

# Electrochemical nucleation theory

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**Abstract** — The kinetic model of electrochemical nucleation of micro- and nanoparticles is studied. The functional dependence of probability of the energy of the particle on the relative radius found earlier is used in nucleation in the statistical Heisenberg model. On the basis of the proposed theory, a simple ratio for calculation of probabilities of kinetic processes is obtained for the case of electrochemical nucleation.

**Index Terms** — micro- and nanoparticles, electrochemical nucleation, kinetic model.

## I. INTRODUCTION

The control of the dimensions of the particles and layers of particles in the electrochemical processes is one of the basic problems of the various forms of electrochemical technologies. The transition from macro- to micro- and nano- technologies is one of the basic tendencies in the development of the modern electrochemical dimensional treatment methods. The nucleation phenomenon plays a dominant role in the nano-treatment processes. The nucleation phenomenon, i.e., the formation of the nuclei, has long been studied in kinetic of phase transition. Along with the particular technological problems of the resolution of the electrochemical questions, are the general approaches to these problems, specifically, the evaluation of the possible dimensions of the particles and their connection with the energetic parameters. The present article is devoted to this question. While the first part of the article is a critique of the conventional thermodynamic approach, in the second part we point out the place of this approach and find its applicability criterion.

The thermodynamic approach makes it possible to obtain simple relations for the radius of the resulting particle  $r_c$  [1]:

$$r_c \sim K\sigma/\mu, \quad (1)$$

where  $\sigma$  is the specific surface energy and  $\mu$  is the change of the volume energy in the phase transition (i.e., upon nucleation),  $K$  is the particle shape factor. The account for the fact that nucleation may take place on the surface of the macroscopic body (or in the pores) reduces in essence the change of the constants in the equation (1) with account for the phenomenological interaction with the surface of the macroscopic material. The further generalization of the results of the thermodynamic relations to the evaluation of the kinetic phenomena reduces to the introduction of the equilibrium thermodynamic potential (with account for formula (1)) and the use of fluctuation theory. However, in this approach the connection between the thermodynamic concepts and the possible statistical model that is able to include the nucleation phenomenon is not a priori evident. At the present time the computational methods are used for the statistical models, but in this case it is difficult to

generalize the solution and compare it with the general thermodynamic relations. Therefore, the analytic solutions are of interest particularly since – in our view – the solution of a similar problem has already been examined ([2-5] where the two-dimensional model that is not completely adequate for our problem was examined) is not entirely suitable for the discussion of the physics on the subject phenomenon. Therefore, the first objective of the present work is to derive the analytic expression that is convenient for the discussion – and to draw conclusions relating to the corresponding nucleation problem. We shall show that the division of the total system energy into the free surface energy and the bulk (corn) energy for the phenomenon of the nucleation of the micro- and nano-particles - as was done in [1] - is quite arbitrary. This division is easily realized for the systems with induced anisotropy.

## II. STATISTICAL MODEL

The classic Heisenberg statistical model for the two-dimensional space that is applicable for the study of the magnetization of the ferromagnetic material is examined in [2]. It is known that the statistical sum and the thermodynamic functions are determined by the local energy minima. We shall use the variation minimum of the exchange energy (in the cylindrical coordinate system) that was proposed in [2]. As in [2 - 5], we examine the low-temperature limit, when a single energy minimum is significant. Therefore, we replace the variation of the free energy by the variation of the energy of statistical model (we will discuss this approximation later):

$$\delta \int T(\rho) dv = 0, \quad (2)$$

the integration is performed over the entire volume  $\mathbf{v}$  of particulars, and

$$T(\rho) = A/2\{(\theta')^2 + a^2(\sin \theta)^2/\rho^2\}, \quad (3)$$

where  $\rho = r/r_c$  is the radial relative coordinate ( $0 < \rho < 1$ ),  $\theta(\rho)$  is the angle between the cylinder axis and the magnetization vector ( $\pi < \theta(\rho) < \pi/2$ ),

$$a^2 = (B-1)/A, \quad (3a)$$

where  $A$  is the exchange interaction constant,  $B$  is anisotropy coefficient [2 - 5].

We will examine the nucleation of cylindrical particle. The exchange energy  $T(\rho)$  is the classic analog in the Heisenberg model for the two-dimensional space (see, for example, [2]). Then follows from (2) and from (3) the known nonlinear equation that was presented, specifically, in [2 - 5]:

$$\theta''(\rho) + \theta'(\rho)/\rho - [a^2 \sin\theta \cos\theta]/\rho^2 = 0. \quad (4)$$

To find the nohomogeneous equation that physically describes the nucleation process, we specify the corresponding boundary conditions in the form

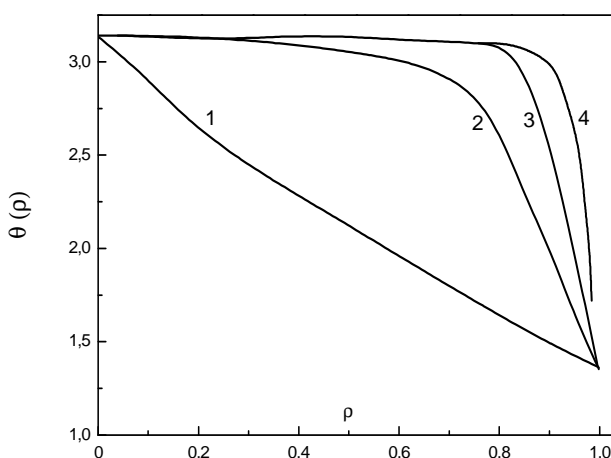
$$\begin{aligned} \theta(\rho) &= \pi, \quad \rho = 0; \\ \theta(\rho) &= \pi/2, \quad \rho = 1. \end{aligned} \quad (5)$$

The analogous problem of determining the magnetization of the infinite cylinder was examined previously [2 - 5], for which was found the analytic relation:

$$\text{tg}\{\theta/2\} = 1/\rho^a. \quad (6)$$

We note that the mathematical solution (6) of the equation (4) was also examined in [2]. This solution is termed the two-dimensional soliton (instanton) and is a rare example of the exact analytic solution of the nonlinear problem.

It is possible to obtain the analytic solution which corresponds only qualitatively to the real situation. We see that the obtained solution does not make it possible to clearly divide the system energy into the surface energy and the core energy. We can consider that this conclusion will remain valid with the increase of temperature. Consequently, the simplified model corresponds to the real physical problem. We shall examine the general case that corresponds to the exactly solvable model. This case makes it possible to find the criterion that determines when the expression (1) can be used adequately. We should present calculation of change of the angle  $\theta$  from the beginning of coordinates (when  $\rho = 0$ ) a cylindrical particle up to its surface (when  $\rho = 1$ ).



**Fig.** Function  $\theta(\rho)$  is the angle of an inclination to an axis of the cylinder (which characterizes energy of a particle in Heisenberg model from the given radius  $\rho$  coordinates of a particle).

If  $a = 1$ , there is no anisotropy in the system, and if  $a > 1$ , the external anisotropy exceeds the exchange interaction in the system.

To compare the results for the two cases, we present the calculated variation of the angle  $\theta$  from the coordinate origin (where  $\rho = 0$ ) of the cylindrical particle to its surface (where  $\rho = 1$ ) (fig.). At the same time, (fig.) let us limit our examination to the two extreme cases of the value of the parameter  $a$ :

(1) curve 1 corresponds to the case  $a = 1$ , which relates to the condition when microscopic anisotropy is absent,

(2) curve 2 corresponds to the case  $a = 10$ , which refers to the condition when microscopic anisotropy exists,

(3) curve 3 corresponds to the case  $a = 50$ ,

(4) curve 4 corresponds to the case  $a = 100$ .

It is shown that, in the first case, it is difficult to isolate the volume of the cylinder that can be attributed to the surface energy, since the angle  $\theta$  changes smoothly as a function of  $\rho$ . In the second case, when  $a = 10$ , a range can be chosen whose volume amounts to the surface energy of the cylindrical particle. In the framework of our qualitative examination, we may conventionally assume, for example, that the surface layer is counted from the value  $\rho \sim 0.8$ . We make this choice using only the shape of curve 2, which sharply decreases for  $\rho > 0.8$ . The volume that defines the surface energy of the cylinder amounts to 30% of the cylinder's volume in this case. When  $a$  increases further (for example, by a factor of  $a = 100$ ), this volume will amount to less than 10% of the cylinder's volume.

### III. TERMODINAMIC ANALIZE

Formation of nanocrystalline structures often depends on the kinetics of nucleation, which includes the thermodynamics of the nucleation process only as an elementary step or event. Thus, the most probable dimensions of the particles in various physicochemical processes are also determined from simple thermodynamic relationships involving thermodynamic functions. The nucleation is usually treated as a chain of sequential processes; that is, the  $N$ -atom nucleus is formed by addition of one atom to an  $(N - 1)$ -atom cluster or by a similar loss of atoms. Constructing a chain of Markov processes, one can obtain the Einstein-Fokker-Planck equation. It is worth noting that the kinetics of the nucleation process is simplified if the process of steady-state nucleation is examined. Therefore, we shall further evaluate the possible dimensions of the particles and their correlation with the energy parameters using the simple ideas and thermodynamic functions.

The further analysis of the kinetic phenomena reduces to description where the velocity of the steady-state stream of formation of the most probable nuclei is defined as [1, 4, 5]

$$J \sim \exp \{- E_a / k T\}, \quad (7)$$

where  $E_a$  is the activation energy of formation of the nucleus. The solution of the problem further reduces to calculation of the magnitude of the activation energy.

Further, we assess how the free energy changes from the center of the particle to its surface. The layer-by-layer change of the free energy of the cylindrical particle is examined. The formula for the energy that was used to obtain the equation of motion has the form

$$\int E(\rho) d v \sim E_a, \quad (8)$$

the integration is performed over the entire volume  $v$  of particulars, and

$$E(\rho) = T + W, \quad (9)$$

- a) where  $T$  is determined in (3), and  $W$  is determined as:

$$W = A (a^2 - 1) \sin^2 \theta / 2 \rho^2. \quad (10)$$

- b) We use the solution (8) in equation (9), and we find:

$$T + W = 2 A a^2 (\rho)^{2a} / [\rho^2 (1 + \rho^{2a})]. \quad (11)$$

Let's analyze solution (11). In that specific case of absence of anisotropy (when  $a^2=1$ ) energy of the surface of the cylinder (at  $\rho^2=1$ ) goes to  $A$ . In a case when  $a^2>1$ , the energy on a surface of the cylinder goes to  $A a^2$ . It is possible to consider given parameter  $A a^2$  as the value of the surface energy.

The energy inside a particle goes to not zero value if  $a^2=1$ . On the other hand the energy is equal to zero if  $a^2>1$ . Characteristic gap of free energy can correspond to phase transition, when in system is infinitesimal anisotropy. Such phase transition can give the result in jump of change of distribution of magnetization. The similar phase transitions are known. It is received here as the simple analytic solutions. The energy  $T$  of particles, in a case  $a^2=1$ , is equal  $A$ .

With decrease of sizes of particles the role of a thermodynamic condition the surface is increasing. The given elementary model showed, that in this case becomes difficult to separate thermodynamic functions on the volumetric thermodynamic functions and the surface thermodynamic functions. It is possible to do using large parameter  $a^2 > 10$ .

#### IV. ELECTROCHEMICAL NUCLEATION

Then we shall investigate the physical nature of the examined anisotropy for the case of electrochemical nucleation. This anisotropy can be generated using the distribution of the electric field in the near-electrode layer,

because the dimensions of the particles become comparable with the dimensions of the layer.

Let the surface energy change in the nucleation process according to the Lippman equation [6]:

$$- d\sigma = q d\varphi, \quad (12)$$

where  $q$  and  $\varphi$  are the charge and potential on the surface. In the approximation of the constant capacity of the double layer  $C$

$$q = C \varphi. \quad (13)$$

We obtain for the change in the surface energy  $\sigma$

$$\sigma = C (\varphi)^2 / 2. \quad (14)$$

The change in the surface energy may be due to the anisotropy introduced above. Actually, if we assume that an asymptotic functional dependence occurs,

$$(\varphi)^2 \sim 1 / \rho^2, \quad (15)$$

then we finally obtain for the parameter  $a^2$  [5]:

$$a^2 / r_c = C / 2, \quad (16)$$

where  $r_c \sim 10^{-6}$  cm is the equilibrium value of the nanoparticle dimension.

For the evaluation, we take the capacity of a mercury electrode that is known to be on the order of

$$C / 2 \sim 10^7 \text{ (1/cm)} \text{ (CGS)} \quad (17)$$

If we confine ourselves to the upper limit of the  $r_c$  value, then we obtain for the evaluation of the dimensionless quantity  $a$

$$a \sim 10. \quad (18)$$

Generally results of consideration have qualitative character.

#### V. KINETIC OF THE NUCLEATION PROCESS

In the framework of the case where formula (7) is applicable, we obtain the formula for the velocity of the steady-state stream of formation of the most probable nuclei in the form (8)

$$J \sim \exp \{- (2 A a^2 D(a) V) / r_c k T\}, \quad (19)$$

where  $V$  is the volume of the particle,

$$D(a) = \int_0^1 \rho d \rho \frac{\rho^{2a}}{[\rho (1 + \rho^{2a})]^2} \quad (20)$$

Let us consider the physical meaning of formula (20).

The factor

$$A a^2 \sim B \quad (21)$$

represents the specific surface anisotropy having an electrochemical nature, and  $\mathbf{D}(\mathbf{a})$  is the fraction of the surface with the given energy. Thus, we come to formula (7), where  $\mathbf{E}_a$  has the meaning of the surface energy of the nanoparticle (which dominates in the given case).

Let us discuss a possible variant of a high-temperature limit of the kinetic theory. With increasing temperature, the processes of growth of a stationary stream due to temperature transitions over the energy barrier of the instanton are possible. The energy height of the barrier (by analogy with magnetic problems) is defined in this case by the magnitude:

$$E_a \sim (BA)^{1/2} / r_c \quad (22)$$

For the potential energy of our topological model, we introduce instead of the usual time a complex time inversely proportional to the temperature [7]. Then we obtain for the evaluation of the potential barrier

$$W \sim (1 - \exp \{- (BA)^{1/2} V / r_c k T\}) \quad (23)$$

The aforementioned effects will be significant only for temperatures

$$k T_c \sim (BA)^{1/2} V / r_c \quad (24)$$

Note that, precisely for such temperatures, the conditions of steady-state kinetics are violated. In this case, no activation processes that we do not examine here will define the kinetics of the process. Therefore, we shall consider the following expression to be the applicability criterion of (16):

$$T < T_c \quad (25)$$

It is clear from simple physical reasons that, when the temperature approaches the critical value  $T_c$ , the formed particles will begin to be destroyed owing to the effect of the temperature. To assess  $T_c$ , we assume that the volume of the particle  $\mathbf{V}$  is on the order of  $10^{-24} \text{ m}^3$ , and

$$E_a / V \sim \text{from } 10^2 \text{ J m}^{-3} \text{ to } 10^1 \text{ J m}^{-3}. \quad (26)$$

Then we obtain for  $T_c$  the range from  $100^0 \text{ K}$  to  $1000^0 \text{ K}$ . Note that an increase in the energy of anisotropy also leads to an increase in the temperature limit at which the conditions of steady-state kinetics are not yet violated conclusion section is not compulsory.

## VI. CONCLUSION

With decrease of the dimension of the particles, the thermodynamic state of its surface will play an ever increasing role in describing its thermodynamic state. This article presents a very simple model that shows it becomes more and more difficult to separate the thermodynamic functions into the core and surface functions.

The physical consequence of the examined model reduced to the fact that this separation into the core energy and the surface energy can be performed if the anisotropy in the system significantly exceeds the close-order isotropic exchange interaction.

The concept of the energy of anisotropy, introduced in theory acquires the meaning of the electrostatic energy of a double electric layer. With the aim of creating equilibrium particles with nanodimensions, the electric capacitance of the system where such a particle is grown should be increased.

For the velocity of the steady-state stream of for motion of the most probable nuclei, we obtain a result that allows us to suggest that effective control is possible over the nucleation process by electrochemical methods

## ACKNOWLEDGMENTS

The author thanks A. I. Dikumar for their participation in discussion of the results.

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