A NEW THEORY OF ELECTROCHEMICAL NUCLEATION

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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 calculating the probabilities of kinetic processes is obtained for the case of electrochemical nucleation.

1. Introduction

The control of the particle size and layers of particles in electrochemical processes is one of the basic problems of the various forms of electrochemical technologies. The transition from macro- to micro- and nanotechnologies is one of the basic tendencies in the development of modern electrochemical dimensional treatment methods. The nucleation phenomenon plays a dominant role in the nanotreatment processes. The nucleation phenomenon, i.e., the formation of the nuclei, has long been studied in the kinetics of phase transition. Along with particular technological problems concerning the solution of electrochemical issues, there are the general approaches to these problems, specifically, the evaluation of the possible particle sizes and their relationship with the energy parameters. The present study is focused on this problem. The first part of the manuscript 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]:

$$r_c \sim K\sigma/\mu \quad , \tag{1}$$

where σ is the specific surface energy and μ is the change in the volume energy in the phase transition (i.e., upon nucleation), and K is the particle shape factor. The account for the fact that nucleation can take place on the surface of a macroscopic body (or in the pores) reduces in essence the change in the constants in equation (1) with allowance for the phenomenological interaction with the surface of the macroscopic material. A 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 the fluctuation theory. However, in this approach, the relationship between the thermodynamic concepts and the possible statistical model that can include the nucleation phenomenon is not a priori evident. At the present time, the computational methods are used for the statistical models; however, 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 because—in our view—the solution of a similar problem has already been examined ([2–5] where a 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 concerning the respective nucleation problem. It will be shown 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 nanoparticles—as was done in [1]—is quite arbitrary. This division can be easily implemented for the systems with induced anisotropy.

2. Statistical model of Heisenberg

The classic Heisenberg statistical model for the two-dimensional space, which 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 where a single energy minimum is significant. Therefore, we replace the variation of the free energy by the variation of the energy of a statistical model (we will discuss this approximation later):

$$\delta \int T(\rho)\, dv = 0, \tag{2}$$

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

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

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

$$a^2 = (B-1)/A\ , \tag{3a}$$

where A is the exchange interaction constant and B is the anisotropy coefficient [2–5].

Examine the nucleation of a cylindrical particle. Exchange energy $T(\rho)$ is the classic analog in the Heisenberg model for the two-dimensional space (see, for example, [2]). The known nonlinear equation, which was presented, specifically, in [2–5], follows from (2) and (3):

$$\theta''(\rho) + \rho^{-1}\theta'(\rho) - \tfrac{1}{2} a^2 \rho^{-2} \sin 2\theta(\rho) = 0. \tag{4}$$

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

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

A similar problem of determining the magnetization of an infinite cylinder was examined previously [2–5], for which the analytic relation was found:

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

Note that the mathematical solution (6) of equation (4) was also examined in [2]. This solution is referred to as the two-dimensional soliton (instanton); it is a rare example of an exact analytic solution of the nonlinear problem.

It is possible to obtain an analytic solution that corresponds only qualitatively to the real situation. It is evident that the obtained solution does not make it possible to clearly divide the system energy into the surface energy and the corn energy. It can be assumed that this conclusion will remain valid with an increase in temperature. Consequently, the simplified model corresponds to the real physical problem. Examine the general case that corresponds to an exactly solvable model. This case makes it possible to find the criterion that determines cases where expression (1) can be used adequately.

We should present the calculation of the change in angle θ from the origin of coordinates (where $\rho = 0$) for a cylindrical particle up to its surface (where $\rho = 1$).

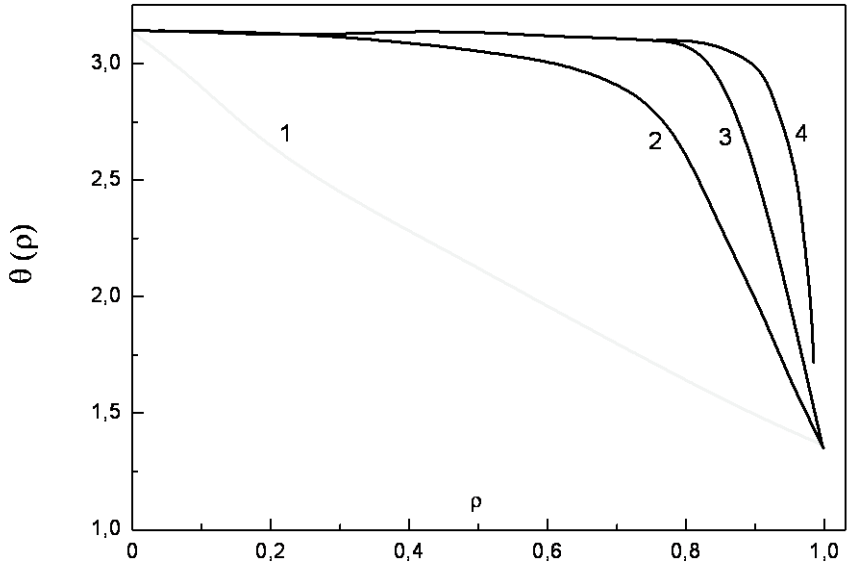

Fig. 1. Function $\theta(\rho)$ is the angle of inclination to the axis of a cylinder (which characterizes the energy of a particle in the Heisenberg model from a given radius ρ in coordinates of the particle).

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 angle θ from the coordinate origin (where $\rho = 0$) of the cylindrical particle to its surface (where $\rho = 1$) (Fig. 1). At the same time, let us limit our examination to the two extreme cases of the value of parameter a (Fig. 1):

(i) curve *1* corresponds to the case of $a = 1$, which refers to the condition where microscopic anisotropy is absent,

(ii) curve *2* corresponds to the case of $a = 10$, which refers to the condition where microscopic anisotropy exists,

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

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

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 angle θ changes smoothly as a function of ρ. In the second case, where $a = 10$, 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 of $\rho \sim 0.8$. 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. As a increases further (for example, by a factor of $a = 100$), this volume will amount to less than 10% of the cylinder's volume.

3. Thermodynamic analysis

The 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 a description where the velocity of the steady-state stream of formation of the most probable nuclei is defined as [1, 4, 5]

$$J \sim exp \{- E_a / k T\}, \tag{7}$$

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

$$\int E (\rho) \, d \, \mathrm{v} \sim E_a , \tag{8}$$

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

$$E (\rho) = T + W \tag{9}$$

where T is determined in (3), and W is determined as

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

We use solution (8) in equation (9), and we find

$$T + W = \frac{4Aa^2\rho^{2a}}{[\rho(1+\rho^{2a})]^2} \tag{11}$$

Let's analyze solution (11). In that specific case of the absence of anisotropy (at $a^2=1$) the energy of the surface of the cylinder (at $\rho^2=1$) goes to A. In a case where $a^2>1$, 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 zero if $a^2>1$. The characteristic gap of free energy can correspond to a phase transition where infinitesimal anisotropy is present in the system. This phase transition can result in a jump of the change in the distribution of magnetization. Similar phase transitions are known. It is received here as simple analytic solutions. The energy T of particles, in a case $a^2=1$, is equal to A.

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

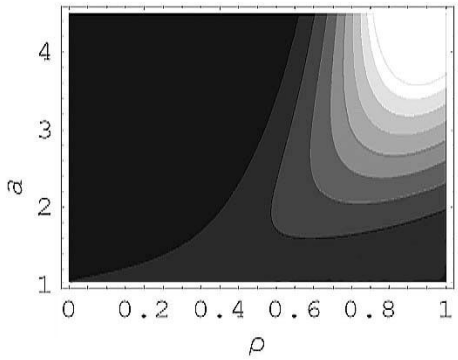

Fig. 2. Density plot for $E(\rho)/A$ as function of ρ and a.

4. Electrochemical nucleation

We shall now 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 particle sizes become comparable with the dimensions of the layer.

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

$$-d\sigma = q d\varphi, \tag{12}$$

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

$$q = C\,\varphi\,. \tag{13}$$

We obtain for the change in the surface energy σ

$$\sigma = C\,(\varphi)^2\,/2\,. \tag{14}$$

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

$$(\varphi)^2 \sim 1/\rho^2, \tag{15}$$

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

$$a^2/r_c = C\,/2, \tag{16}$$

where $\boldsymbol{r_c} \sim 10^{-6}$ 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

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

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

$$a \sim 10\,. \tag{18}$$

Generally, results of consideration are qualitative.

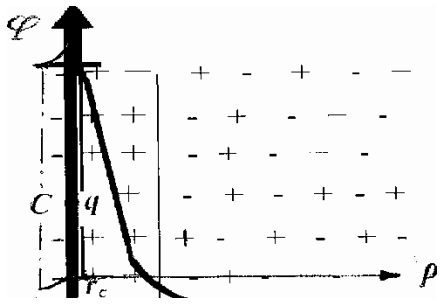

Fig. 3. Scheme of the physical process of nucleation for the case of electrochemical nucleation. The charge is q, the potential is φ. The capacity of the double layer is C. The relative coordinates of particle is ρ, the radius of particle is r_c.

5. 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):

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

where V is the volume of the particle

$$D(a) = \int_0^1 (\rho)\ \text{I}\Theta/[\rho\ (\ \mathbf{1} + \rho\text{I}\Theta)\text{I}]\ d\ \rho\,. \tag{20}$$

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

Factor

$$A\, a^2 \sim B \ , \tag{21}$$

represents the specific surface anisotropy having an electrochemical nature, and $D(a)$ is the fraction of the surface with the given energy. Thus, we come to formula (7), where 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:

$$E_a \sim (B\, A)^{1/2} / r_c \tag{22}$$

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, for the evaluation of the potential barrier, we obtain

$$W \sim (1 - exp\, \{- (B\, A)^{1/2}\, V / r_c\ k\, T\}). \tag{23}$$

The aforementioned effects will be significant only for temperatures

$$k\, T_c \sim\ (B\, A)^{1/2}\, V / r_c\ . \tag{24}$$

Note that, precisely for these 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):

$$T < T_c \tag{25}$$

It is clear from simple physical considerations that, when the temperature approaches 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 V is on the order of 10^{-24} m^3, and

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

Then we obtain for T_c the range from 100^0 to 1000^0 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 have not yet been violated.

5. Conclusions

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

The physical consequence of the examined model reduced to the fact that this separation into the corn 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 the 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 this particle is grown should be increased.

For the velocity of the steady-state stream for the motion of the most probable nuclei, we obtain a result that suggests that it is possible to effectively control the nucleation process by electrochemical methods.

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