

On the Possibility of Using the Cahn–Hilliard Model to Describe Electrodeposition of Nanostructures

S. A. Baranov^{a, b, c}

^a*Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD–2028 Republic of Moldova*

^b*Shevchenko Transdnestrian State University, Tiraspol, Republic of Moldova*

^c*Département de Génie Physique, École Polytechnique de Montréal, C.P. 6079, succ. Centre-ville, Montréal H3C 3A7, (Québec) Canada*

e-mail: baranov@phys.asm.md, sabaranov07@mail.ru

Received February 22, 2016

Abstract—The possibility of using the Cahn–Hilliard theory in the process of electrodeposition of nanostructures is studied. A correlation between the microscopic parameters included in the calculation formulas and the experimental kinetic coefficients is found. The theoretical results can explain the choice of the optimal parameters of electrochemical deposition.

Keywords: electrochemistry, nucleation of nanoparticles, phase transitions

DOI: 10.3103/S1068375517020028

INTRODUCTION

It has been demonstrated in recent research studies (e.g., [1]) focused on electrochemical co-deposition of alloys containing Co and W that nucleation plays a key role in obtaining these elements (nanoparticles, NPs) upon the formation of galvanic coatings consisting of nanostructures. Let us mention right away that although nucleation is always an appreciably complex kinetic process (e.g., [2, 3]), the investigation of the tendency of the formation of these structures from NPs may primarily depend on using a correct model for calculating the thermodynamic functions.

This study aims to discuss the possibility of assessing the NP size by finding the functional relationship between the thermodynamic parameters. We believe that this is of prime interest in the elaboration of the theory of processes related to nanonucleation (in particular, in electrochemistry). Nanonucleation is broadly understood both as a process of electrodeposition of NPs and etching nanodots (nanoholes).

Let us provide explanatory estimations from [1], which in particular allow one to assess the relevance of this theoretical study. Weston et al. [1] applied the model that was used in the Cahn–Hilliard–Hillert (CHH) theory [4–10] to interpret the fabrication of nanocrystalline coatings from an intermetallic compound with a composition close to that of Co₃W. According to this model, the size of the nanostructures being separated (NPs or concentration fluctuations that correspond to the NP size) is assessed using

the formula derived in the CHH theory and is written as (the notation is taken from [1]):

$$\lambda \approx 4\pi(|K/G_{xx}|)^{1/2}, \quad (1)$$

where λ is the wavelength corresponding to the NP size and is estimated as $\sim(6–10) \times 10^{-9}$ m. The magnitude of λ is related to the macroscopic properties of the coating, such as its microhardness (in the well-known interpretation of the Hall–Petch relations).

Parameter K can be denoted as a gradient energy term (the details are provided below) that is determined by the value $\sim(10^{-8}–10^{-10})$ J/m and G_{xx} is the specific energy due to the change in chemical potential as the NP phase is separated. According to [1], this parameter strongly depends on the ratio between the Co and W concentrations in the coating. This specific energy can vary over a broad range, e.g., $\sim(1–10) \times 10^9$ J/m³. The alteration in NP size can be related to changes in the G_{xx} parameter, which needs to be substantially varied to interpret the experimental data. The latter statement is one of the conclusions drawn in [1].

Weston et al. [1] further demonstrated that at a certain tungsten concentration in the deposited layer, the NP size decreases abruptly, which is supposed to correspond to formula (1). The G_{xx} parameter is expected to change by no less than an order of magnitude.

We would like to discuss the estimation of the parameters included in formula (1) more thoroughly. Thus, the following reasoning can be used to estimate K :

the phenomenological parameter of specific surface energy σ_{in} , which has the order of magnitude

$$\sigma_{in} \sim (0.1-1) \text{ J/m}^2, \quad (2)$$

should be multiplied by the effective film thickness of the surface layer Δ_{in} , for which the following approximation can be used:

$$\Delta_{in} \sim (0.1-1) \times 10^{-7} \text{ m}. \quad (3)$$

Hence, the relationship

$$K \sim \Delta_{in} \sigma_{in} \quad (4)$$

is proposed to assess the K value.

$K \sim 10^{-8} \text{ J/m}$ is used for further estimations [1]. If $G_{xx} \sim 10^{10} \text{ J/m}^3$, the size of the NPs (the λ value according to [1]) lies in the nanosized range, which corresponds to the experimental data.

Meanwhile, the theory used in [1] is similar to the theory of micromagnetism [11–13], where the domain wall (DW) with size δ (a parameter identical to λ) is determined in the Bloch–Landau–Lifshitz–Döring (BLLD) theory as

$$\delta_{LL} \approx (\alpha/A_a)^{1/2}, \quad (5)$$

where $\alpha \sim 10^{-11} \text{ J/m}$ is the exchange interaction energy (i.e., the value smaller than K from (1) by several orders of magnitude) and A_a is the anisotropic energy, which is also lower than the corresponding G_{xx} value. In crystalline hard magnetic materials, the anisotropic energy can be of the order of magnitude $\sim 10^5 \text{ J/m}^3$, while in soft magnetic and amorphous materials, $\sim 1 \text{ J/m}^3$. The order of magnitude of the size of DW can be easily estimated: it is greater than the size of λ (i.e., a nanoparticle) by several orders of magnitude and corresponds to the microsized scale. Except for the numeric magnitude, both theories utilize at least the same calculation formulas and, therefore, the same mathematical models.

Hence, this work, looking ahead towards the further studies of this series, was broadly aimed at building the appreciably simple mathematical models to describe the nucleation phenomena; the parameters included in the final formulas need to be experimentally accessible. One of the major requirements for the theory described below is the possibility to obtain analytical expressions for the size of an equilibrium nanoparticle, which is a crucial condition for the practical prediction of coating properties upon electrodeposition. This will allow us to find and expand the area of application of the theory and obtain new results.

We suggest using the following order of presenting the material to achieve this goal:

(1) To ascertain the relationship between the earlier nucleation theory with the CHH theory [4–10] proposed in [1];

(2) To discuss the example of the theory variant close to the CHH theory but taking into account the case when the shape of an NP approaches a cylinder shape; and

(3) To study the possibility of wider use of the simplified variant of the theory similar to the CHH theory for the problem of phase transitions in the case when the shape of the resulting NPs is noncylinder.

We suggest that the key result of the study should be determining the role of each theoretical model in the problem of investigating an electrochemical NP, which emerges during the formation of galvanic coatings, similar to the case discussed in [1].

In the first part of the study, we will discuss the old variants of the nucleation theory in the ideology proposed by J.W. Gibbs.

The main focus is placed on generalizing the results of these theories; some new conclusions have been drawn in our opinion. The main idea is to demonstrate the relationship between the previous theories and the Landau theory of phase transitions that has been further developed into the Ginzburg–Landau–Abrikosov (GLA) theory.

In our next articles we intend to report the results of the original studies of the author that are primarily based on the chiral models used in modern statistical physics, the theory of micromagnetism, and the theory of elementary particles. In particular, this will allow considering only the two-dimensional models. A simplified version of the theory will be proposed to study the higher dimensional models.

BRIEF HISTORY: THE CURRENT STATE OF THE PROBLEM AND THE LINE OF RESEARCH IN NUCLEATION THEORY

Let us provide a brief scheme showing how the nucleation theory has been developed in a simplified table that makes no claims to thoroughly cover this topic, in the same order as it is given in the text of this article.

This scheme of development of the nucleation theory is far from complete (according to the citation) and is appreciably simplified. However, a number of the most interesting ideas of nucleation theory in the author's opinion are presented in the references section. In this case, it is by no means a comprehensive bibliography but just shows the overall tendency of theory development (and only from the author's point of view). References to other modern directions of nucleation theory are provided below.

However, if one makes a rougher classification, all theoretical studies could be subdivided into two parts:

(1) The thermodynamic theory that studies the stage of generating the critical equilibrium size of a

Table

1. The thermodynamic nucleation theory (TNT)	J.W. Gibbs theory [14] Theories proposed by M. Volmer, A. Weber, T. Erdey–Gruz, R. Becker, and W. Döring [15–18] Theory proposed by Ja.I. Frenkel [19]
2. The phenomenological theory of phase transitions	Landau’s theory [11, 20, 21]. Ginzburg–Landau (GL) theory: GLA theory
3. The kinetic methods for calculating the nucleation time	Methods proposed by A.N. Kolmogoroff (W. Johnson, R. Mel) and methods proposed by Ya.B. Zeldovich [22–26]; methods proposed by I.M. Lifshits, V.V. Slezov, and S. Wagner [27]
4. The theory of spinodal decomposition as applied to the nucleation theory	The theory proposed by J.W. Cahn, D.J.E. Hilliard, M. Hillert [4–9] and development of the theory by A.G. Khachaturyan [10]
5. Statistical nucleation theory for the case of a classical (continual) nonlinear two-dimensional model (the Heisenberg sigma models)	The instanton theory developed by A.A. Belavin and A.M. Polyakov [28] (as well as G. Woo [29]) and used by S.A. Baranov et al. [30–33] for nucleation and the theory of micromagnetism
6. Directions and other variants of the nucleation theory	F.F. Abraham; K. Binder; J.D. Gunton, J.S. Langer; S.R. Martin; O. Penrose; T.L. Hill; R. Kaishev; D. Kashchiev et al. [34–49]

nanoparticle nucleation center (in our classification it is mostly items 1, 2, 4, 5, and partially 6);

(2) The kinetic theory of growth of a new phase after a critical size is achieved (in our classification, it is 1, 3, and partially 6).

Only the first part (the processes of formation of particles of a critical size) will be studied in this article.

The key result of the kinetic theories is that after a nucleation center of a critical size is formed, its growth slows (at a different rate in different theories). Other critical nucleation centers are typically formed during this period of time. Therefore, the energy relationships emerging during the description of the first stage of nucleation are of interest for the electrochemical deposition discussed in this article. We will not take into account the coalescence processes and all the variants of the kinetics of absorption of smaller nucleation centers by larger ones. Let us assume that in the experimental situation under discussion [1] everything takes place in the Δr region where an NP is formed (Fig. 1).

Khachaturyan [10] demonstrated that the development of a quasi-periodic concentration instability can be suppressed. This statement was subsequently proved by the calculations made by Binder [36, 37].

In this study, we will not focus on the questions related to proving the possibility of the quasi-periodicity of the NP segregations, although they often play a crucial role. Let us discuss the dependence between the NP size and the thermodynamic parameters; the questions related to quasi-periodicity need to be discussed separately, since more complex models need to be developed in this case.

The formation of nanocrystalline structures is often determined by nucleation kinetics, with the ther-

modynamics of the nucleation process being only an elementary component. However, a simplified consideration can be used for the nucleation process (hereinafter, referred to as steady-state). In this case, if the most plausible size of NPs determined from the simple thermodynamic relations can be generated, the nucleation kinetics can be regarded as a chain sequence of processes. First, an NP nucleation center is formed in a fluctuating manner. This very nucleation center typically grows to reach the equilibrium size r_c . After it passes over the so-called equilibrium energy barrier, it can continue growing (its growth is described with a series of Markovian processes or, in a simplified manner, by the Frenkel–Zeldovich equation [2, 3, 22–24]); however, this growth will slow. The Einstein–Fokker–Planck equation [23] can be used to describe the kinetics in the simplest case.

The so-called process of steady-state nucleation is known to often take place in electrochemistry [1–3]. As a model, it ends at the stage when an NP with size $r \sim r_c$ is formed. The size of NPs and their relationship with the energy parameters can be derived based on the quasi-equilibrium thermodynamics. The further manipulations are reduced to the following semi-qualitative reasoning [19] according to which the dimensionless rate of a steady-state flow of the formation of the most plausible nucleation centers will be written as

$$J \sim \exp\{-\Delta E_c/kT\}, \quad (6)$$

where ΔE_c is the activation energy of the formation of an equilibrium nucleation center. The dimension of this activation energy is [J] per elementary particle (or degree of freedom). Hence, the dimensionless parameter

$$G = \Delta E_c/kT \quad (7)$$

is known as the Gibbs number and characterizes the rate of equilibrium nucleation.

The preexponential factor, which contains the so-called Zeldovich factor and a combination of other constants [2, 3, 14–19, 22, 23], as well as the possible entropy component, is omitted in formula (6). All the preexponential kinetic coefficients are clearly important, and a number of studies have focused on their calculation. However, it is always possible (and should be done) to single out this exponential component of the process related to an important physical parameter, the activation energy, when analyzing an experimental situation.

In this study, the solution of the problem will be reduced to calculating the change in the free energy needed for the formation of an NP, which actually, up to a constant, coincides with the activation energy and is a part of (6) and (7). However, this definition of the activation energy is not unequivocal. Therefore, we will subsequently often speak, instead of the activation energy ΔE_c , about the change in the free energy of the $\Delta G_c(N)$ system (related to a certain physical model) required for the formation of an NP of size r_c , which is prescribed in an abstract multidimensional (2, 3...N-dimensional) space.

Hence, the range of problems to be solved has been outlined: estimation of the most plausible radius r_c of an NP and the activation energy ΔE_c (or changes in the free energy of the $\Delta G_c(N)$ system depending on the thermodynamic parameters that are determined or calculated for this specific system). Let us start the discussion with the conventional Gibbs theory. We will demonstrate that it does not contradict the CHH theory and, therefore, the GLA theory.

DEVELOPMENT OF SOME REPRESENTATION UNDER THE GIBBS NUCLEATION THEORY

Historically, a number of researchers, who lived in different time periods and studied different thermodynamic and kinetic processes, have made an equal contribution to the classical approach to the problem of nucleation. The fundamental ideas have been developed by Gibbs (e.g., [14]). Volmer, Becker, Döring, and Frenkel subsequently developed these ideas to a different extent [15–19]. This list of scientists associated with the classical nucleation theory can be continued; thus, let us denote this theory as the classical nucleation theory (CNT).

Below we will extrapolate the CNT to an abstract multidimensional space by assuming it to be a topological projection when taking into account the coordination spheres following the first one. Simultaneously, we will demonstrate that the CNT and the CHH theory at least do not contradict one another using fairly simple examples. Let us note that during the formation of a spherical nucleation center of radius r_N in three-dimensional space (the so-called droplet

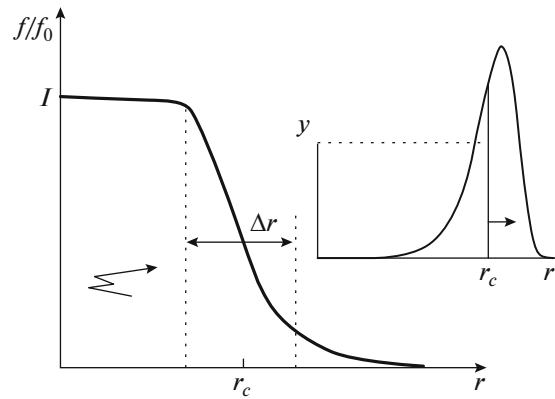


Fig. 1. Qualitative appearance of relative changes in distribution function (normalized to equilibrium distribution function) depending on NP size, where r_c are most probable NP values of radius (corresponding to λ from Eq. (1) [1–3]). Inset in top right-hand corner shows diagram of changes in radii of formed nanoparticles depending on number of all NPs (along Y axis) in space of their radius r , with maximum lying near r_c . Particles smaller than r_c either reach this size or are destroyed. Particles larger than r_c are of no interest, since particles of size r_c emerge in abundance.

model, which will be discussed below), the change in the Gibbs free energy G_N ($N=3$) consists of the difference between two energies: the positive surface energy G_{3P} and the negative volumetric energy G_{3V} (which reduces the potential barrier for the formation of nanoparticles) [14–19]:

$$G_3 = G_{3P} - G_{3V} = 4\pi r^2 \gamma_3 - (4/3)\pi r^3 \mu_3, \quad (8)$$

where γ_3 is the surface energy depending on surface tension, which usually varies within the range of $\sim(0.1-1)$ J/m². The μ_3 value is the gain in the difference between chemical potentials resulting from nucleation (J/m³). Equating the derivative of G_3 with respect to variable r to zero will yield the r_{3c} value:

$$r_{3c} = k_3 \gamma_3 / \mu_3, \quad (9)$$

where for our situation, $k_{N=3} = 2$.

Substitution of r_{3c} from Eq. (9) into Eq. (8) allows one to calculate the dependence between the activation energy and γ_3 and μ_3 [14–19]:

$$\Delta G_3 = (16\pi/3) \left(\gamma_3^3 / \mu_3^2 \right). \quad (10)$$

This parameter acts as the energy barrier (Fig. 2) in the CNT. Let us mention that ΔG_3 is determined as one-third of the surface energy G_{P3} [2, 3, 14–19]:

$$\Delta G_3 = G_{3P} / 3. \quad (11)$$

Hence, in the CNT it is sufficient to know the surface energy value G_P and determine which portion of it generates ΔG (it will be demonstrated below that in the multidimensional CNT model this is reduced to a multiplier factor, which is related to the dimension of the model geometry). If the nascent NP has a shape of

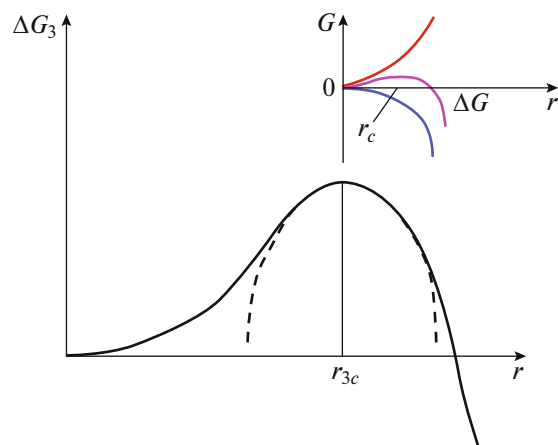


Fig. 2. Schematic representation of energy barrier in region of nanoparticle formation for three-dimensional theory. This scheme is also valid for two-dimensional theory. Dashed curve shows quadratic dependence for barrier ΔG_2 , which is accurate for homogeneous two-dimensional nucleation [3]). Inset in top right-hand corner shows schematic diagram of surface (ascending) and volumetric (descending) energies that result in formation of this energy barrier ΔG (this schematic diagram is valid for any space dimensionality).

a faceted crystal instead of spherical shape, this can be taken into account under the droplet model by adding the known multiplier factors Θ in (10) or (11) (e.g., [3]). Three-dimensional nucleation on a substrate, when the nanoparticle volume and surface area depend on a single parameter, the contact angle, is also discussed. In this case, it is sufficient to add the multiplier factor Φ (e.g., [3]) in Eq. (11). It has been proved [3, 41–45] that a combination of these cofactors allows one to make allowance for all similar cases of nucleation (we will specify the other cases below).

Let us discuss the two-dimensional situation as an example, when the surface energy is set on a circle (it is determined by the γ_2 value with dimension J/m), while the increment of chemical potential μ_2 has the dimension J/m². Formal multiplication by the effective thickness of a film being formed yields these values from the parameters used in the case of three-dimensional nucleation. Let us also mention that two-dimensional nucleation often takes place as heterogeneous nucleation on the surface [3, 41–47], making it necessary to make a correction (in particular, for the surface tension energy). However, we refrain from making the notation too cumbersome (e.g., see [3, 41–47] for more detail); thus, the following formulas will be obtained for the two-dimensional Gibbs free energy G_2 , similar to the previous case:

$$\begin{aligned} G_2 &= 2\pi r\gamma_2 - \pi r^2\mu_2; \\ r_{2c} &= k_2\gamma_2/\mu_2, \quad \text{where } k_2 = 1; \\ \text{and } \Delta G_2 &= G_{2P}/2 = \pi(\gamma_2^2/\mu_2). \end{aligned} \quad (12)$$

The generalized result can be obtained by introducing the concept of a multi-dimensional system. The corresponding formulas (see below) can be used and the phenomenological parameters (γ_n as the specific surface area that is also related to the surface tension; and μ_n , the specific change in the internal energy) can be determined for this purpose. These parameters need to be additionally defined because of the changes in the space dimension. Without getting into details, let us report the result, namely, how the r_{nc} and ΔG_n depend on the space dimension introduced. The nanoparticle radius (when the multimetric Gibbs free energy has an extremum) is determined as

$$r_{nc} = (n-1)(\gamma_n/\mu_n), \quad k_n = (n-1), \quad (13)$$

while the energy barrier

$$\Delta G_n = G_{nP}/n, \quad (14)$$

where the physical meaning of G_{nP} is the surface energy and

$$G_{nP} \sim (\gamma_n)^n / (\mu_n)^{n-1}.$$

Spinodal decomposition is known to be an almost activationless process [2], indicating that ΔG_n decreases.

The important threshold case also follows from these formulas. Hence, in the one-dimensional space, the system cannot be divided into a finite number of sections corresponding to new phases. Division into new phases in the one-dimensional case takes place endlessly [22], which corresponds to

$$r_{1c} = 0,$$

since $k_1 = 0$.

The generalized relationship for factor $k(i)$ can be obtained for the convex surfaces in the droplet model from the general principle of the CNT (the functional dependence of γ on coordinate r is neglected here):

$$k(i) \sim \frac{S'(r)r}{V'(r)},$$

which makes it possible to estimate the energy barrier ΔG if the surface energy and the introduced value $k(i)$ are known:

$$\Delta G_i \sim G_P/[k(i) + 1].$$

The following result can be expected for electrochemistry: in ΔG_n , the degree of dependence on the increment of the chemical potential can differ from the results derived from formulas (8)–(12). According to [3, 16, 17, 41, 42], these values can be correspondingly proportional to the cathode overpotential η_k . Then, the following relationship can be observed depending on the dimensionality of the system:

$$\Delta G_n \sim 1/(\mu_n)^{n-1} \sim 1/(\eta_k)^{n-1}, \quad (15)$$

which was studied experimentally for $n = 2$ and 3 , according to formulas (8)–(12) (e.g., [3, 17, 41]).

Some other general conclusions follow from Eqs. (13) and (14). Hence, if the short-range environment involves the coordination spheres following the first one, the NP radius tends to infinity, while the energy barrier required for the formation of a nanoparticle tends to zero. These conclusions support the validity of the ideas that the CNT is based on.

Since ΔG (see Eq. (14)) depends on the surface energy G_p and a geometry factor (e.g., k_i and Θ or Φ), determination of the activation energy is reduced (under the CNT) to studying the surface tension [43–46]. In this context, let us explain how to attain formal agreement between formulas (1)–(5), which are derived from the CHH (or BLLD) theory and, for example, formula (9) or (12), derived from the CNT. Let us discuss the situation with appreciably small NPs when the dependence between surface tension and the NP size is expected to manifest itself. (As some dependences of this kind were previously discussed in [43–47], we will not thoroughly analyze this dependence.) Let us make the simplest assumption about changes in surface tension as the NP decreases, namely,

$$\gamma_{\text{eff}} \approx \gamma/r_{\text{rel}}, \quad (16)$$

where $r_{\text{rel}} = r_c/\Delta_{\text{in}} > 1$ is the introduced dimensionless parameter and Δ_{in} is the thickness of the surface layer (see Eq. (3)) (the CNT is inapplicable if $r_{\text{rel}} < 1$ but is conjugated with the CHH theory as demonstrated below). Then, a formula similar to (8) and (12), without allowance for the factor of space dimensionality k_n , will be written as

$$r_c \approx \gamma_{\text{eff}}/\mu \approx \Delta_{\text{in}}\gamma/r_c\mu, \quad (17)$$

and the transition to formulas (1)–(5) follows from the CHH theory:

$$r_c^{\text{CHH}} \approx (\Delta_{\text{in}}\gamma/\mu)^{1/2}, \quad (18)$$

which is valid if

$$K \rightarrow \Delta_{\text{in}}\sigma_{\text{in}} \equiv \Delta_{\text{in}}\gamma; \quad \mu \rightarrow G_{\text{CHH}}. \quad (19)$$

Hence, there is a formal coincidence between the CHH theory and the CNT. The suggested consideration is not accurate, since one should also take into account the derivative of γ_{eff} when finding the minimum of the Gibbs free energy G . One of the variants of the theory was discussed in [45]. The dependence between the surface tension and particle size was found using the Gibbs–Tolman–König–Buff equation. The resulting equilibrium size of the NP was obtained in the following form:

$$r_c \sim r_c^{\text{CNT}} \left(1 + F\left(\delta_T/r_c^{\text{CNT}}\right)\right).$$

The physical meaning of this formula can be interpreted as follows. If a particle is larger than Δ_{in} , its size corresponds to the result obtained using the CNT. If a

particle is smaller than Δ_{in} , the r_c corresponds to a certain parameter δ_T . Rekhviashvili et al. [45] demonstrated that F is the analytical function from which the δ_T parameter corresponding to the so-called Tolman length can be singled out by series expansion. Comparison to the result obtained using the CHH theory enables determining the physical meaning of this length. The δ_T length agrees well with the size λ or δ_{LL} . We will discuss the theories that initially did not involve singling out the surface layer in NPs in more detail; the question about the consistency between the activation energy in the CHH theory and CNT will be reported as a conclusion.

THE THEORY DEVELOPED BY LANDAU (GINZBURG–LANDAU–ABRIKOSOV) AND THE THEORY BY CAHN–HILLIARD– HILLERT WITH RESPECT TO NANONUCLEATION

First, we will discuss the earliest variant of the Landau theory (LT) [20, 21] and then derive formulas (1)–(5). The first postulate of the theory consists in assuming that it is possible to expand the free energy in series with respect to a certain parameter called the order parameter. This parameter (using the theory of symmetry) is supposed to characterize the phase transition. As previously mentioned in [30–32], the variant of CNT can be regarded as the simplified variant of the LT, where the following value is used as an order parameter:

$$\eta_{\text{TTN}}^2 = (r - r_c)^2 / (r_c)^2. \quad (20)$$

Of course, one can choose a different order parameter (e.g., see [10, 20–24, 47–49]); however, it is important to demonstrate that the CNT and the LT can be mutually reduced to one another. Therefore, the following expression can be easily derived from the results of the previous section for the two-dimensional nucleation centers for the increment of Gibbs free energy (see details in [3]):

$$\Delta G_2 = 2\pi r_{c_2}\gamma_2 - \pi r_{c_2}\gamma_2 (r - r_{c_2})^2 / (r_{c_2})^2. \quad (21a)$$

A similar expansion near r_c is also obtained for the three-dimensional nucleation centers, but up to terms of the order η_L^3 (see details in [3]), which is usually simplified as

$$\Delta G_3 \sim A_c (r_{c_3})^2 - A_{lc} (r - r_{c_3})^2 / (r_{c_3})^2, \quad (21b)$$

where $A_c = (4\pi/3)\gamma_3 (r_{c_3})^2$, $A_{lc} = 4\pi\gamma_3 (r_{c_3})^2$.

(Let us emphasize once again that in the general case there will be a term with the power $(r - r_{c_3})^3 / (r_{c_3})^3$.) As mentioned previously, formula (21a) is accurate for two-dimensional nucleation centers if complications associated with heterogeneous nucleation are not taken into account. We note that expansion can be per-

formed for other parameters as well, or the thermodynamic function can simply be postulated.

The next (second) postulate of the LT makes allowance for the dependence between thermodynamic energy and thermodynamic functions (temperature, pressure, etc.) by reducing this relationship to the dependences of the serial expansion coefficients on these parameters at a certain order parameter [20, 21]. Another linear term with respect to the order parameter should also be added to the interaction with the external field.

First, let us discuss in more detail the simplest, earlier variant of the LT described in [20, 21]. We will combine the fundamental views about changes in the symmetry of a thermodynamic system upon phase transition; although symmetry is a qualitative parameter, the introduced order parameter η_L allows one to justify the shape of expanding the thermodynamic potential with respect to it into a series:

$$\Phi(E, p, T, \eta_L) = \Phi_0 + E\eta_L + A_0\eta_L^2 + B_0\eta_L^3, \quad (22)$$

where the serial expansion coefficients, as mentioned previously, depend on thermodynamic functions. The equality of some serial expansion coefficients to zero results, in particular, from epy symmetry of the phase obtained during the phase transition. The linear term corresponding to $E\eta_L$ in this notation is also associated with the interaction with the external field, which will be neglected in the further discussion. It has been demonstrated [20, 21, 48] that the LT for the functional written as Eq. (22) is the phenomenological theory that allows one to describe the phase transitions using the serial expansion coefficients obtained either experimentally or by model calculations. In our situation, as one can easily see, the number of terms in the expansion corresponds to the dimensionality of space n introduced earlier (hence, Eq. (21a) suggests that expansion to η_L^2 is sufficient for the two-dimensional space; expansion to η_L^3 , for the three-dimensional space, etc.). From this perspective, expansion to the appreciably high powers η_L^n is needed to describe the spinodal decomposition (we will demonstrate below that this can be avoided by making the model more complicated).

The following relationship was assumed for the coefficient in the quadratic term η_L^2 in the first variant of the theory [20, 21]:

$$A_0 \sim (T - T_c)/T_c,$$

where T_c is the phase transition point (which is immaterial in our case). This was additionally substantiated by the fact that the corresponding summand can become indefinitely small near the phase transition point T_c . Symmetry of the system was also used for justifying the fact that some serial expansion coefficients in the region near the phase transition point are zero.

Shang-Keng Ma [48] demonstrated that the first variant of the theory [20, 21] works poorly in the nucleation region (region $\Delta\bar{r}$ in Figs. 1, 2) if the density fluctuations in the system are too high. Identically, the fluctuations in order parameter η_L can also be of macroscopic size in the spinodal region, near the phase transition point, which should be taken into account when further developing the theory [47–49]. Allowance for the higher powers $(\eta_L)^N$ is equivalent of examining a multidimensional model in the CNT.

The CHH theory is actually based on the improved variant of theory [20, 21], the so-called GL theory. When discussing the further generalization of the GL theory, we use the Hamiltonian block with specific energy density written as [48]

$$H(\Sigma) = \alpha(\nabla\Sigma)^2 + A_1\Sigma^2 + C_1\Sigma^4 + \dots, \quad (23)$$

where the order parameter Σ is the generalized spinor (the linear member characterizing the interaction with the external field is omitted for the sake of simplicity). Let us refer to this model as the GLA model. It is important that in this Hamiltonian, there is the macroscopic relationship between blocks: namely, the term $\alpha(\nabla\Sigma)^2$ in its simplest form [47–55]. We will subsequently speak about the kinetic energy in the GLA theory.

Let us illustrate how formula (1) is derived using the particular case of Hamiltonian (23). For simplicity, we will confine ourselves to two terms of expansion and introduce a parameter for further convenience, which determines, as we will see below, the reciprocal value of the most probable NP radius:

$$a^2 = A_1/\alpha. \quad (24)$$

We also assume that the proposed expansion was carried out under the Heysenberg model (i.e., the simplest spin system). Next, we proceed to the generalized variables (the angles characterizing spin coordinates) for which the equation [28–33] can be easily derived from the condition of action with Hamiltonian (23), i.e., the Euler–Lagrange equation. This equation can be reduced to

$$\theta''(\rho) + ((L-1)/\rho)\theta'(\rho) - F[(a, \rho), \cos\{\theta(\rho)\}, \sin\{\theta(\rho)\}] = 0, \quad (25)$$

where L is the dimensionality of the spinor space (or the number of components of the order parameter) and the polynomial $F[(a, \rho), \cos\{\theta(\rho)\}, \sin\{\theta(\rho)\}]$ is an analytical function that will be further defined for each particular case. Equation (25) is derived from the most general principles. In it, angle θ is represented as the axial angle [48], e.g., in three-dimensional space.

Equation (25) for two-dimensional space will be discussed in detail in another study. Below, we confine ourselves to one-dimensional space; i.e., the case when $L = 1$ (see Eq. (25)), which corresponds to the CHH theory. We obtain an equation similar to that for

magnetic spin (the one-dimensional case) reported in [11, 53–56]:

$$\theta''(\rho) = (a/2) \sin\{2\theta(\rho)\}. \quad (26)$$

If Eq. (26) is integrated for the boundary conditions that mean spin flip, solutions identical to those in [11] can be obtained depending on their specification:

$$\cos\{\theta(\rho)\} = -\tanh\{a\rho\}. \quad (27a)$$

However, depending on which function $F[(a, \rho), \cos\{\theta(\rho)\}, \sin\{\theta(\rho)\}]$ was selected, this result can be represented in the form (as in [13] or [50–56]):

$$\sin\{\theta(\rho)\} = \tanh\{a\rho\} \quad (27b)$$

(which is not of crucial significance for our problem).

In order to simplify the final expression when looking for a partial solution, the boundary conditions were chosen in the manner described in [11]; i.e., it was assumed that in the extreme case

$$\rho \rightarrow \infty (\rho \rightarrow -\infty),$$

the initial values of functions are determined as

$$\theta(\rho) = 0 \text{ and } \theta'(\rho) = 0.$$

The choice of boundary conditions in the nucleation problem is not crucial. We note that a more general case with different boundary conditions was discussed in [53, 55]; the qualitative form of the solution is shown in Fig. 3.

The model described is known as the pendulum model of one-degree-of-freedom (MP1). For our purpose, both the linearized and the nonlinear models provide the same result for the domain wall size and, as shown below, the activation energy. However, as mentioned earlier, it can be demonstrated for the nonlinear model that development of a quasi-periodic concentration instability [10, 36, 37] can be suppressed.

Hence, the domain wall size (see the previous formulas (1), (5), (18), and (27a)) is a key parameter for our problem, which also determines the size of the nucleation center:

$$\delta_{LL} = 1/a = (\alpha/A)^{1/2}, \quad (28)$$

and it fully agrees with the value obtained using formula (1).

The general solution for formula (26) is also often written as [55]:

$$\theta(\rho) = 2 \arctan\{\exp[a(\rho - \rho_0)]\},$$

which does not change the main result written as Eq. (28). In the mathematical theory of nonlinear equations, this model is very convenient, since it is an example of an integrable nonlinear equation. Surprisingly, for our purpose, the linearized and nonlinear MP1 yield identical physical (and fundamental) results. Looking ahead, we note that it is very important both for the

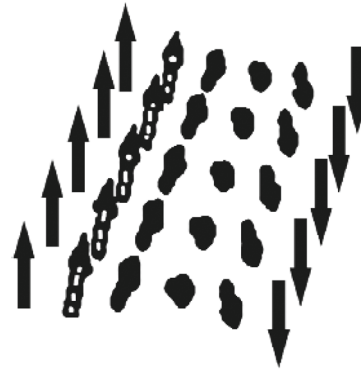


Fig. 3. Qualitative solution in form of domain wall represented as energy vectors for visual clarity.

size of the nucleation center and, as we demonstrate below, for the energy barrier.

Since this physical result is so important, let us also discuss its physical meaning for the nucleation process according to [10], which is of methodological interest. Since nucleation is a metastable process, it is described, for example, as the state of a constrained extremum on the free energy hypersurface in a multi-dimensional space. Of course, the system can leave this metastable state and reach the state of another minimum by overcoming the saddle point on the free energy hypersurface that separates these two minima (the reverse processes are also possible). These saddle points determine the probability of metastable processes. From considerations of the statistical thermodynamics of quasi-equilibrium processes, the probability of this process is

$$W \sim \exp\{-Q/kT\}, \quad (29)$$

where Q is the extremal value of the thermodynamic activation potential near the saddle point, which involves both the activation energy of a unit event and energy expenditure related to changes in the state configuration. All the expenditures are determined by the Gibbs free energy of system F near the saddle point, which actually determines the thermodynamic activation potential. Let us assume concentration c to be the variable with respect to which we expand the free energy in the Landau method. According to [10], we will obtain expansion of the thermodynamic potential with respect to variable c and the rate of variation in c with respect to a spatial coordinate (for the one-dimensional case being analyzed):

$$\Phi = \alpha(c')^2 + A_1 c^2. \quad (30)$$

We obtain the Euler equations from the extremum conditions, in a way similar to the previous one:

$$c'' = (A_1/\alpha)c, \quad (31)$$

which can be derived from Eq. (26) by expanding $\sin\{2\theta(\rho)\}$ because the linear model and MP1 yield the same results.

The solution to Eq. (31) yields formulas (1), (5), and (18), as well as formula (28) derived above. Katsnel'son and Olemskoi [52] called this case a system with a scalar order parameter. This system clearly has the same solution as the one-dimensional spin system (26) with the order parameter depending on the value $L = 1$.

Formulas (1), (5), (18), and (28) can also be derived using a simpler method [51]. If we assume the following type of expansion (not analytical, the one having a simple pole at $\eta_L = 0$) for a certain model energy functional (the reasoning behind this expansion can be found in the Appendix):

$$\Phi = 1/2(\alpha/\eta_L + A_1\eta_L), \quad (32)$$

then, after finding the extremum, we will obtain the order parameter:

$$\eta_L = (\alpha/A_1)^{1/2}. \quad (33)$$

In conclusion, let us discuss the important question about the energy barrier that we have in the CHH or LGA models. We use the solution to Eq. (26) to calculate it: it is substituted into the corresponding Hamiltonian and the target energy is calculated using the formula

$$\Delta E_{LL} = 1/2 \int_{-\infty}^{\infty} [\alpha\theta'^2 + A_1 \sin^2\{\theta\}] d\rho = (\alpha A_1)^{1/2}. \quad (34)$$

Meanwhile, the concept of domain wall energy can be introduced for this energy barrier using equivalent reasoning. The domain wall energy can be calculated as follows (see details in [13, 50, 51]):

$$\Delta E_{LL} = \alpha/2 \int_{-\pi/2}^{\pi/2} \sqrt{A_1 \cos^2 \theta} d\theta = (\alpha A_1)^{1/2}. \quad (35)$$

In the CHH theory described at the very beginning of this article, the energy barrier is also determined from Eqs. (34) and (35). We note that a formula similar to Eqs. (34) and (35) can be derived from Eq. (32) using the solution to Eq. (33). Hence, we provide this formula once again in the notation assumed above and it will be used in the following form:

$$\Delta E_{\text{CHH}} \sim (\alpha A_1)^{1/2}. \quad (36)$$

Here, the energy barrier is the geometric mean of two competing energies. Formulas similar to (35) are derived in some other models, in particular, for the two-dimensional theory, thus confirming its importance in the nucleation theory.

In the theory of micromagnetism, the models yielding Eq. (35) (and Eq. (28)) have been generalized and made more complex (e.g., [50, 55, 56]). For one

coordination variable (in our terminology, in the one-dimensional case), all these complications allow one to integrate the resulting differential equations. They do not cause any fundamental changes in the results that would be substantial for our problem. However, they can be useful for many particular applications, including the nucleation problem.

Hence, if the electrostatic interaction with the energy density

$$w_e \sim (E^2), \quad (37)$$

where E is the electric field strength ($E \sim \eta_k$), is discussed as anisotropy, then when it is higher than anisotropy, the nanoparticle size is determined by the following formula [50, 56]:

$$\delta_e = (\alpha/w_e)^{1/2} \sim 1/\eta_k. \quad (38)$$

Since this result is very important (Eqs. (35), (28)), let us discuss the role of the energy barrier in the CNT and the CHH theory below, in the results and discussion section.

DISCUSSION OF THE RESULTS OBTAINED BY APPLYING THE THEORY TO ELECTROCHEMICAL NUCLEATION

Weston et al. [1] demonstrated that the NP radius calculated (with allowance for the estimations for the competing energy parameters K and G_{xx}) using the CHH theory agrees with the experimental data. Hence, it is fair to assume that the CHH theory satisfactorily describes the available experimental data on the electrochemical codeposition of the alloys containing Co and W.

The studies mentioned above explain the role of the CNT and its limiting passage to the CHH theory, which is possible even under an experimental situation of electrochemical deposition. However, we believe that the choice of a preferred theory should also be based to a significant extent on studying the kinetics of the deposition process. We mean the fact that, at first sight, estimations of the energy barriers in these theories (the CNT and the CHH theory) seem to be different.

According to the well-known ideas put forward by Erdey-Gruz and Volmer, the rate of nanoparticle formation should be related to the difference in the chemical potential denoted as μ in the CNT and as A_1 in the CHH theory. According to [17], these values can be proportional to the cathode overpotential. Hence, one needs to study the dependences of the rate of NP kinetic deposition and cathode overpotential η_k . Having determined these dependences, one could determine the validity of a certain model. However, a discussion of the possibility of implementing these experiments lies beyond the scope of this paper.

We now turn to comparing the prediction of the theoretical models and the experiment. As noted in [1], it is sufficient to demonstrate that calculation of the size of the NP radius, with allowance for the reasonably estimated values included in the formulas from the CHH theory used there, agrees with the experimental data obtained in those studies. However, let us not forget that according to the LGA theory (and the equivalent CHH theory), manifestations of the features depending on changes in chemical potential and, therefore, on cathode overpotential η_k are shown in the final section of this study, which should affect different models.

Today, we believe that there are no reliable data about these abnormal dependences between the rate of formation of nucleation centers and cathode overvoltage η_k . A possible reason for this is that the classical experiments (e.g., [17]) are related to optical detection, or any other type of imaging, of a nanoparticle. Hence, one can believe that there is a good chance that nanoparticles have differentiated their surface from their volume; i.e., their further growth occurs according to the principles of the CNT, which has been detected in the classical experiments [17, 41].

However, in connection with these conclusions, it would be interesting to demonstrate that there is no contradiction between the formulas for activation energy in the CNT and the CHH theory, as well as in the one-dimensional case of GLA. Indeed, the activation energy in the CNT can be determined, to an order of magnitude, by the energy that is needed for the aggregation of the particles and corresponds to the chemical potential μ multiplied (for the linear case) by the defect size, which, according to Eq. (18), is estimated as

$$r_c^{\text{CHH}} \approx (\Delta_{\text{in}}\gamma/\mu)^{1/2}. \quad (39)$$

In this case, the final formula can be easily derived:

$$\Delta G \sim (\Delta_{\text{in}}\gamma\mu)^{1/2}, \quad (40)$$

which corresponds to the formulas in the CHH and LGA theories (e.g., compare with Eq. (35)).

The following conclusion can be drawn from the modern views of the theory of phase transitions with respect to the process of electrochemical nucleation. The long-range field emerging as an electrostatic field of the surface layer will always destroy the long-wave fluctuations. Therefore, the chemical nucleation process is described well by the classical models (i.e., those corresponding to the CNT). This statement will be thoroughly confirmed in our next study (see also [30–33]).

CONCLUSIONS

The classical thermodynamic nucleation theory (TNT) is broadly discussed in this study. When nanoparticles are small and it is impossible to differen-

tiate between the surface and bulk portions of the nanoparticles, this theory should be replaced by the GL theory. Cahn, Hilliard, and Hillert (CHH) [4–9] developed this theory with respect to nanonucleation, while Khachatryan [10] further developed it. Some other researchers have made a significant contribution to the theory [34–58].

The CNT and the CHH theory were shown not to contradict to one another; in the model discussed in this study, they can be represented by mathematical expressions for the r_c parameter of the same form (Eqs. (1), (5), (18), (28), and (33)). Therefore, the regions where the CNT and CHH (BLLD) theory coincide have been found.

In our opinion, an important methodological condition has been obtained, stating that isolation of the surface portion of energy is not required and it can be replaced (generalized) by the expansion of the Gibbs free energy of the system into a series with respect to some parameters, in accordance with the Landau theory. Generalization of the Landau theory for the situation referred to as the GLA model, is exactly equivalent to the CHH theory under a certain approximation.

Indeed, the long-range field always exists during the electrochemical processes as a near-electrode layer. It will always destroy a certain type of system fluctuations characterizing any type of phase transitions. Therefore, electronucleation in electrochemistry is bound to behave in a classical manner close to the descriptions in the CNT. However, we believe (and this will be demonstrated in the next articles) that the latter statement is not so perfect as there are some limitations resulting from the modern fluctuation theory of phase transitions.

Phase transitions in the modern fluctuation theory of phase transitions are classified with respect to space dimensionality (n , according to the denotations already used in our article) and the number of components of the order parameter (L , according to the denotations already used in our article). Transitions with the same dimensionality of the order parameters belong to the same universality class. The phase transitions possessing completely different physical properties can enter this universality class. Nucleation is usually attributed to the universality class that corresponds to the Ising model with $n = 3$ and $L = 1$. There is a need to discuss other models as well.

The CHH (BLLD) theory should be extrapolated to the cases when $L = 2$ and 3, which will be done in our further studies. This will allow us to be more specific about the application areas for each theory.

APPENDIX

The size of quantum NPs (case A) and classical NPs (case B) can be calculated using a scheme similar to Eqs. (32) and (33), which is proposed at the end of

this article and utilizes the generalized nonanalytic expansion of Gibbs free energy with respect to the order parameter. We will further describe this procedure more thoroughly. For now, let us present the key methodological examples of the calculation that supports this procedure for different examples.

(1A) First, we would like to demonstrate the quantum case, which allows us to determine the size of a hydrogen atom and estimate the ionization energy of a hydrogen atom [59, 60]. The Schrödinger Hamiltonian for an electron of a hydrogen atom is written as

$$H = -\frac{\hbar^2}{2m_e}\Delta_r - \frac{e^2}{r}, \quad (\text{A1})$$

where Δ_r is the Laplace operator. In order to solve the problem, one needs to determine the eigenvalues and eigenfunctions of the Hamiltonian operator.

The solution of the problem can be significantly simplified by representing the total atom energy as a generalized sum (identical to Eq. (33)), where the terms of the series depend on its size a_a . From the physical considerations, this series is written as follows (below we will explain the physical meaning of each term):

$$E_a = A_a/(a_a)^2 - B_a/(a_a), \quad (\text{A2})$$

where for a hydrogen atom, $A_a = \hbar^2/2m_e$, $B_a = e^2$, \hbar is the Planck constant, and m_e and e are electron mass and charge, respectively. Let us explain how this formula was derived.

The $\hbar^2/[2m_e(a_a)]$ value corresponds to the kinetic energy of an electron. We use Heisenberg's uncertainty principle and obtain for the electron momentum that

$$p \sim \hbar/a_a, \quad (\text{A3})$$

note that the kinetic energy in classical physics is determined from the expression

$$E_k = p^2/(2m_e). \quad (\text{A4})$$

The electrostatic potential energy of an electron in the field of an atomic nucleus is determined by the second term in (A2):

$$E_p = -e^2/a_a. \quad (\text{A5})$$

As one can see from (A2), the total energy consists of two competing summands. The first summand (kinetic energy) increases the system's energy due to the quantum effect of increasing the electron momentum when an attempt is made to reduce its localization by prescribing atom size a_a .

The second summand corresponds to the electrostatic attraction between an electron and the nucleus; it is supposed to reduce the energy of an atom when its size a_a is reduced.

The minimal E_a , which is used to calculate the a_a value, is determined from

$$\partial E_a/\partial a_a = -2A_a/(a_a)^3 + B_a/(a_a)^2 = 0. \quad (\text{A6})$$

It can be found easily by solving Eq. (A6) that

$$a_a = \hbar^2/(m_e e^2) = 0.528 \times 10^{-10} m, \quad (\text{A7})$$

the *Bohr radius* of a hydrogen atom. By using it, we will also easily determine the ionization energy of a hydrogen atom:

$$E_{\text{ion}} = -e^2/[2(a_a)^2] = -13.6 \text{ eV}. \quad (\text{A8})$$

(2A) Let us discuss the problem about the possibility of confining a quantum particle (we denote the linear dimension of confinement as a_j) to a shallow potential well with the characteristic dimension scale λ and depth U_0 . In this case, the kinetic energy of an electron, according to the uncertainty principle, can be as high as

$$E_k \sim \hbar^2/(2m_e \lambda^2). \quad (\text{A9})$$

Let us use the previous formulas to write the total energy of a localized electron in a potential well as a generalized sum, where the terms of the series depend on the dimensions of the confinement of electron a_j (which can be either smaller or greater than λ):

$$E_j \sim \hbar^2/(2m_e (a_j)^2) - (\lambda/a_j)^L U_0, \quad (\text{A10})$$

where λ is the dimensionality of the potential under study (the system where an electron is located, which can be an ultrathin wire, a plane, or a 3D crystal). Hence, the potential energy is modulated with a dimensionless factor $(\lambda/a_j)^L$. It is clear that the region with characteristic dimension λ will make a significant contribution to localization. In order to make this parameter dimensionless, one needs to correlate it with the localization parameter of electron a_j that we need to find.

Similar to the first case under study, the total energy consists of the two competing summands. The first summand (the kinetic energy) increases the energy of the system due to the quantum effect of increasing the electron momentum when an attempt to reduce its localization is made, while the second summand tries to localize the electron within the potential well.

The case of a one-dimensional potential is of the greatest interest, when $L = 1$ (for $L = 2$, one needs to solve the Schrödinger equation [60], while for $L = 3$, there is no localization under this model). By using the test for the extrema of the energy (identically to how it was used in (A6)), we find a very simple and illustrative formula:

$$a_j(L = 1) \sim \lambda(E_k(\lambda)/U_0) \quad (\text{A11})$$

i.e., if $E_k(\lambda) > U_0$, the localization radius will be greater than dimension λ , and vice versa.

For the sake of completeness, let us provide the formula for localization at $L = 2$ [60]:

$$a_j(L = 2) \sim \lambda \exp\{E_k(\lambda)/U_0\}, \quad (\text{A12})$$

whose radius increases exponentially as the kinetic energy of a particle rises.

(B) For the classical situation of calculating the size of an NP (or a DW), we used the term of the exchange interaction energy written as the formula

$$E_{\text{ex}} = \alpha/(a_{\text{ex}}). \quad (\text{A13})$$

A similar analytical dependence was used in Eq. (33).

Since this formula is important, let us describe how it was derived in more detail than it was done in [51] (the constant $\alpha = 1$ will be used further for the sake of simplicity).

The two nearest spins in a classical Heisenberg ferromagnet rotated by a small angle with respect to one another increase the exchange interaction energy by $\sim(-\cos\varphi)$.

In our case, if one examines the continual threshold of the Heisenberg model of a lattice, the interspin angle, when passing from one to the second neighboring spin, can be expanded into a series:

$$-\cos\varphi \approx -(1 - \varphi^2/2). \quad (\text{A14})$$

We are interested only in the functional dependence of this energy set in Eq. (A14) on the size of the NP or DW, i.e., on a_{ex} . Let us make allowance only for the fact that the increment of energy, which makes a contribution when varying the energy for the two nearest spins, changes by an order of magnitude:

$$(\varphi^2/2). \quad (\text{A15})$$

If the interspin distance in the lattice is b , the angular variable φ can be roughly substituted using the formula

$$\varphi^2 \approx (b/a_{\text{ex}})^2. \quad (\text{A16})$$

The direction of the spin flip in the continual model occurs after all the layers rotate by angle π (in this case, the spins flip in the opposite direction to one another). The number of rotation layers is estimated as

$$\pi(a_{\text{ex}}/b). \quad (\text{A17})$$

Now, by multiplying (A16) by (A17) and using (A15), we obtain the first term of formula (33) (and (A13)) for the exchange interaction energy. In our case, it looks as follows:

$$E_{\text{ex}} \approx (b/a_{\text{ex}}). \quad (\text{A18})$$

The numerical coefficient $\pi/2$ is higher than the accuracy of the method used to derive the formula.

This reasoning is valid if the size of an NP or a DW is much greater than value a that is equal to the inter-

atomic distance in the crystal. Only in this case we proceed to the continual approximation, where the quick rotation of the two nearest spins by angle $\sim\pi$ is substituted by a slow rotation of the system by the distance a_{ex} .

ACKNOWLEDGMENTS

This study was supported by the Academy of Sciences of the Republic of Moldova (project no. 15.817.02.05.A).

The author thanks Yu.D. Gamburg, A.I. Dikumar, and M.P. Anisimov for their valuable advice and discussion.

REFERENCES

1. Weston, D.P., Gill, S.P.A., Fay, M., Harris, S.J., et al., *Surf. Coat. Technol.*, 2013, vol. 236, pp. 75–83.
2. Weston, D.P., Harris, S.J., Shipway, P.H., Weston, N.J., et al., *Electrochim. Acta*, 2013, vol. 55, pp. 5695–5708.
3. Gamburg, Yu.D. and Zangari, G., *Theory and Practice of Metal Electrodeposition*, New York: Springer-Verlag, 2011.
4. Cahn, J.W. and Hilliard, D.J.E., *J. Chem. Phys.*, 1958, vol. 28, no. 2, pp. 258–267.
5. Cahn, J.W. and Hilliard, D.J.E., *J. Chem. Phys.*, 1959, vol. 30, no. 5, pp. 1121–1124.
6. Cahn, J.W. and Hilliard, D.J.E., *J. Chem. Phys.*, 1959, vol. 30, no. 5, pp. 688–699.
7. Cahn, J.W., *Trans. Metall. Soc.*, 1968, vol. 242, pp. 166–170.
8. Cahn, J.W. and Larché, F.C., *Acta Metall.*, 1982, vol. 30, pp. 51–56.
9. Hillert, M., *Metall Trans A*, 1975, vol. 6, no. 1, pp. 5–19.
10. Khachatryan, A.G., *Theory of Structural Transformations in Solids*, New York: Wiley, 1983.
11. Landau, L.D. and Lifshits, E.M., *K teorii dispersii magnitnoi pronitsaemosti ferromagnitnykh tel. Sbornik trudov* (The Theory of Dispersion of the Magnetic Permeability of the Ferromagnetic Bodies: Collection of Research Works), Moscow: Nauka, 1969, vol. 1, pp. 128–143.
12. Vonsovskii, S.V., *Magnetizm* (Magnetism), Moscow: Nauka, 1971.
13. Brown, W.F., Jr., *Micromagnetics*, New York: Wiley, 1963.
14. Gibbs, J.W., *The Collected Works of J. Willard Gibbs*, Vol. 1: *Thermodynamics*, New York: Longmans and Green, 1928.
15. Volmer, M. and Weber, A., *Z. Phys. Chem.*, 1926, vol. 119, pp. 277–239.
16. Erdey-Gruz T. and Volmer, M. *Z. Phys. Chem.*, 1931, vol. 157, pp. 165–170.
17. Vetter, K.J., *Electrochemical Kinetics, Theoretical Aspects*, New York: Academic, 1967.
18. Becker, R. and Döring, W., *Ann. Phys.*, 1935, vol. 24, pp. 719–730.

19. Frenkel, Ja.I., *J. Chem. Phys.*, 1939, vol. 7, pp. 200–201.
20. Landau, L.D., *Phys. Z. Sowjetunion*, 1937, vol. 11, pp. 26–36.
21. Landau, L.D., *Phys. Z. Sowjetunion*, 1937, vol. 11, pp. 545–553.
22. Kolmogoroff, A.N., *Bull. Akad. Sci. URSS. Cl. Sci. Math. Nat.*, 1937, pp. 355–359.
23. Zeldovich, J.B., *Acta Physicochim. URSS*, 1943, vol. 18, pp. 1–17.
24. Lifshits, I.M. and Slezov, V.V., *J. Phys. Chem. Solids*, 1961, vol. 19, pp. 35–49.
25. Belavin, A.A. and Polyakov, A.M., *JETP Lett.*, 1975, vol. 22, pp. 245–248.
26. Woo, G., *J. Math. Phys.*, 1977, vol. 18, pp. 1264–1266.
27. Baranov, S.A., *Surf. Eng. Appl. Electrochem.*, 2011, vol. 47, no. 4, pp. 316–330.
28. Baranov, S.A., Laroze, D., Vargas, P., and Vazquez, M., *Phys. B*, 2006, vol. 372, pp. 320–323.
29. Baranov, S.A., Gamburg, Yu.D., and Dikumar, A.I., *Surf. Eng. Appl. Electrochem.*, 2007, vol. 43, no. 3, pp. 172–175.
30. Laroze, D., Baranov, S.A., Vargas, P., and Vazquez, M., *Phys. Status Solidi C*, 2007, vol. 4, no. 11, pp. 4170–4173.
31. Baranov, S.A., Dikumar, A.I., and Gamburg, Yu.D., *Surf. Eng. Appl. Electrochem.*, 2008, vol. 44, no. 2, pp. 98–105.
32. Baranov, S.A., *Mold. J. Phys. Sci.*, 2014, vol. 13, nos. 3–4, pp. 214–221.
33. Baranov, S.A., *Handbook of Nanoelectrochemistry: Electrochemical Synthesis Methods, Properties and Characterization Techniques*, Zurich: Springer-Verlag, 2015, pp. 1057–1069.
34. Abraham, F.F., *Homogeneous Nucleation Theory*, New York: Academic, 1974.
35. Martin, C.R., *Science*, 1994, vol. 266, pp. 1961–1966.
36. Puri, S. and Binder, K., *J. Stat. Phys.*, 1994, vol. 77, no. 1, pp. 145–172.
37. Binder, K., *Rep. Prog. Phys.*, 1987, vol. 50, pp. 783–859.
38. Gunton, J.D. and Droz, M., *Introduction to the Theory of Metastable and Unstable States, Lect. Not. Phys.*, New York: Springer-Verlag, 1983.
39. Penrose, O., *J. Stat. Phys.*, 1997, vol. 89, pp. 305–320.
40. Hill, T.L., *Nano Lett.*, 2001, vol. 1, no. 3, pp. 111–112.
41. Kaishev, R., *Izbrani trudove* (Collected Works), Sofia: Bolg. Akad. Nauk, 1980.
42. Kashchiev, D., *Nucleation: Basic Theory with Applications*, Oxford: Butterworth, 2000.
43. Roldugin, V.I., *Fizikokhimiya poverkhnosti* (Physical Chemistry of a Surface), Dolgoprudnyi: Intellekt, 2008.
44. Rekhviashvili, S.Sh., Kishtikova, E.V., and Rozenberg, B.A., *Russ. J. Phys. Chem. B*, 2009, vol. 3, no. 6, pp. 1008–1014.
45. Rekhviashvili, S.Sh., Kishtikova, E.V., and Rozenberg B.A. *Tech. Phys.*, 2009, vol. 54, no. 12, pp. 1731–1735.
46. Rekhviashvili, S.Sh. and Kishtikova, E.V., *Tech. Phys.*, 2011, vol. 56, no. 1, pp. 143–146.
47. Ono, S. and Kondo, S., *Molecular Theory of Surface Tension in Liquids*, Berlin: Springer-Verlag, 1960.
48. Ma, S.-K., *Modern Theory of Critical Phenomena*, Benjamin, W.A., Ed., Massachusetts: Adv. Book Progr. Reading, 1976.
49. Fleury, P.A., *Science*, 1981, vol. 211, no. 4478, pp. 125–131.
50. Hubert, A., *Theorie der Domänenwände in geordneten Medien* (Theory of Domain Walls in Ordered Media), Berlin: Springer-Verlag, 1974.
51. Kittel, C., *Introduction to Solid State Physics*, New York: Wiley, 1963.
52. Katsnel'son, A.A. and Olemskoi, A.I., *Mikroskopicheskaya teoriya neodnorodnykh struktur* (Microscopic Theory of Heterogenic Structures), Moscow: Mosk. Gos. Univ., 1987.
53. Shirokobokov, M.Ya., *Zh. Eksp. Teor. Fiz.*, 1945, vol. 15, pp. 57–68.
54. Landau, L.D. and Lifshits, E.M., *Teoreticheskaya fizika. Tom 8. Elektrodinamika sploshnykh sred* (Theoretical Physics, Vol. 8: Electrodynamics of Continuous Media), Moscow: Nauka, 1982.
55. Kosevich, A.M., Ivanov, B.A., and Kovalev, A.S., *Nelineinye volny namagnichennosti. Dinamicheskie i topologicheskie solitony* (Nonlinear Wave Magnetization. Dynamics and Topological Solitons), Kiev: Naukova Dumka, 1983.
56. Malozemoff, A.P. and Slonczewski, J.C., *Magnetic Domain Walls in Bubble Materials*, New York: Academic, 1979.
57. Ivanov, D.Yu., Critical phenomena in pure liquids, *Vestn. Sib. Gos. Univ. Telekomm.*, 2009, vol. 3, pp. 94–104.
58. Anisimov, M.A., *Critical Phenomena in Liquids and Crystals*, Philadelphia: Gordon and Breach, 1991.
59. Feynman, R.P., Leighton, R.B., and Sands, M., *The Feynman Lectures on Physics, Pasadena, CA: Calif. Inst. Technol.*, 1963, vol. 1.
60. Landau, L.D. and Lifshits, E.M., *Teoreticheskaya fizika. Tom 3. Kvantovaya mekhanika, nerelativistskaya teoriya* (Theoretical Physics, Vol. 3: Quantum Mechanics and Nonrelativistic Theory), Moscow: Nauka, 1974.

Translated by D. Terpilovskaya