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REVIEW

Electrochemical phase formation: some fundamental concepts

Alexander Milchev

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Abstract The article comments upon some basic concepts related to the electrocrystallization phenomena. Short stories about the founders of the classical nucleation and crystal growth theory M. Volmer, W. Kossel, I.N. Stranski, R. Kaischew, and L. Krastanow are also included.

Keywords Half-crystal position · Equilibrium form · Effective overpotential · Nucleation work

Introduction

When I received the invitation to contribute to the special issue *Electrochemistry—Past, Present and Future* of JOS-SEC, the question that I asked myself first was: *Am I the suitable person?* Later, I realized that, at least in my close Bulgarian circles, I was among those scientists who should have sufficient experience to do the job in a proper way. Therefore, I accepted the invitation.

How did it all start in my case? Recently, one of my younger colleagues asked me: *Why did you decide to study chemistry?* Frankly, the main reason was that I hated chemistry in secondary school. In the end, I had to take a school-leaving chemistry examination and that was how I finally learned something on that subject. Two years later, after the obligatory military service, when I had to decide what to study next, it seemed that perhaps chemistry was still comparatively fresh in my head. I passed the admission examination and joined the Chemistry Department of Sofia University in the autumn of 1962.

At that time, Professor Rostislaw Kaischew, the first coworker and close friend to the famous Bulgarian scientist Ivan Stranski, was the head of the Physical Chemistry Department. R. Kaischew was also reading lectures to students, and we liked him a lot because he was not only a brilliant lecturer but also an open-minded person. His lectures were never spoilt by making lists of absentees, angry remarks at those who were a few minutes late, etc.

In June 1967, I had to take my exam on Physical Chemistry and that was my first personal contact with Rostislaw Kaischew. I still remember the subject on which I had to talk: *Entropy and thermodynamic probability.* Kaischew listened to me carefully and when I finished, he asked a single question:

-Is that all you know?

When I confirmed, he just put an “excellent” mark in my student’s record book. Already at the door, I heard him say:

-And if you have any interests in physical chemistry, come to me.

A. Milchev (✉)
Rostislaw Kaischew Institute of Physical Chemistry,
Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria
e-mail: amilchev@ipc.bas.bg

I must admit that at that time, my interests were slightly different: some bridge and poker, sport, some girls and, of course, lectures, and practicals. The group of my friends in the student days was not very devoted to science. Of course, we took our exams, moved from one course to another, and finally received a good education. Most of our lecturers were very good, indeed.

After the last semester, when I had to do my diploma work, I remembered Kaischew's words. At that time, he was Vice President of the Bulgarian Academy of Sciences (BAS), and one morning, I found myself waiting in front of his study. He came shortly after, said "Good morning" and invited me to come in. I did and explained my case.

> -Very well—Kaischew said—It is good that you came. Now, go to the Institute of Physical Chemistry, find Svetoslav Toschev and tell him that I am sending you. He knows what to do.

That is how Rostislaw Kaischew determined my scientific career for the next 42 years: *electrocrystallization—nucleation and growth of metals and alloys.*[1]

In the following sections, I discuss some fundamental concepts in this scientific field.

The half crystal position and the equilibrium form

One of the first things I learned in S. Toschev's research group was what *half-crystal position* means. The concept was defined simultaneously and independently by the German physicist Walther Kossel and the Bulgarian physical chemist Iwan Stranski in 1927 [1–3]. In this way, the two scientists laid the foundations for the molecular-kinetic studies of crystal growth phenomena supplementing the classical statistical-thermodynamic works of J.W. Gibbs [4–6] and M. Volmer [7–9] (Photo 1, 2, and 3).

In an infinitely large three-dimensional (3D) crystal (Fig. 1), the building unit (atom, ion, molecule) in the *half-crystal position* is bonded with a one-dimensional (1D) semi-infinite crystal row, with a two-dimensional (2D) semi-infinite crystal lattice and with a three dimensional (3D) semi-infinite crystal block. Attaching or detaching one atom[2] to and from the half-crystal position results in a new half-crystal position, and this makes the position a repeatable step in the successive building and disintegration of the bulk crystals.

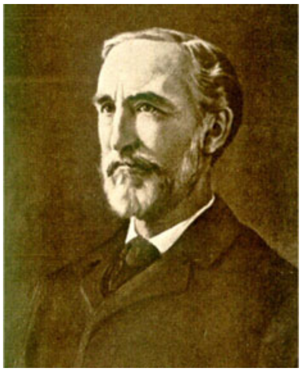

Photo 1 J.W. Gibbs (1839–1903)

Suppose now that the cubic crystal in Fig. 1a is a finite crystal with n atoms in the edge and therefore consists of n^3 atoms. Then, it is not difficult to show that if the crystal is disintegrated accounting only for the bond energy ψ_1 between first neighboring atoms for the total bond energy W of the crystal lattice one obtains:

$$W = 3n^3\psi_1\left(1 - \frac{1}{n}\right) \tag{1}$$

Thus for the bond energy per single atom (W/n^3) it results,

$$\frac{W}{n^3} = 3\psi_1\left(1 - \frac{1}{n}\right) \tag{2}$$

which means that all building units in an infinitely large crystal ($n \rightarrow \infty$) are connected as the atom in the *half crystal position*, the separation work $\varphi_{1/2}$ being equal to $3\psi_1$. Therefore, it appears that namely the energy $\varphi_{1/2}$ is which determines the equilibrium of a bulk crystal with the ambient phase.

Equation 2 allows us to evaluate the size at which a cubic crystal should be considered "infinitely large." Thus, assuming that for $n \geq 100$, $W/n^3 \approx \varphi_{1/2} = 3\psi_1$, it appears that a cubic crystal consisting of $n^3 = 10^6$ atoms, i.e., having a linear size of approximately 30 nm should already have the properties of the "infinitely large" crystalline phase.

Photo 2 M. Volmer (1885–1965)

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[1] Svetoslav Toschev, my first teacher in the field of electrocrystallization from whom I learned a lot, died in a mountain accident in 1971, and since that time, I have been working independently and in collaboration with my older and younger colleagues and coworkers.

[2] For the sake of simplicity here and henceforth, we assume that the building units are atoms.

Photo 3 Walther Kossel (1888–1956; *left*) and Iwan N. Stranski (1897–1979; right) (Germany, the early fifties)

In 1931, Stranski and Kaischew [10] made another important step in the development of the crystal growth theory by determining the equilibrium form of the homopolar crystals. The considerations were based on the simple assumption that in a finite crystal the atoms that are bonded weaker than the atom in the half crystal position should leave the crystal surface. Thus, accounting for the *first* and *second* neighbor interaction energies ψ_1 and ψ_2, one obtains $\varphi_{1/2}=3\psi_1+6\psi_2$, and this leads to the appearance of the octahedral <111> and the rombododecahedral <110> faces (Fig. 2). If interactions between *third* neighbors ($\varphi_{1/2}=3\psi_1+6\psi_2+4\psi_3$) are taken into consideration, the <211> faces appear, too. Interactions between more distant neighbors turned out to have no effect on the equilibrium form. Note that the abovementioned values of $\varphi_{1/2}$ hold good only for simple cubic crystals. For crystals with *face-* and *body-centered* cubic lattices for the separation work $\varphi_{1/2}$, one obtains $\varphi_{1/2}=6\psi_1+3\psi_2+12\psi_3$ and $\varphi_{1/2}=4\psi_1+3\psi_2+6\psi_3$, respectively. The results for the equilibrium form of homopolar crystals obtained by Stranski and Kaischew [10] were experimentally verified and confirmed 3 years later by Straumanis [11, 12] (see also [13] and the references cited therein). Note that practically, the same results follow also from the Wulff's rule (Gibbs–Curie–Wulff theorem [4–6, 14, 15]) according to which the total free surface energy of any crystal having the equilibrium form displays a minimum at a constant volume V. Thus, for each crystallographic face j, it follows that

$$\frac{\sigma_j}{h_j}=\lambda \tag{3}$$

or

$$\sigma_1:\sigma_2:\sigma_3:\ldots=h_1:h_2:h_3\ldots \tag{4}$$

where σ_j are the specific free surface energies of the crystal faces which contact only the parent phase, h_j are the distances between the crystal faces and the Wulff's point (Fig. 3), and λ is a material constant, which depends on the crystal size. In 1951, the Wulff's rule was generalized by Kaischew [16], who accounted also for the *crystal–substrate* interactions in case of heterogeneous nucleation. Thus, for the crystal faces, which contact the foreign substrate, it follows that

$$\sigma_1-\beta_1:\sigma_2-\beta_2:\sigma_3-\beta_3:\ldots=h_1^*:h_2^*:h_3^*\ldots \tag{5}$$

where β_i are the specific free adhesion energies giving the work per unit surface area that has to be done to separate the crystal from the foreign substrate, and h_j^* are the distances between those faces and the Wulff's point. Combining Eqs. (4) and (5), one obtains the following general formula characterizing the equilibrium form of crystals on a foreign substrate:

$$\frac{\sigma_{hkl}-\beta_{hkl}}{\sigma_{hkl}}=\frac{h_{hkl}^*}{h_{hkl}} \tag{6}$$

In 1933, Iwan Stranski, who was the first lecturer in Physical Chemistry at Sofia University, applied for a professorship in the Faculty of Physics and Mathematics. The Special Commission elected by the Faculty Council decided to consult about Iwan Stranski's contribution to the crystal growth field not only with Bulgarian reviewers but also with well-known international experts. Three honored German scientists were selected: Professor Kurt Spangenberg from the Mineralogy-Petrography Institute and Museum at the University and Technical High School of Breslau, Professor Max Volmer from the Institute of Physical Chemistry and Electrochemistry at the Technical High School, Berlin, and, last but not least, Professor Walther Kossel himself, from the Institute of Physics at the Technical High School, Danzig.

Being aware of the typical Bulgarian skepticism, I am fully convinced that one of the main reasons for this

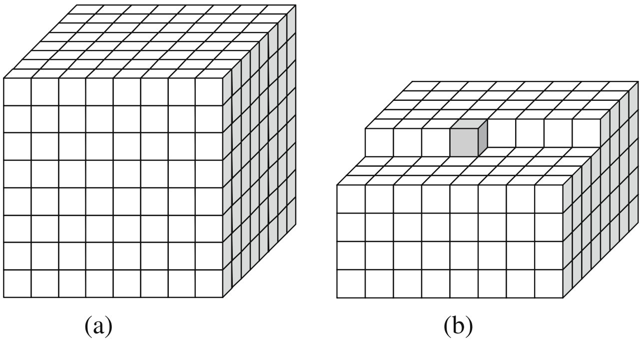

Fig. 1 The Kossel cubic crystal (**a**) and the atom in the half-crystal position (**b**)

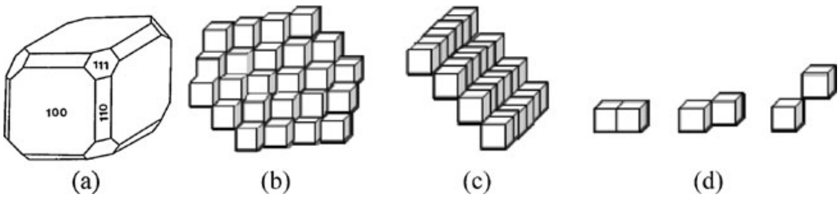

Fig. 2 The simple cubic crystal (**a**), the <111> (**b**), and <110> (**c**) faces in the cubic lattice and the first, second, and third neighboring atoms (**d**)

decision was the strong interest of the Commission members in the experts' opinion not only on the significance of Stranski's work but also, and particularly, on the remarkable coincidence of the brilliant ideas of W. Kossel and I. Stranski leading to the definition of the concept *half-crystal position*.

What follows are short excerpts from the German scientist's letters addressed to the Commission member Lubomir Chakalow,[3] at that time Professor in the Mathematical Faculty of Sofia University and regular member of the Bulgarian Academy of Sciences.

> *…Professor Stranski made a good name for himself with his works in the field of crystal growth. The numerous earlier works in this field are mainly of a purely descriptive nature i.e. the fact that the substance deposits on the crystal bodies with a different velocity in the different directions was considered just as a fact, from which the formation of different polyhedric forms follows. On the contrary, Mr. Stranski directs his attention to the main question: what are the physical reasons for the deposition of substance with different velocities? Mr. Stranski finds these reasons in the difference of the attachment energies to the different sites of the crystal lattice and calculates these energies for heteropolar crystals by means of the Madelung's lattice potentials.*
>
> *… The consequences of all these works are very important because they moved the whole field from the stage of descriptive to the stage of exact sciences. The achievements of Mr. Stranski are so astonishing also because he got familiar with the problem and solved it himself without having any preliminary contacts with older researchers.*
>
> *Prof. Dr. Max Volmer, 09 March 1933, Charlottenburg, Germany*
>
> *…In his fundamental work "On the theory of crystal growth" published in 1928 in Zeitschrift für Physikalische Chemie 136:259, Mr. Stranski published his theoretical considerations and calculations concerning the crystal growth phenomena on the lattice of NaCl. Since in this paper he formulated basic ideas independently of Professor W.Kossel, he calculated, approximately simultaneously with him the values of the separation works of single ions on the surface of a NaCl crystal, which differed significantly depending on their lattice position. Most successfully, he went further than Mr. Kossel taking into account not only the attraction but also the repulsion forces between oppositely charged particles in this ionic lattice. Also, again ahead of Mr. Kossel, Mr. Stranski considered not only separate ions but, for the first time, separation works of ionic pairs and bigger ionic complexes*
>
> *Prof. Dr. Kurt Spangenberg, 15th April 1933, Breslau, Germany*
>
> *Since 1928 I have followed Mr. Stranski's work with great interest and I believe I am familiar with and understand his scientific achievements. At that time he submitted a picture of the crystal growth processes very close to my own considerations, which I had presented shortly before that at the Academy of Goettingen, meaning that Mr. Stranski could not have been familiar with them. Therefore, his work aroused my vivid interest. The first paper of Mr. Stranski was already much richer than mine and his considerations, even of the most simple cases, convinced me that he has not only found a new idea but has also thought it over in a most profound way.*
> *Prof. Dr. Walther Kossel, 23th April 1933, Danzig, Germany*

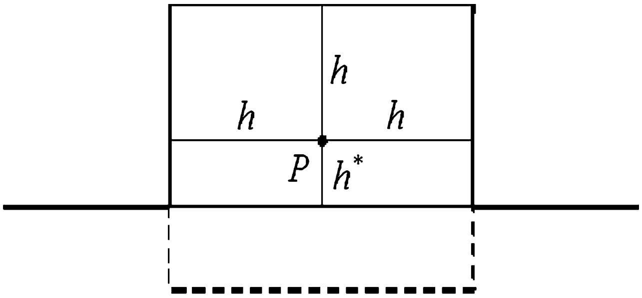

Fig. 3 The cross section of a simple cubic crystal formed on a foreign substrate, h and h^* being the distances between the Wulff's point P and the different crystallographic faces

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[3] Professor Lubomir Chakalow (1886–1963) was among the best Bulgarian mathematicians of the twentieth century, and nowadays, the mathematical gymnasium in Sofia is named after him.

No comments! I suppose, however, that the reader might be interested how I could gain access to these 77-year-old and most valuable documents. The answer is simple—just another lucky coincidence! For 25 years, my family and the family of Professor Lubomir Chakalov's son—Vladimir Chakalov, a professor of mathematics, too—lived in the same building, on the same floor, and we are good neighbors and good friends. One day, not too long ago, Vladimir showed me his father's archives, and I was allowed to take everything concerning Iwan Stranski as a valuable gift.

Speaking of coincidences, I would like to cite Stranski's comments on the subject in a lecture given to the members of the Rotary Club, Berlin in 1963 [17]:

> *… It is quite clear that every discovery or knowledge will be made or attained, sooner or later, if not by one then by another scientist and, beside that, in a form, which does not carry personal features. If the foundations of the kinetic theory of gases had not been laid by Clausius, this would have been done by somebody else. If the theory of relativity had not been developed by Einstein, it would have been inevitably developed by other authors. This is simply the consequence of the existence of nature and the striving of mankind to unravel it.*
> *… It is the opposite with art. Firstly, the creation of a certain work of art could not be predicted in any circumstances, even by chance. If Beethoven had not composed his 9th Symphony this could not have been done by anybody else. If Goethe had not written his "Faust", nobody else would have been able to do it in the same way.*
> *…Therefore the works of art are unique and directly related to their authors.*

Back to science again, I will comment upon the next decisive step in the development of the molecular-kinetic approach to the nucleation-growth phenomena—the theory of *mean separation works* created by Iwan Stranski and Rostislaw Kaischew [18–20] and published between March and June 1934 (see also the historical review article of R. Kaischew [21] as well as his selected works [22]).

Theory of mean separation works and elementary acts of single ions/atoms attachment and detachment to and from the crystal surface

Introducing the concept *half-crystal position*, W. Kossel [1] and I. Stranski [2, 3] shed light on the equilibrium state of bulk, infinitely large crystals. Naturally, what had to be done next was to use the molecular-kinetic approach for a theoretical description of the equilibrium of small, finite crystals with the ambient phase. That was one of the purposes of the Stranski–Kaischew's theory of mean separation works [18–20]. Apparently, in a finite crystal, the energy contribution of the edge and corner atoms cannot be neglected and must be taken into account in the total energy balance. Thus, the authors' main idea was that the equilibrium state of small crystals should be expressed through the equality of the *mean separation work* $\overline{\varphi}_{hkl}$ of the atoms from the crystal faces <*hkl*>, which contact the ambient phase.

Suppose now that a simple cubic crystal consisting of n^2n' atoms is formed on a foreign substrate (Fig. 4). Then, accounting only for the first neighbor interaction energies ψ_1 for the total bond energies $W(n^2)$ and $W(nn')$ of the atoms in the upper and the front crystal face, one obtains

$$W\left(n^2\right) = 3\psi_1 n^2\left(1 - \frac{2}{3n}\right) \tag{7}$$

and

$$W(nn') = 3\psi_1 nn'\left[1 - \frac{1}{3n} - \frac{1}{3n'}\left(1 - \frac{\psi_1'}{\psi_1}\right)\right] \tag{8}$$

respectively, ψ_1' being the bond energy between a crystal atom and its first neighbor in the foreign substrate. Correspondingly, for the mean separation works $\overline{\varphi}_{n^2} = W(n^2)/n^2$ and $\overline{\varphi}_{nn'} = W(nn')/nn'$ it results

$$\overline{\varphi}_{n^2} = 3\psi_1\left(1 - \frac{2}{3n}\right) \tag{9}$$

$$\overline{\varphi}_{nn'} = 3\psi_1 - \frac{\psi_1}{n} - \frac{\psi_1 - \psi_1'}{n'} \tag{10}$$

Thus the condition $\overline{\varphi}_{n^2} = \overline{\varphi}_{nn'}$ yields

$$\frac{n'}{n} = 1 - \frac{\psi_1'}{\psi_1} \tag{11}$$

which transforms into the condition for the equilibrium form of a crystal formed on a foreign substrate (Eq. (6)), bearing in mind that the specific free surface and adhesion energies can be defined as $\sigma=\psi_1/2d^2$ and $\beta = \psi_1'/d^2$, respectively, d being the atomic diameter

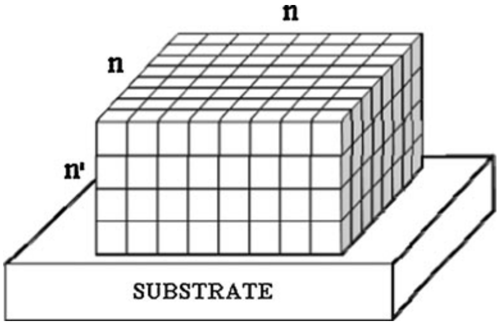

Fig. 4 A simple cubic crystal consisting of n^2n' atoms formed on a foreign substrate

for which the simple relations hold (see Figs. 3 and 4): $nd=2h$ and $n'd=h+h^*$ [23].

Furthermore, he authors consider also the process of nucleus formation deriving theoretical expressions for both the nucleation work and the rate of two- and three-dimensional nucleation from a vapor phase. As emphasized by Kaischew [21], namely the theory of mean separation works "*…threw at last the long searched for bridge between the molecular-kinetic treatment of Kossel and Stranski and the statistical-thermodynamic theory of Volmer, and thus the foundations for development of an unified theory of the crystallization processes were laid down.*" Those who may be interested in the theory of mean separation works could find a more detailed description also in [24].

Finally, I must not forget to mention also the Stranski–Krastanow's studies of the epitaxial crystal growth [25], which were part of the L. Krastanow's doctor work performed under Stranski's supervision and defended by L. Krastanow on July 4, 1938. Additional information on the Stranski–Krastanow growth mechanism can be found in the excellent paper of E. Bauer [26], who proposed a classification of the epitaxial crystal growth modes in 1958.

In 1941, Iwan Stranski left Bulgaria, invited by W. Kossel to join the University of Breslau as a Visiting Professor, and this is how his academic career in Germany started. Unfortunately, the Iron Curtain, which split Europe into "East" and "West" after the Second World War, also severed Stranski's contacts with his close Bulgarian coworkers and friends, and they were reestablished after 28 long years.

In Sofia, the examinations of crystal growth phenomena were continued by L. Krastanow and R. Kaischew. Krastanow directed his efforts to solving problems related to phase transitions in atmosphere [27–29], whereas Kaischew initiated his electrocrystallization studies. He applied the molecular-kinetic approach to the case of electrochemical phase formation, and the obtained results were included in two fundamental works: *On the theory of electrocrystallization* [30] and *On the electrochemical potential of small electrodes* [31]. Unfortunately, these were published only in Bulgarian, probably because of the restrictions of the established totalitarian regime that replaced the Bulgarian Kingdom in 1945. What follows is a brief description of Kaischew's main results (for more details see also [24]).

The frequencies of attachment W_{+i} and detachment W_{-i} of a single ion/atom to and from the ith site of the crystal surface are given by

$$W_{+1} = p_i c \exp(-V_i/kT)\exp(-\alpha ze\,E/kT) \tag{12}$$

$$W_{-i} = q_i \exp\left(-V_i^*/kT\right)\exp[(1-\alpha)ze\,E/kT] \tag{13}$$

where c is the ionic concentration, E is the electrode potential difference between the crystal, and the solution, p_i and q_i are frequency factors, V_i and V_i^* are the corresponding energy barriers, the difference $V_i^* - V_i = \varphi_i$ giving the separation work from the ith site of the crystal surface and the other symbols have their usual meaning.

The state of stable equilibrium between the electrolyte and the infinitely large crystal is determined by the equality of the frequencies of attachment $W_{+1/2}(E_\infty)$ and detachment $W_{-1/2}(E_\infty)$ of a single ion/atom to and from the half crystal position at a potential difference $E=E_\infty$, and from Eqs. 12 and 13, it results to

$$\frac{W_{-1/2}(E_\infty)}{W_{+1/2}(E_\infty)} = \frac{\xi_{1/2}}{c}\exp\left(-\varphi_{1/2}/kT\right)\exp(zeE_\infty/kT) = 1 \tag{14}$$

Here, $\xi_{1/2}=q_{1/2}/p_{1/2}$ and the difference $V_{1/2}{}^*-V_{1/2}=\varphi_{1/2}$ gives the separation work from the half-crystal position. As discussed by Kaischew [30], the last expression coincides with the equation of Nernst, $zeE_\infty=kT\ln(c/c^0)$ if at the standard state ionic concentration $c=c^0$ the potential difference is denoted by $E_\infty \equiv E^0=-(kT/ze)\ln c^0$.

Suppose now that a cathodic overpotential $\eta>0$ is applied to the bulk crystal,[4] i.e., the potential difference between the crystal and the solution becomes $E=E_\infty-\eta$ and the system is deviated from the equilibrium state. In this case, for the ratios $W_{-1/2}(\eta)/W_{+1/2}(\eta)$ and $W_{-i}(\eta)/W_{+i}(\eta)$, it results to

$$\frac{W_{-1/2}(\eta)}{W_{+1/2}(\eta)} = \exp(-\Delta\tilde{\mu}/kT) \tag{15}$$

$$\begin{aligned}\frac{W_{-i}(\eta)}{W_{+i}(\eta)} &= \frac{\xi_i}{\xi_{1/2}}\exp\left[\left(\varphi_{1/2}-\varphi_i\right)/kT\right]\exp(-\Delta\tilde{\mu}/kT)\\ &= \exp\left[\left(\tilde{\mu}_i-\tilde{\mu}_{1/2}\right)/kT\right]\exp(-\Delta\tilde{\mu}/kT)\end{aligned} \tag{16}$$

where $\Delta\tilde{\mu} = ze\eta > 0$ is the electrochemical supersaturation and $\tilde{\mu}_{1/2}$ and $\tilde{\mu}_i$ are the electrochemical potentials of the atoms in the half-crystal position and in the ith site of the crystal surface, respectively.

Kaischew considered also the equilibrium of small crystals in contact with solution of their ions applying the principle of detailed balance. Bearing in mind that the equilibrium state does not depend on the mechanism of its establishment, he assumes that the equilibrium of the upper face of the cubic crystal (Fig. 4) with the ambient phase is expressed through the equality of the probabilities of

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[4] In this paper, the cathodic overpotential η is considered as a positive quantity.

attachment P_{+n^2} and detachment P_{-n^2} of n^2 atoms to and from the top layer, which results in:

$$\frac{P_{-n^2}}{P_{+n^2}} = \prod_{1}^{n^2} \frac{W_{-i}(\eta)}{W_{+i}(\eta)}$$
$$= \exp\left[\left(-n^2\tilde{\mu}_{1/2} + \sum_{1}^{n^2}\tilde{\mu}_i\right)/kT\right]\exp\left(-n^2\Delta\tilde{\mu}/kT\right) = 1 \qquad (17)$$

Taking the logarithm of this expression, one obtains

$$\Delta\tilde{\mu} = \frac{\sum_{1}^{n^2}\tilde{\mu}_i}{n^2} - \tilde{\mu}_{1/2} = \bar{\tilde{\mu}}_{n^2} - \tilde{\mu}_{1/2} \approx \varphi_{1/2} - \bar{\varphi}_{n^2} \qquad (18)$$

$\bar{\tilde{\mu}}_{n^2}$ being the mean electrochemical potential of the atoms in the top layer of the upper face of the cubic crystal. Thus, it appears that the equilibrium between the small crystal and the electrolyte solution at a fixed supersaturation $\Delta\tilde{\mu}$ is expressed through the equality of the mean separation works $\bar{\varphi}_{hkl}$ of the atoms from all crystallographic faces constituting the equilibrium form. It is not difficult to show that Eq. 18 coincides with the Gibbs–Thomson equation

$$\Delta\tilde{\mu} = \frac{2\sigma\upsilon_M}{r_c} \qquad (19)$$

σ being the potential dependent specific free surface energy at the *crystal/solution* interface boundary (see e.g., [24]). In Eq. 19, $r_c \equiv h_c = n_c d/2$ is the radius of the sphere, a segment of which could be inscribed in the cubic crystal, and $\upsilon_M = d^3$ is the volume of the single atom. Namely, the crystal of linear size r_c, which stays in a metastable equilibrium with the supersaturated parent phase, is defined as a *critical nucleus* in the classical nucleation theory.

Assuming that at the supersaturation $\Delta\tilde{\mu}$, the cubic crystal of Fig. 4 is the critical nucleus consisting of $N_c = n_c^2 n_c'$ atoms, for the nucleation work $\Delta\tilde{G}(N_c)$ in terms of the theory of mean separation works, it results [31]:

$$\Delta\tilde{G}(N_c) = \sum_{1}^{N_c}\left(\bar{\varphi}_{i,n^2} - \varphi_i\right) \approx \sum_{1}^{N_c}\left(\tilde{\mu}_i - \bar{\tilde{\mu}}_{i,n^2}\right) \qquad (20)$$

which coincides with the formula for the nucleation work derived in the classical works of Gibbs [4–6] and Volmer [7–9]. Kaischew derived also explicit theoretical expressions for the work of formation of two-dimensional nuclei on the faces of a three-dimensional crystal, which contact the ambient phase [30]. Later, Budevski and coworkers performed profound theoretical and experimental studies of the two-dimensional electrochemical nucleation and those who are interested in this subject can find a thorough description of the obtained results in the monograph of Budevski et al. [32] (see also [24, 33]).

I should say that, namely, these two Kaischew's works, [30] and [31], laid the foundations of the electrocrystallization studies in Bulgaria, first in the Physical Chemistry Department of Sofia University and then also in the Institute of Physical Chemistry, Bulgarian Academy of Sciences founded in 1958 and headed by him till the end of 1988.

As I already mentioned above, Rostislaw Kaischew was not only an outstanding scientist but also an open-minded and most respectable person who had a lot of friends in the crystal growth world. Most of them visited him in Sofia, and this was how I met a number of outstanding scientists: A. N. Frumkin, one of the best electrochemists of the twentieth century (Photo 4), J. B. Zeldovich, named by Andrey Sakharov "a man of universal scientific interests," whose scientific activities covered a really broad range of fields—from adsorption, catalysis, and cavitation to nuclear physics, astrophysics, physical cosmology, and general relativity (Photo 5), Sir F.C. Frank, who discovered,

Photo 4 A.N. Frumkin (*left*) and R. Kaischew (*right*) with shepherds in Rila mountain, Bulgaria (the fifties)

together with W.K. Burton and N. Cabrera, the spiral growth mechanism of crystals, Dorothy Hodgkin, the Nobel prize winner who deciphered the structure of vitamin B_{12} and of insulin, and many others.

I suppose, it is not well known that A. N. Frumkin have also contributed to the field of liquid and solid small phases. In 1935, Frumkin and Fuchs published a paper entitled *On the vapor pressure of small droplets and crystals* [34], in which the Stranski–Kaischew kinetic method developed in the theory of mean separation works was essentially used. I am sure, too, that few people know that in 1965, Peter Rebinder and Rostislaw Kaischew, regular members of the Russian and Bulgarian Academies of Sciences, respectively, suggested to the Nobel Committee to award the Nobel Prize to M. Volmer and A.N. Frumkin for their significant contributions to the field of electrochemistry. Unfortunately, the Nobel Committee reached a different decision.

In 1962, L. Krastanow was elected President of the Bulgarian Academy of Sciences, and R. Kaischew became his Vice President. This is the reason why the period between 1962 and 1968 was jokingly called the "Golden Century of Bulgarian Physical Chemistry." In 1966, Iwan Stranski was elected Foreign Member of BAS, and he visited Bulgaria in 1969, after 28 years spent abroad (Photo 6).

I met Iwan Stranski for the first time when he visited the Institute of Physical Chemistry in 1975. I remember that Kaischew was taking him to the different labs, explaining briefly the goals of the scientific research and then leaving him with the head of the research group who presented recent scientific results. Stranski listened carefully, asked one or two questions or made some remarks and at the end usually smiled, and said in a low voice: "And now tell me the last anecdote, please, but hurry up because Rostislaw may come and then we will have problems, the two of us!"

Iwan Stranski died in 1979 in Bulgaria, his home country, and nowadays, a street in Sofia is named after him. In 2005 Bulgarian National Television telecasted the movie "*The master of crystal growth*" devoted to Iwan Stranski and directed by S. Stefanov, the son of my colleague S. Stoyanov with whom we worked side by side in the Institute of Physical Chemistry, BAS during the last 40 years. In Germany, an Institute in the Technical University, Berlin and the Metalurgical Institute in Oberhausen both bear his name. More information about Iwan Stranski's scientific career can be found in the "in memoriam" articles of R.Lacmann [35] and I. Gutzow [36].

Photo 5 J.B. Zeldovich (*left*) and R. Kaischew (*right*), Sofia, 1979

Photo 6 *Left to right* R. Kaischew, I.N. Stranski, and L. Krastanow, Sofia, 1975

The Gibbs–Thomson equation, the effective overpotential and the nucleation work

I will now return back to the Gibbs–Thomson equation and to the nucleation work, which lie at the root of the classical theory of phase formation. It might be suitable to start with the general theoretical formula for the thermodynamic work of formation of an *N*-atomic cluster of the new phase:

$$\Delta\widetilde{G}(N) = -N\Delta\widetilde{\mu} + \widetilde{\Phi}(N) \tag{21}$$

In this expression, the term $-N\Delta\widetilde{\mu}$ accounts for the energy gained when *N* single particles of the supersaturated parent phase turn into an *N*-atomic cluster of the new phase having a lower thermodynamic potential and $\widetilde{\Phi}(N)$ is the energy contribution of the "nucleus-substrate" and the "nucleus-solution" interface boundary. In 1936, Iwan Stranski defined this important quantity in a most general form [37]:

$$\widetilde{\Phi}(N) = N\varphi_{1/2} - \sum_{1}^{N}\varphi_i \tag{22}$$

The physical significance of Eq. 22 can be explained in the following way. Suppose that *N* atoms are detached from an infinitely large crystal (i.e. from the half crystal position) thus consuming the energy $N\phi_{1/2}$. If after that the detached atoms form an N-atomic cluster on the foreign substrate, the energy gained will be equal to the sum $\sum_1^N \varphi_i$ of the individual separation works of the N atoms. Clearly, the difference $\widetilde{\Phi}(N)$ accounts for the uncompensated energy due to the interaction of the N-atomic cluster with both, the ambient phase and the foreign substrate and is equal to the cluster's total free surface and adhesion energies. Another theoretical formula for the same quantity reads:

$$\widetilde{\Phi}(N) = \widetilde{G}(N) - N\widetilde{\mu}_{1/2} \tag{23}$$

where $\widetilde{G}(N) = \sum_1^N \widetilde{\mu}_i$ is the Gibbs free energy of the N-atomic cluster formed on the foreign substrate (see e.g. [24] and the references cited therein). Note that defined in this way, the theoretical formulas for $\widetilde{\Phi}(N)$ and $\Delta\widetilde{G}(N)$ (Eqs. 21–23) can be used without any restrictions of the clusters' size and apply even to single atoms.

In case of sufficiently large clusters, the number N of atoms can be considered as a continuous variable and $\Delta\widetilde{G}(N)$ as a differentiable function. Then, the condition for a maximum of the nucleation work at the critical nucleus size, $\left[\mathrm{d}\Delta\widetilde{G}(N)/\mathrm{d}N\right]_{N=N_c} = 0$, applied to Eq. 21 yields [38],

$$\Delta\widetilde{\mu} = \left[\frac{d\widetilde{\Phi}(N)}{dN}\right]_{N=N_c} \tag{24}$$

which represents a general formula of the Gibbs–Thomson equation. Explicit expressions for the size N_c of the critical nucleus and for the work $\Delta\widetilde{G}(N_c)$ of critical nucleus formation of three dimensional clusters on a foreign substrate read:

$$N_c = \frac{a^* \upsilon_M^2}{\Delta\widetilde{\mu}^3} \tag{25}$$

$$\Delta\widetilde{G}(N_c) = \frac{1}{2}\frac{a^* \upsilon_M^2}{\Delta\widetilde{\mu}^2} \tag{26}$$

Here, a^* is a material constant, which can be found in each particular case by means of the generalized Gibbs–Curie–Wulff theorem (Eqs. 3–6). Thus for crystalline nuclei with a face centered cubic lattice, which contact the substrate with their cubic, <100>, or octahedral, <111>, face, it results: $a^*_{<100>} = 8\sigma^3_{<100>}\ [1-(\beta_{<100>}/2\sigma_{<100>})]$ and $a^*_{<111>} = 16 \times \sqrt{3}\sigma^3_{<111>}\ [1-(\beta_{<111>}/2\sigma_{<111>})]$, respectively, etc. In the case of liquid droplets formed on a foreign substrate, the expressions for N_c and $\Delta\widetilde{G}(N_c)$ read:

$$N_c = \frac{32}{3}\frac{\pi\sigma^3\upsilon_M^2}{\Delta\widetilde{\mu}^3}F(\gamma_o) \tag{25$'$}$$

$$\Delta\widetilde{G}(N_c) = \frac{16}{3}\frac{\pi\sigma^3\upsilon_M^2}{\Delta\widetilde{\mu}^2}F(\gamma_o) \tag{26$'$}$$

Here, γ_0 is the wetting angle determined by the specific free surface and adhesion energies according to $\cos\gamma_0=(\beta-\sigma)/\sigma$ and $F(\gamma_0)=1/2-(3/4)cos\gamma_0+(1/4)cos^3\gamma_0$ is the so-called *wetting angle function*. It is worth noting that combination of Eqs. 25 and 26 yields a simple relation between the three most important physical quantities in the classical nucleation theory, N_c, $\Delta\widetilde{G}(N_c)$ and $\Delta\widetilde{\mu}$ [24]:

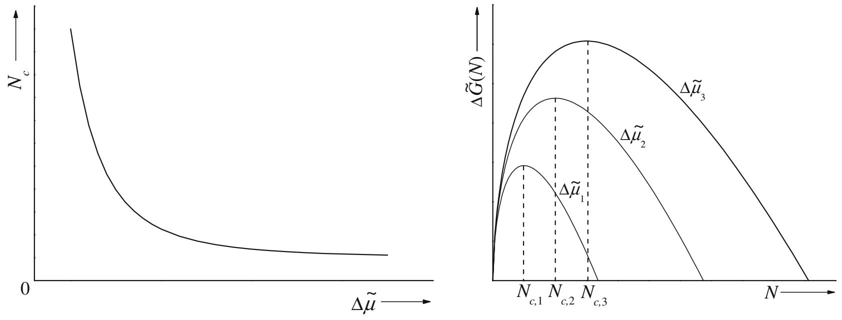
$$\Delta\widetilde{\mu} = \frac{2\Delta\widetilde{G}(N_c)}{N_c} \tag{27}$$

Equation 27 is another formula for the Gibbs–Thomson relation (Eqs. 19 and 24) and can be obtained also combining Eqs. 25′ and 26′. Figure 5 shows schematically the N_c vs $\Delta\widetilde{\mu}$ and the $\Delta\widetilde{G}(N)$ vs N relationships according to the classical nucleation theory.

According to Kaischew [31], the equilibrium potential E_r of any spherical cluster with a radius r is given by

$$E_r = E_\infty - \frac{2\sigma\upsilon_M}{zer} \tag{28}$$

and the difference E_r–$E=\eta_r$ defines an effective overpotential, the corresponding effective supersaturation being $\Delta\widetilde{\mu}_r = ze\eta_r$. Bearing in mind Eq. 19, the formula 28 can be rewritten as [39, 40]:



(a) (b)

Fig. 5 N_c vs $\Delta\widetilde{\mu}$ (**a**) and $\Delta\widetilde{G}(N)$ vs N (**b**) relationships according to the classical nucleation theory. The critical nuclei at the supersaturations $\Delta\widetilde{\mu}_1 > \Delta\widetilde{\mu}_2 > \Delta\widetilde{\mu}_3$ consist of $N_{c,1} < N_{c,2} < N_{c,3}$ atoms

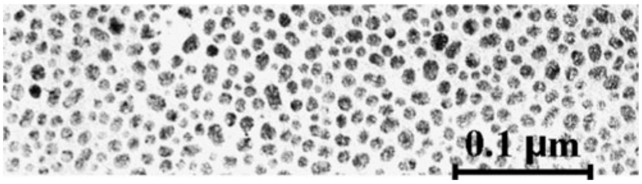


Fig. 6 Silver crystals evaporated on a carbon film [40] (courtesy of A. Panov and with permission from Prof. R. Jacobson, Chief Editor of *The Imaging Science Journal*, formerly *The Journal of Photographic Science*)

$$\eta_r = \eta - \frac{2\sigma \upsilon_M}{zer} = \eta\left(1 - \frac{r_c}{r}\right) \tag{29}$$

or

$$\eta_r = \eta\left(1 - \frac{N_c^{1/3}}{N^{1/3}}\right) \tag{29'}$$

Equations 29 and 29′ show that solid or liquid clusters having exceeded the critical radius r_c (number of atoms N_c) will grow irreversibly at the effective overpotential $\eta_r > \eta$, the effective supersaturation being $\Delta\widetilde{\mu}_r = ze\eta_r > 0$. On the contrary, clusters of radius $r < r_c$ will dissolve because for them the electrochemical system will be effectively undersaturated, $\eta_r < \eta, \Delta\widetilde{\mu}_r = ze\eta_r < 0$. As for the critical nuclei of radius $r = r_c$, ($N = N_c$), they will stay in a metastable equilibrium with the supersaturated parent phase since for them $\eta_r = 0, \Delta\widetilde{\mu}_r = ze\eta_r = 0$. Namely, the theoretical expression for the effective overpotential η_r (Eq. 29) was used by Konstantinov, Panov, and Malinowski [40] to interpret the results of their model studies of photographic development, which is a typical process of electroless metal deposition.

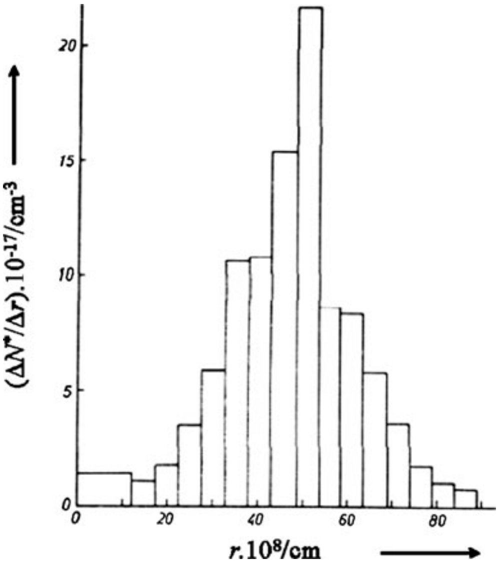


Fig. 7 Size distribution of silver crystals before development [40] (courtesy of A. Panov and with permission from Prof. R. Jacobson, Chief Editor of *The Imaging Science Journal,* formerly *The Journal of Photographic Science*)

The photographic process takes place in two stages—(1) *exposure* of a light-sensitive material, most frequently a silver halide, e.g., AgBr, which leads to the formation of a "latent image" consisting of silver nano-clusters and (2) *development* during which the latent image centers grow to visible size and form the real photograph. The process of development can be presented as a reaction taking place in a galvanic cell of the type $Ag/Ag^{+}//Red\text{-}Oxy/Pt$, in which the redox system is a Fe^{2+}/Fe^{3+} solution [40] (see also the references cited therein, as well as the book of T.H. James [41]). The equilibrium potential $E_{Fe^{2+}/Fe^{3+}}$ of the ferrous-ferric electrode can be varied by varying the concentration of the Fe^{2+}/Fe^{3+} couple, whereas concentration of silver ions in the same solution determines the equilibrium potential E_∞ of bulk silver at the corresponding temperature *T. Thus, the cathodic overpotential* $\eta > 0$*, which determines the growth of the latent image clusters during development, is given by* $\eta = E_\infty - E_{Fe^{2+}/Fe^{3+}}$, and the effective overpotential is expressed by Eq. 29.

In 1973, Konstantinov, Panov, and Malinowski [40] (see also [42–46]) modeled the process of photographic development depositing silver clusters on a carbon film by evaporation in vacuum (Fig. 6) and then treating them in a developer with a known value of η. The size distribution of silver crystals before development is presented in Fig. 7, the ordinate giving the number density ΔN^{*} referred to the corresponding size range Δr. Figure 8 shows size distribution histograms obtained after treating the crystals in developers with overpotentials η=0.0668 V and η=0.0507 V, respectively, in presence of 1.10^{-3} M solution of $AgNO_3$ and temperature T=298 K. The distinct minima at 30.10^{-8} cm and 39.10^{-8} cm correspond to the radii r_c of the critical nuclei at the two overpotentials.

Finally, Fig. 9 demonstrates the results of detailed experimental studies performed at different overpotentials η and illustrating the validity of the Gibbs–Thomson Eq. 19 in a most convincing way. The slope of line 1 corresponds to a specific surface free energy of the "silver-solution" phase boundary σ_{Ag}=9,2.10^{-5}Jcm^{-2}, whereas in presence of a gelatin overlayer, which is the case of real photographic materials (line 2), the value of σ_{Ag} lowers to 4.10^{-5}Jcm^{-2}. As seen from Fig. 9, the size of the critical nuclei varies from r_c=1,92.10^{-6} cm (N_c=8,7.10^{5} atoms) at η= 0.010 V to r_c=0,24.10^{-6} cm (N_c=1,7.10^{3} atoms)[5] at η= 0.0815 V. Note that the two values of r_c are smaller than

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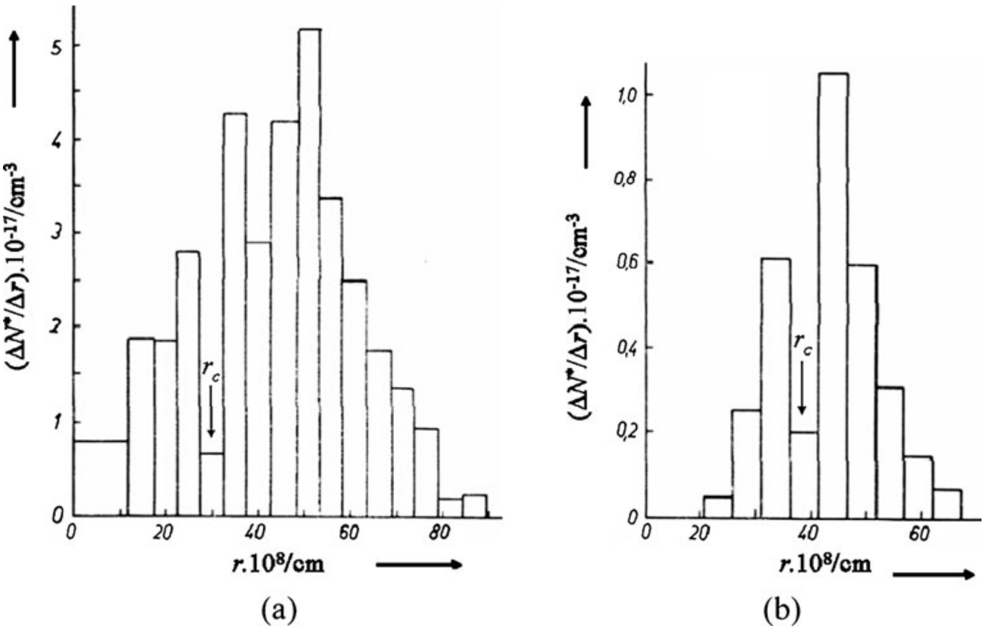
[5] These values of N_c are based on the assumption for hemispherical silver crystals (γ_0=90^0, $F(\gamma_0)$=1/2), which is a frequently used approximation for the silver–carbon system.



(a) (b)

Fig. 8 Size distribution of silver crystals after development. **a** η=0.0668 V and **b** η=0.0507 V [40] (courtesy of A. Panov and with permission from Prof. R. Jacobson, Chief Editor of *The Imaging Science Journal*, formerly *The Journal of Photographic Science*)

30 nm, which was the estimation for an "infinitely large" crystalline phase based on Eq. 2.

The classical nucleation theory developed by Gibbs and Volmer [4–9] operates with macroscopic physical quantities, continuous variables and differentiable functions. Therefore, it applies to sufficiently large clusters of the new phase. Apparently, the same refers to the molecular-kinetic Stranski–Kaischew's theory of mean separation works [18–20] based on average statistical quantities. A short comment of J.W. Gibbs [6] unambiguously shows that he has also had a clear idea about the macroscopic nature of the classical approach to the phase formation phenomena:

> *Let the pressure of the phase of which the stability is in question be denoted by p', and that of the other phase of the same temperature and potentials by p". A spherical mass of the second phase and of a radius determined by the equation*
>
> $$2\sigma = (p'' - p')r \qquad \text{(I)}$$
>
> *would be in equilibrium with a surrounding mass of the first phase. This equilibrium, as we have just seen, is unstable, when the surrounding mass is indefinitely extended. A spherical mass a little larger would tend to increase indefinitely. The work required to form such a spherical mass, by a reversible process, in the interior of an infinite mass of the other phase, is given by the equation*
>
> $$W = \sigma s - (p'' - p')\upsilon'' \qquad \text{(II)}$$
>
> *The term σs represents the work spent in forming the surface, and the term (p"-p')υ" the work gained in forming the interior mass. The second of these quantities is always equal to two-thirds of the first. The value of W is therefore positive, and the phase is in strictness stable, the quantity W affording a kind of measure of its stability. We may easily express the value of W in a form which does not involve any geometrical magnitudes, viz.,*
>
> $$W = \frac{16\pi\sigma^3}{3(p'' - p')^2} \qquad \text{(III)}$$
>
> *where p", p' and σ may be regarded as functions of the temperature and potentials. It will be seen that the stability, thus measured, is infinite for an infinitesimal difference of pressures, but decreases very rapidly as the difference of pressures increases. These conclusions are all, however, practically limited to the case in which the value of r, as determined by equation (I), is of sensible magnitude.*[6]

Since Gibbs considered a *spherical mass*, it seems reasonable to assume that a *radius of sensible magnitude* should be evaluated to at least 2 or 3 atomic diameters, which means spherical clusters consisting of 50 to 100 atoms or more. Clearly, clusters of that size can never be obtained by means of direct nucleation experiments. An evaluation based on Eqs. 25′ and 26′ for σ_{Ag}=9,2.10^{-5} J and T=298 K shows that even for 10-atomic hemispherical silver clusters, the nucleation work $\Delta\widetilde{G}$ (10) has a value of 3,6.10^{-19} J (87,5 kT

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[6] Note that Max Volmer [9] also cited this comment of Gibbs and apparently shared his opinion. Equation (III) is analogous to Eqs. (26) and (26′) of the present article but refers to homogeneous nucleation from a vapor phase.

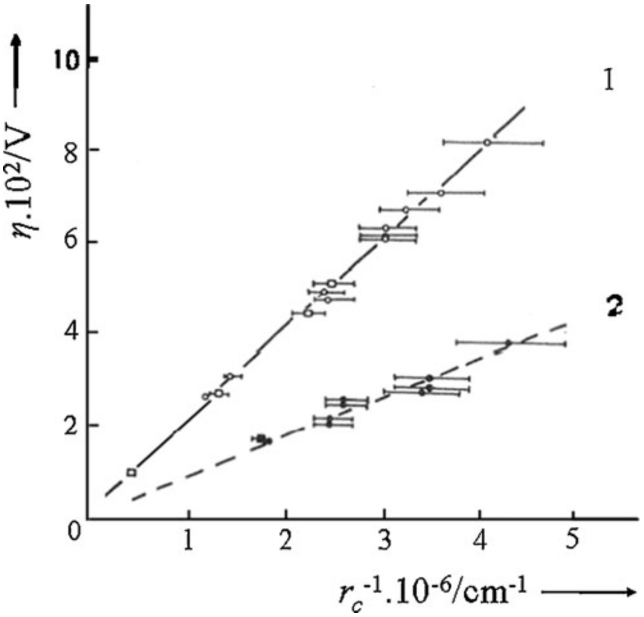


Fig. 9 η versus r_c^{-1}relationships (*1*) in absence and (*2*) in presence of a gelatin overlayer (after [46], see also [42, 44, 45])

units), which makes the stationary nucleation rate $J_0 \sim \exp\left[-\Delta\widetilde{G}(N_c)/kT\right]$ practically equal to zero. Indeed, detailed experimental studies of the nucleation kinetics performed in various physical systems unambiguously show that the size of the critical nuclei does not exceed several atoms. Namely, this fact initiated the atomistic considerations of the phase formation kinetics, first in the case of heterogeneous nucleation from a vapor phase [47–49] and then also in case of electrocrystallization [50–52] (see also [24]).

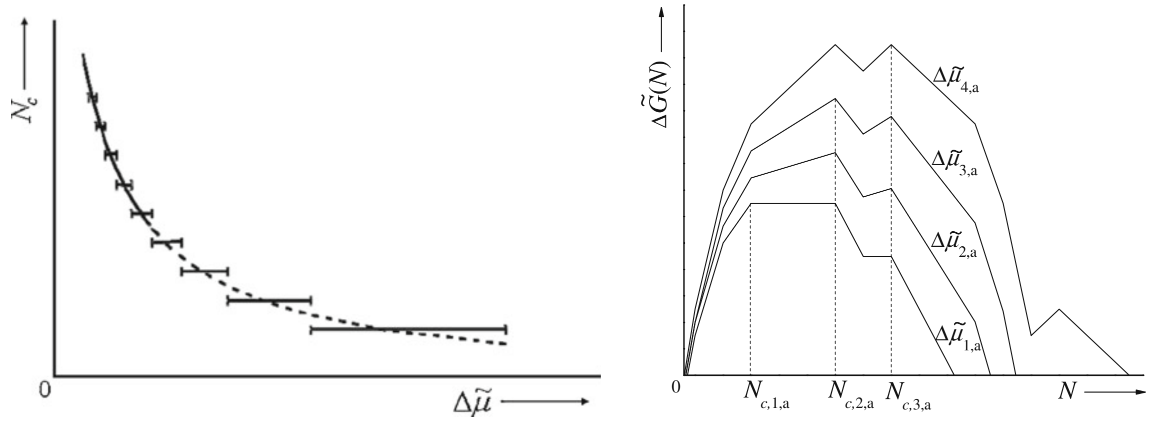
Without entering into the details of this subject, I will only point out that due to the discrete character of the clusters' size alteration at small dimensions, it turns out that to each critical nucleus corresponds a supersaturation interval and not a fixed supersaturation. With decreasing the supersaturation, the intervals become shorter and turn into the fluent curve predicted by the classical nucleation theory (Fig. 10a). As for the $\Delta\widetilde{G}(N)$ vs N relationship, it contains several minima and maxima, the highest maximum corresponding to the work $\Delta\widetilde{G}(N_c)$ of formation of the critical nucleus within the corresponding supersaturation interval (Fig. 10b). Thus, the $N_{c,2,a}$—atomic cluster is a critical nucleus for all supersaturations $\Delta\widetilde{\mu}$ from the interval $[\Delta\widetilde{\mu}_1, \Delta\widetilde{\mu}_4]$, except for $\Delta\widetilde{\mu}_4$ at which the critical nucleus consists of $N_{c,3,a}$ atoms.

The discrete change of the clusters' size affects also the shape of the supersaturation dependence of the stationary nucleation rate J_0 which turns from a fluent curve at low to a broken straight line at high supersaturations (Fig. 11), the slopes of the straight line portions giving the size N_c of the corresponding critical nuclei [24, 38, 50–52] according to:

$$N_c = kT\frac{d\ln J_0}{d\Delta\widetilde{\mu}} - \alpha \qquad (30)$$

Experimental studies of the nucleation kinetics of silver on glassy carbon [53, 54] and of copper on palladium [55] performed in wide overpotential intervals provided the possibility to determine the free energy excess $\widetilde{\Phi}(N_c)$ and the nucleation work $\Delta\widetilde{G}(N_c)$ of critical nuclei consisting of 1 to 4 atoms using the general theoretical expressions (21)–(23). This was certainly an important result bearing in mind the decisive role of small clusters in the first-order electrochemical phase transitions. A detailed comparative analysis of experimental data for the stationary nucleation rate J_0 based on the classical and the atomistic nucleation theories can be found also in [24, 38].

The atomistic nucleation theory is sometimes considered as a theory for high supersaturations, but this definition is



(a) (b)

Fig. 10 N_c vs $\Delta\widetilde{\mu}$ (**a**) and $\Delta\widetilde{G}(N)$ vs N (**b**) relationships according to the atomistic nucleation theory [24]

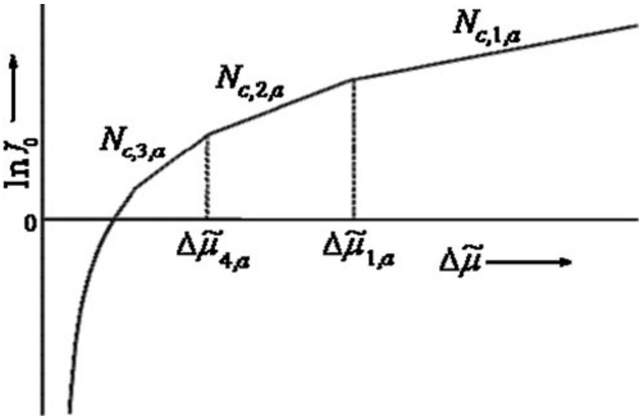


Fig. 11 Supersaturation dependence of the stationary nucleation rate

not quite precise. The reason is that in the case of heterogeneous nucleation, the size of the critical nuclei depends strongly on the specific "cluster-foreign substrate" interaction. For example, the 4-atomic silver cluster was found to be the critical nucleus within the overpotential interval 0.025÷0.051 V, $\Delta\tilde{\mu}=(4\div8).10^{-21}$ J [54] and a simple evaluation based on the classical formula (25′) for $\sigma_{Ag}=9{,}2.10^{-5}$ J and $\gamma_0=180^0$, $F(\gamma_0)=1$ shows that at $\eta=0.025$ V ($\Delta\tilde{\mu}=4.10^{-21}$ J), a homogeneous (spherical) silver cluster should consists of $1{,}2.10^5$ silver atoms. Apparently, this is a value high enough to rank $\Delta\tilde{\mu}=4.10^{-21}$ J among the low supersaturations. Therefore, the experimentally determined value of $N_c=4$ atoms [54] is due to the strong interaction between the cluster's atoms and the glassy carbon surface. All this means that the atomistic nucleation theory must be defined as a theory for small critical nuclei, and one should not forget that a small nucleus does not necessarily mean high supersaturation.

In 1976, I read a paper by Graham Hills published in *Electrochimica Acta*, and it came to my attention that one of the obtained experimental results could have had a different interpretation than the offered one. So, I wrote him a short letter explaining my point of view. The answer arrived a month later, and it was unexpectedly exciting: Professor Hills, who at that time worked in the University of Southampton, was inviting me to join his group for 1 year with the support of the British Council. I suppose that readers from former Eastern Block countries, who were born around or before the early sixties, would remember very well that such a visit could only take place on one condition: the Bulgarian state security service had to give the final go-ahead. I duly applied for permission, and I got it: being invited for 1 year in the spring of 1976, I was allowed to go to Southampton for 3 months in the autumn of 1978!

I spent three wonderful months in England, and this is how I met also the other members of the Southampton electrochemistry group: Martin Fleischmann, Alan Bewick, Laurie Peter, Derek Pletcher, and others. I stayed in the hotel for the first week, but after that, Graham invited me to live in his house, and we had enough time to talk at length not only about science but also about art, music, and politics. Graham suggested to me to work with his PhD student Ben Scharifker from Venezuela, which we did—very often until the small hours of the morning! I must admit that it was me who insisted to work that hard. The main reason was that in Sofia, after having received the permission to go to Southampton, one member of the Communist party made violent efforts to convince me that my trip would just be a waste of time because nothing worthwhile could possibly be achieved within 3 months. Probably, I went too far with my efforts to prove the opposite! Later on, the results from this joint work were included in Ben's thesis and were also published [56].

In 1980, Graham and Ben visited Sofia, and we spent a nice week together, not only working but also visiting some beautiful places in my country. The two dear guests were able to learn something about the Bulgarian way of life, as well. Late one evening, after visiting Professor R. Kaischew at his home, where his wife cooked a special Bulgarian dinner for us, I asked Ben about his impressions of the stay in Sofia. His answer was: "I have the feeling that I met a remarkable person!" Ben meant Rostislaw Kaischew, and I think that he was right (Photo 7)!

The people in the photograph, right to left, are: Ben Scharifker, Rector of the University "Simon Bolivar" in Caracas in the period 2005–2009, now President of the Academy of Physical, Mathematical and Natural Sciences of Venezuela, Rostislaw Kaischew, Sir Graham Hills, Principal and Vice-Chancellor of the University of Strathclyde, Glasgow in the period 1980–1991, and

Photo 7 *Right to left* B. Scharifker, R. Kaischew, G. Hills, and A. Milchev in the court of the Samokov's monastery, 1980

Photo 8 R. Kaischew and A. Milchev, March 1, 1998, Institute of Physical Chemistry, BAS, Sofia

myself, the author of the article you are reading. I look a bit different now, 31 years later.

Conclusion

The main purpose of this review was to comment upon some fundamental concepts related to electrocrystallization, and I hope that the subjects have been properly selected. I would like to think that the reader has also enjoyed the short stories about the founders of the contemporary nucleation and crystal growth theory: M. Volmer, W. Kossel, I.N. Stranski, R. Kaischew, and L. Krastanow. More on, this subject can be found in the book *Rostislaw Kaischew—life dedicated to science* compiled by S. Stoyanov and myself and published in 2003 [57]. The first part of it contains R. Kaischew's recollections of the remote past when the studies of crystal growth started. The second part contains memories of R. Kaischew written by 12 of his closest followers and coworkers. Perhaps, it is worth translating this book in English, and we have to think about that (Photo 8).

On March 1, 1998, Rostislaw Kaischew celebrated his 90th anniversary. He passed away 4 years later, on November 19, 2002, with his intellectual capacity and clarity of thought preserved up to his very last days. Nowadays, the Institute of Physical Chemistry, BAS, and a street nearby are named after him.

As for myself, I am trying to do my best for my science. Of course, I am not sure that I always succeed but I am trying.

Acknowledgments I would like to express my sincere gratitude to Prof. V. Chakalov and to his daughter, Dr. L. Chakalova, for their help and friendship.

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