

## Review

Review article

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## Surface energy in microwires. Review

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### Abstract

The research involves using an analytical solution of the Gibbs–Tolman–Koenig–Buff equation to calculate the microwire surface tension. The classical theory of nucleation and the statistical theory of density were used to determine dependencies for the surface energy of a cylindrical particle. It was shown that within the linear theory, both approaches produce similar results. However, within the nonlinear theory, the results may differ. The article presents an analysis of the analytical solutions of equations for a cylindrical surface within the van der Waals linear and nonlinear theories.

**Keywords:** Gibbs–Tolman–Koenig–Buff theory, Tolman length, Van der Waals theory, Surface energy, Cylindrical surface

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## 1. Introduction

The study of the nanoscale effects of solid nanoparticles is extremely important due to the rapid development of nanotechnologies [1–3]. A number of monographs [1–9] (not limited to these papers) have been dedicated to problems associated with the description of surface effects. However, these issues are extremely complex and have not yet been completely solved even for the simplest of models. Therefore, it appears to be interesting to consider some of the problems if only for simple geometric surfaces, for example, for a cylindrical surface [11–16].

Elongated nanoparticles (this part discusses solid nanoparticles), which can be nanowires or nanowhiskers (hereinafter NWs), are often used in micro- and nanoelectronics. Such materials often have unique electrical, magnetic, optical, and other properties, which makes it possible to use NWs in modern devices (see, for example, [1–3] and the literature cited therein).

Obtaining NWs is technologically challenging. However, this task can be facilitated by using appropriate theoretical models which enable the most basic mathematical modeling of technological processes. The scope of this article does not include a detailed discussion of the technological challenges associated with obtaining filamentary nanoobjects. However, it is worth mentioning that at present they can be produced using a wide range of materials. For example, the list of technologies that we provide below can be easily expanded. For instance, the following technologies are used to grow NWs: gas-phase epitaxy, chemical and electrochemical deposition, molecular beam epitaxy, magnetron deposition method, laser ablation, etc. Recently, nanowires have also been produced by the Taylor–Ulitsky method (see, for example, [3]). Among the most suitable methods of theoretical modeling which allow understanding the kinetics and details of NWs growth are various types of dynamic modeling. Modeling does not only allow obtaining information about the kinetics of the process, but also allows calculating the morphology of the growth surface. It also allows taking into account the spatio-temporal fluctuations that are significant

for the kinetics of the studied process. We are not going to discuss the results of these studies in detail; however, we would like to note that these results tend to be contradictory and differ depending on the group of researchers. In addition, they are not well-founded for large systems and the real calculations are always limited by the upper limit to the number of particles in the system associated with a reasonable counting time. This is the main source of contradictions in the modeling results. To be more precise, for example, some authors get negative values for the limit value of the Tolman parameter, while others predict positive values for the same parameter within similar systems. Therefore, it is undoubtedly of interest to somehow systematize the previously obtained (more verified) results substantiated within the framework of the general approaches of thermodynamics and the simplest models of statistical physics (see, for example, [1, 2]). The content of these results, as will be shown below, allows establishing some general regularities, which can become the starting point for any model calculations.

Therefore, the purpose of this work is to combine the most general results describing nanonucleation and its main thermodynamic parameters, for example, surface energy and its corresponding surface tension, etc., with general thermodynamic results if only for the simplest case of NW. To achieve this goal, we conducted a detailed analysis of the results which we had obtained earlier, defined the main tasks to be performed as a result of this analysis, and presented a number of new results.

## 2. Thermodynamic approach to a cylindrical particle

We considered an isolated system consisting of two three-dimensional phases with different densities and interfaces between them. In this section, we use the results of the monograph [9].

The initial equation is the Gibbs adsorption equation.

$$d\sigma = -\Gamma d\mu, \quad (1)$$

where  $\Gamma$  is adsorption and  $\mu$  is chemical potential. To build a thermodynamic model, equation (1) is extended as follows:

$$d\sigma = -\frac{\Gamma}{\Delta\rho}d(\Delta p) = -\delta\left(2 + \frac{\delta}{R}\right)d(\Delta p), \tag{2}$$

$$\mu = \frac{\Delta p}{\Delta\rho}, \quad \Gamma = \frac{\Delta V}{\omega} \Delta\rho,$$

where  $\Delta\rho$  is the difference in the densities of the coexisting phases,  $\delta$  is the thickness of the transition layer (Tolman length), and  $\Delta V$  is the volume of the interfacial transition layer with a thickness of  $\delta$ .

The combination of the formulas produces the following differential equation:

$$\frac{d \ln \sigma}{d \ln R} = \frac{\frac{2\delta}{R} + \left(\frac{\delta}{R}\right)^2}{2 + \frac{2\delta}{R} + \left(\frac{\delta}{R}\right)^2}. \tag{3}$$

Equation (3) is analogous to the well-known Gibbs–Tolman–Koenig–Buff equation (see [3–9]) for a cylindrical surface.

To solve equation (3), the dimensionless variable  $R/\delta$  is introduced. As a result,

$$\ln \frac{\sigma}{\sigma^{(\infty)}} = -\int_{R/\delta}^{\infty} \left( \frac{2x+1}{2x^3+2x^2+x} \right) dx. \tag{4}$$

The integral in (4) is found by integrating rational functions (i.e. by expanding the integral function into partial fractions [9]). The final result can be represented as [9] (see Fig. 1):

$$\sigma = \frac{\sigma^{(\infty)}R}{\delta} \sqrt{\frac{2}{2\left(\frac{R}{\delta}\right)^2 + 2\frac{R}{\delta} + 1}} \exp\left(-\operatorname{arctg}\left(\frac{1}{1+2\frac{R}{\delta}}\right)\right). \tag{5}$$

When  $R \gg \delta$ , (5) is transformed into a well-known analogue of the Tolman formula:

$$\sigma = \frac{\sigma^{(\infty)}}{1 + \frac{\delta}{R}}, \tag{6}$$

where Tolman parameter  $\delta$  must have the same sign with the radius of curvature  $R$  of the surface (i.e.  $\delta > 0$ ).

The monograph [9] (assuming that Eulerian curvature is small) offers a more general formula for the surface tension of an arbitrarily curved surface as a function of the two main radii of curvature.

When  $R \ll \delta$ :

$$\sigma / \sigma^{(\infty)} \sim 0.645(R/\delta)$$

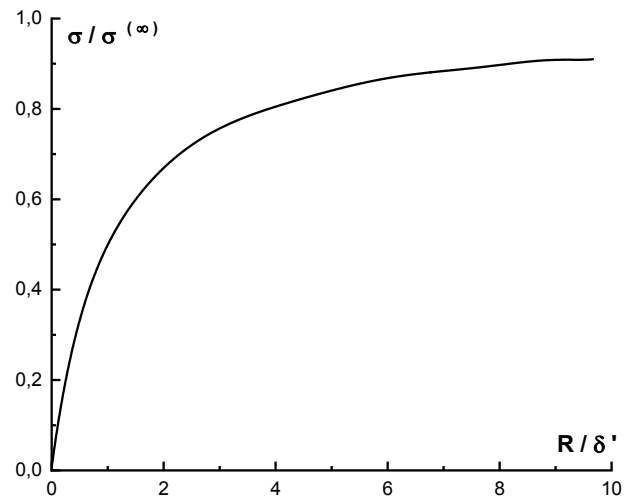


Fig. 1. Functions graphs of solution (5) (see [9])

from (5) follows Rusanov’s formula [6, 9] for a cylindrical particle.

### 3. Linear Theory

First, we will consider the linear theory proposed in [9], which will help us when choosing the van der Waals equation. As the resulting function, we accept the value proportional to the volume density of the fragments of the  $n(x)$  particles which the cylindrical particle consists of. This allows obtaining in the linear approximation a simple equation, which, importantly, can be solved analytically [9]:

$$n'' + \frac{n'}{r} - \frac{1}{\delta^2}(n-1) = 0, \tag{7}$$

where  $r$  is the coordinate of the radius of the nanocylinder. In our equation, the value of the volume density of the particles  $n(0)$  in the center per unit was pre-normalized, which is not important but will be very convenient for our purposes later on.

The function  $n(x)$  (the dimensionless variable:  $x = r/\delta$  is introduced) is proportional to the volume density function, which we designate as  $N(x)$  (see below).

A particular physical solution (7) is used, which has the form of [9]:

$$n(x) = cK_0(x), \tag{8}$$

where  $K_0(x)$  is a modified Bessel function.

Now, we find the real physical quantity called the normalized function of the volume density of

particles  $N(r/\delta)$ . For it, the boundary conditions can be described as:

$$\begin{aligned} N(r/\delta) &\rightarrow n(0) \equiv n(R) = 1, \\ N(+\infty) &\rightarrow n(+\infty) = 0. \end{aligned} \tag{9}$$

Using solution (8) and conditions (9), we get:

$$N(r/\delta) = \begin{cases} 1, & r \leq R, \\ \frac{K_0(r/\delta)}{K_0(R/\delta)}, & r > R, \end{cases} \tag{10}$$

which is shown schematically in Fig. 2.

Using (10) in [9], we derive the equation:

$$\frac{d \ln \sigma}{d \ln x} = \frac{1}{x \{K_0(x) / K_1(x_0)\} + 1}. \tag{11}$$

If  $x \gg 1$ :

$$\frac{K_0(x)}{K_1(x_0)} \rightarrow 1,$$

As a result,

$$\frac{d \ln \sigma}{d \ln x} = \frac{1}{x + 1},$$

where follows the Tolman formula (6).

When  $x \ll 1$ :

$$\frac{K_0(x)}{K_1(x)} \approx x \ln \frac{2}{\gamma x},$$

where  $\gamma = 1.781$ , and

$$\frac{d \ln \sigma}{d \ln x} = \frac{1}{x \ln \frac{2}{\gamma x} + 1}.$$

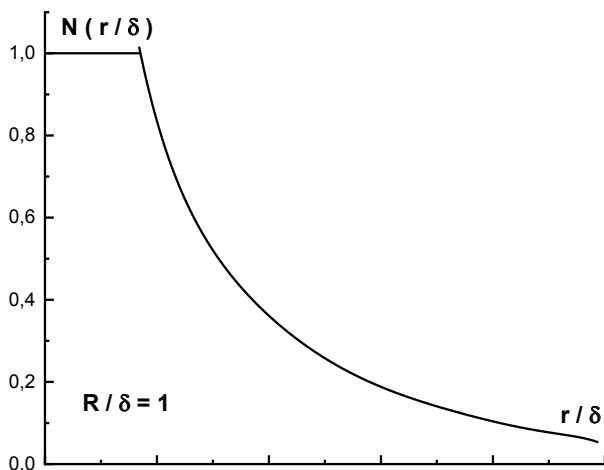


Fig. 2. Volume density function,  $N(r/\delta)$  (10)

As follows from the graph (Fig. 2), it can be assumed that the emerging nanocylinder reaches thermodynamically equilibrium dimensions  $R \sim \delta$  (with a relative volume density of its constituent fragments equal to one). This equilibrium dimension  $\sim \delta$  in the Cahn–Hilliard–Hillert theory was defined in [7, 10–15]. Around the equilibrium dimension  $R \sim \delta$ , there is an “atmosphere” of the volume density of the nanoparticle components (or discharged nanoparticle fragments),  $N(r/\delta)$ , which asymptotically approaches zero only within the  $r/\delta \rightarrow \infty$  limit, since in this case the forces are not short-range.

This modeling result physically meant that the equilibrium nanocylinder (solid phase) was surrounded by an infinite “atmosphere” of its fragments. Therefore, the thermodynamic growth of cylindrical nanoparticles beyond their equilibrium dimensions in the presented approximation is not limited. This result is in line with the classical theory of nucleation (CTN).

The section above showed that to describe the dependence of surface tension on the Tolman parameter  $\delta$ , a differential equation was used, which was the Gibbs-Tolman-Koenig-Buff equation (GTKB). It is obvious that the linear theory presented here based on the linear dependence of the density on the coordinate (equation (7)), is in line with the GTKB theory [9] and, accordingly, with the classical theory of nucleation.

#### 4. Nonlinear theory

Let us move on to the nonlinear analogue of the differential equation (7). Let us introduce an interaction space  $D$  relevant for nanonucleation (correlation radius).

Since we do not know the differential equation, we have the right to propose a simplest model that within the boundaries coincides with the model used for the linear theory (a correspondence between the linear theory and CTN).

Then, based on the previous equation (7), the nonlinear equation could be modeled as follows:

$$n_1'' + \frac{1}{r} n_1' + \frac{1}{\delta_1^2} \exp\{-n_1\} = 0, \tag{12}$$

where  $n_1(r)$  is a function similar to the function  $n(r)$  but for a nonlinear equation.

Choosing the function in the form of  $\frac{1}{\delta_1^2} \exp\{-n_1\}$  is undoubtedly an arbitrary decision when modeling an unknown functional. However, if we expand the exponent  $\frac{1}{\delta_1^2} \exp\{-n_1\}$ , we can obtain equation (7).

On the other hand, in our opinion, the function  $\frac{1}{\delta_1^2} \exp\{-n_1\}$  models the short-range force of the interaction between fragments which occurs in the model of  $N$ -dimensional fractal cluster [12].

The physical solution (taking into account the normalization) is presented as:

$$n_1 = 2 \ln[1 - X_1^2], \tag{13}$$

where (see below):

$$X_1 = r / (2\sqrt{2}\delta_1). \tag{14}$$

It should be noted that we chose a solution that satisfied the following conditions:

$$n_1(0) = n_1'(0) = 0$$

A correspondence between the radius  $D$  and the Tolman parameter  $\delta_1$  is introduced through the normalization integral:

$$\int_0^\infty \frac{2\pi r dr}{1 + (r^2)/(8\delta_1^2)} = 8\pi\delta_1^2 = \pi D^2, \tag{15}$$

from which it was derived that

$$D = 2\sqrt{2}\delta_1. \tag{16}$$

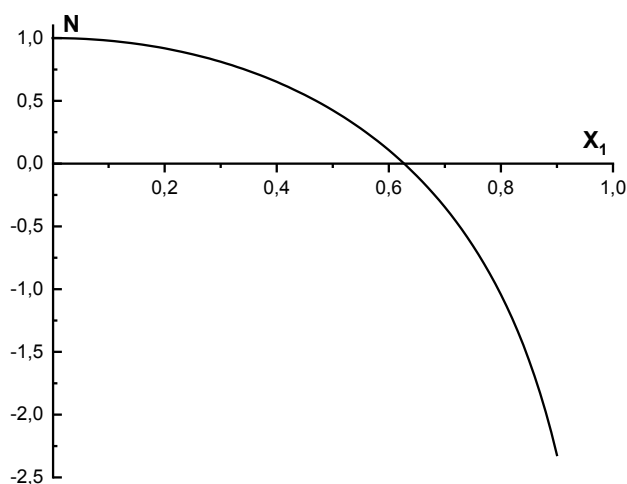
This means that the radius  $D$  and the Tolman length are related by the relation (16) presented here. The coupling coefficient for these values is of a model character, however, we can state that by an order of magnitude  $D \sim \delta_1$ .

As a result, the function of the volume density of particles can be represented as:

$$N = 1 + 2 \ln[1 - X_1^2]. \tag{17}$$

It should be noted that there is no analytical correspondence between solutions (10) and (17). As evidence, we provide a graph for solution (17), which is shown in Fig. 3.

The difference between solutions of the linear and nonlinear equations (Fig. 2 and 3) is fundamental. In the first case, as we have



**Fig. 3.** Plot of function (17) obtained from solution of Eq. (13). Only the solution for  $N$ , when this function is greater or equal to zero, has a physical sense

already noted, the thermodynamic growth of cylindrical nanoparticles beyond their equilibrium dimensions ( $R \sim \delta$ ) is not limited. This result is in line with the classical theory of nucleation (CTN). In the case of the nonlinear equation (equation (12)), the growth of the nucleus is ultimately limited, which will be discussed below.

### 5. Surface energy for nanowires

If the droplet sizes are comparable with the Tolman length, there is a problem associated with an additive calculation of surface energy from the volume part of the energy. It is possible that in some cases negative Tolman lengths are due to inappropriate approaches used to solve this problem.

An alternative method is to use the model density profile in the van der Waals theory (see, for example, [16]). This theory was also proposed in a generalized form by L. D. Landau to describe phase transitions. It should be noted that all these theories became the theoretical foundation for a series of works by Cahn and Hilliard. Below we use a version of the theory similar to the theory of V. L. Ginzburg, L. D. Landau, and A. A. Abrikosov.

We consider a particular case of applying these theories, when the nucleus of the condensed phase is shaped as a long cylinder. We used a cylindrical coordinate system, for which the characteristic spin function [16] is represented by the angle function  $\theta(\rho)$  relative to the cylinder axis  $z$ . The physical interpretation of the spin



function differs from the interpretation of the concentration density, but in the style of the Landau’s theory it can be assumed that these quantities are both order parameters. In our case, this order parameter characterizes the energy state (of the atom) in the nanoparticle as a function of the radius of the base of the cylinder. The free energy in this model can have the following form [16]:

$$H_{g,c} = \frac{A}{2} \left[ \theta'^2 + \frac{\sin^2 \theta}{r^2} \right], \tag{18}$$

where  $\theta(r)$  is the angle between the cylinder axis and the magnetization vector and  $r$  is the radial coordinate. Thus, unlike the previous three-dimensional problem, this time we considered a two-dimensional problem. The solution of the three-dimensional problem is reduced to numerical methods and this problem will be dealt with in another paper.

The model kinetic energy in (18) is a classical analogue of the exchange energy in the Heisenberg model for the two-dimensional space in a continuous approximation, which corresponds in our case to the infinite cylinder model. It can be assumed that the kinetic energy in (18) coincides in form with the kinetic energy of a quasiparticle (in cylindrical coordinates). This fact is not accidental and is due to the fact that the studied model allows accurate analytical solutions in the form of quasiparticles, nonlinear waves known as instantons (or skyrmions [16]). It should also be noted that in our case these quasiparticles are topological compositions rather than dynamic particles. Therefore, in our case the virtual kinetic energy of the topological instanton is meant by the kinetic energy.

The theory considered below is scale invariant, which allows us to introduce a relative coordinate:

$$\rho = \frac{r}{R_c}, \tag{19}$$

where  $R_c$  is the equilibrium radius of the droplet. Now, let us consider the topological space as the initial droplet. Then, there is a condition of  $0 \leq \rho \leq 1$ . The proposed continuum model of energy (18) appears to be a Heisenberg model in which the interacting spins act as energy states of the particles associated with the constant exchange

interaction  $A$  (with the dimension for the exchange energy [J/m]).

Using (18), it is simple to derive the Euler-Lagrange equation:

$$\theta''(\rho) + \frac{\theta'(\rho)}{\rho} - \frac{\sin \theta \cos \theta}{\rho^2} = 0. \tag{20}$$

For simplicity, it is sufficient to only use a particular solution of this equation describing the nucleation process under simple boundary conditions:

$$\theta(\rho) = \begin{cases} \pi, & \rho = 0, \\ \frac{\pi}{2}, & \rho = 1. \end{cases} \tag{21}$$

The solutions of equations (20) and (21) look simple:

$$\tan\left(\frac{\theta}{2}\right) = \frac{1}{\rho}, \tag{22}$$

which is convenient for further analysis.

Let us introduce the model surface energy to obtain the Euler-Lagrange equations for the scale invariant theory:

$$\theta_a''(\rho) + \frac{\theta_a'(\rho)}{\rho} - \frac{a^2 \sin \theta_a \cos \theta_a}{\rho^2} = 0, \tag{23}$$

where  $a^2$  is the ratio of anisotropy energy to exchange interaction constant  $A$ . Parameter  $a^2$  was determined in [16]:

$$a^2 = \frac{B}{A} + 1, \tag{24}$$

The definition of the anisotropy function was also given there:

$$\frac{B \sin^2 \theta_a}{2\rho^2}, \tag{25}$$

where  $B$  is a positive energy quantity, the dimension of which coincides with  $A$ .

For agreement with the previous solution, we assume that there is no anisotropy in (23) when  $B = 0$ , and when  $B > 0$ , it is present. The solution of equation (8) is as follows:

$$\tan\left(\frac{\theta_a}{2}\right) = \frac{1}{\rho^a}. \tag{26}$$

It should be noted that solutions (22) and (26) join analytically, therefore, the indices are further

omitted. Let us consider one general solution (26). This solution is shown schematically in Fig. 4.

It is easy to show that the function  $\theta(\rho)$  when  $a = 1$  and  $0 < \rho \leq 1$  has no inflection point. This point only appears when  $a > 1$ . This means that the surface layer in our model can only exist at  $a > 1$ . In this case, a certain volume whose energy is the surface energy of the cylindrical particle can be chosen as the surface layer. For definiteness, let us suppose, for example, that the surface layer begins to clearly manifest itself when  $a > 4$ . Thus, we assume that at  $a = 1$ , there is no anisotropy in the system, and the Tolman length actually coincides with the droplet size. If  $a \gg 1$ , within the proposed model, the specific anisotropy exceeds the exchange interaction, and in relation to the droplet there appears a parameter (Tolman length) that characterizes the dimension of the interfacial region. The case of  $a < 1$  corresponds to the negative surface energy (in Fig. 4 this case is shown for  $a = 0.5$ ) and is not considered in detail in this article since it is associated with the instability of the condensed phase.

The change in the free energy from the center of the particle to its surface can be estimated. This estimation allows the physical interpretation of the introduced model parameters and their comparison with the conventional energy characteristics that are used to describe the nucleation process.

Let us first consider the layer-by-layer change in the free energy of a cylindrical droplet. We will use again the formula for the energy that we used to derive the equation of motion. It is as follows:  $E(\rho) = T + U$ . Considering solution (26), we find that the kinetic energy is equal to the potential energy:  $T = U$ . This important result for the closed dynamic system is associated with the virial theorem for the finite motion, and in our case can be used to check if our approach to problem solution was correct. For total energy, we have:

$$E(\rho) = T + U = 4A \left( \frac{a}{\rho} \right)^2 \frac{\rho^{2a}}{(1 + \rho^{2a})^2}. \tag{27}$$

It follows from (27) that for  $a = 1$  and  $\rho \rightarrow 1$ , the equality  $E(\rho) = A$  is satisfied. When  $B > 0$ , the cylinder surface energy tends to  $Aa^2 \sim B$  and the higher the  $B$  value, the higher the limit. Therefore, just this parameter  $B$  can be associated with the parameter of specific thermodynamic surface

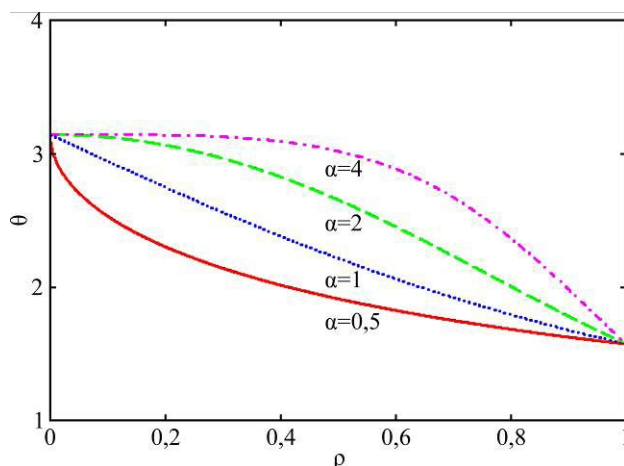


Fig. 4. Diagrams of solution (26) at different values of parameter  $a$

energy used in thermodynamic theories provided that these energies have different dimensions.

A sharp increase in free energy (see Fig. 5) depending on parameter  $a$  is associated with the phase transition that occurs in the system in the event of an infinitesimal anisotropy. To find the total energy of the particle assigned to the cylinder length unit, it is necessary to take the integral of  $E(\rho)$  over the cylinder volume. Let us start with a qualitative analysis of the model. It should be noted that for the particular case of  $a = 1$  and  $B = 0$ , this integral must be equal to  $A$  (up to factor). Then, there is no other energy in the system;  $A$  is the only internal model energy

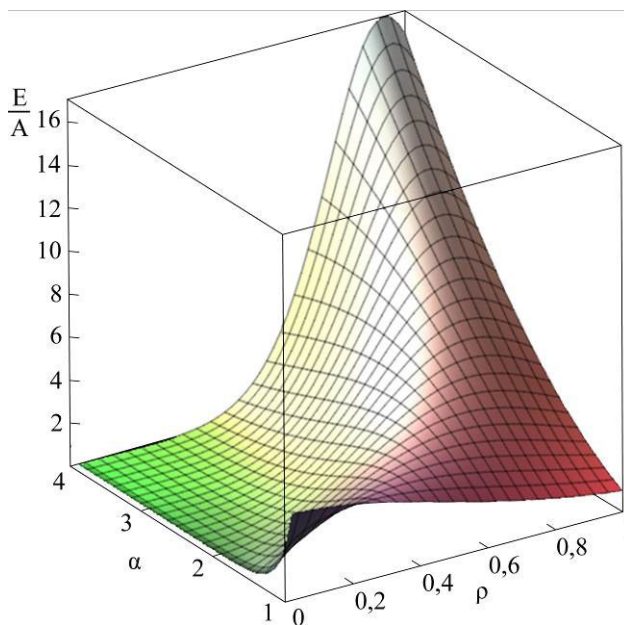


Fig. 5. Three-dimensional dependence of energy on parameters  $a$  and  $\rho$

of the system. In another limiting case, a high value of  $a$  is sufficient for the total energy to tend to anisotropy energy  $B$ . In the general case, the total specific energy (for the cylinder length unit) will be as follows:

$$W = 2\pi \int_0^1 E(\rho) \rho d\rho = 8\pi a^2 A \int_0^1 \frac{\rho^{2a-1} d\rho}{(1+\rho^{2a})^2} = 2\pi a A. \quad (28)$$

According to the Cahn–Hilliard theory, the energy of the activation barrier is proportional to the geometric average of two energy parameters:  $E_c \sim \sqrt{AB}$ . Unlike the proposed theory, the Cahn–Hilliard theory is not scale invariant, and the quantity of  $B$  has a dimension of  $\text{J}/\text{m}^5$ . In our case, the integral formula derived from (28) for the activation energy has the same form, which indicates that these theories coincide when calculating the average activation energy (in the volume unit). Therefore, it can be concluded that the proposed theory qualitatively coincides with the Cahn–Hilliard theory.

## 6. Conclusions

A decrease in the size of the condensed phase leads to an increase in the relative proportion of surface atoms. As a result, the influence of the interfaces increases. What is more, the size dependence of the surface tension is due to the Tolman length, i.e. the thickness of the interfacial (transition) layer. This is especially evident in nanoparticles, the radius of which is ones to tens of nanometers.

The final section of the article provided the results related to the van der Waals gradient theory, which can be summarized as follows. If only one form of energy is present during the formation of a nanoparticle, which acts as exchange interaction  $A$ , it is not correct to separate additive energies of the system into the surface energy and the energy of the nanoparticle volume within the framework of the proposed model. However, in this case, it would be possible to introduce the average energy of the entire nanoparticle and to derive Rusanov’s linear formula for surface energy based on geometric considerations. Typically, Rusanov’s formula is assumed to be universally applicable. This fact is not confirmed when our model is complicated by anisotropy energy.

The concept of anisotropy energy, which is introduced into the theory in the form of the

proposed model as a modified Rapini potential, leads to the emergence of surface energy. It should be noted that the conventional Rapini potential has no multiplier of the form of  $1/\rho^2$  [16]. The anisotropy energy can become the energy of a double electric layer (in electrochemistry). However, in the case of the formation of extremely small equilibrium particles with differentiated surface energy, the electric capacity of the nanosystem where this nanoparticle is formed should be increased. Thus, it can be assumed that the nanonucleation process can be efficiently controlled.

The main result of all parts of the work can be considered obtaining a profile of surface energy from the thermodynamic parameters of the system, which allows expanding to a certain extent the understanding of capillary phenomena in nanosystems.

The question of the Tolman length, which determines the dimensional effect of the surface tension and the scope of the theory, requires separate consideration. According to the thermodynamic definition, the Tolman length is numerically equal to the distance between the equimolecular surface and the tension surface [4, 5]:

$$\delta = z_e - z_s, \quad (29)$$

where  $z_e$  and  $z_s$  are the positions of the equimolecular surface and the tension surface on the same half-axis. The equimolecular surface corresponds to the condition  $\Gamma = 0$ . The dividing surface, for which the Laplace equation is valid, is the tension surface. The tension surface is generally taken as a true dividing surface.

The equimolecular surface and the tension surface are always located inside the interfacial transition layer, so the thickness of this layer can be taken as the maximum value of the Tolman length  $\delta$ . For larger droplets, the Tolman length can be considered to be a constant value related to a flat surface. By definition, the Tolman length for a flat dividing surface is:

$$\delta = \frac{\Gamma}{\Delta n}, \quad \Delta n = n_1 - n_2, \quad (30)$$

where  $n_{1,2}$  are volume densities of coexisting phases in equilibrium. There is contradictory information about numerical values and even the sign of the Tolman length. It follows from (30)



that the sign of  $\delta$  depends on the sign of Gibbs adsorption on the tension surface. You can determine the sign of the Tolman length if you use the well-known formula for the density distribution profile in the flat interfacial region:

$$n(z) = \frac{n_1 + n_2}{2} - \frac{\Delta n}{2} \operatorname{th}\left(\frac{z}{z_0}\right), \quad \Delta n > 0, \quad (31)$$

where  $z$  is the coordinate;  $z_0$  is the parameter characterizing the slope of the density distribution profile. Formula (31) specifies a density distribution profile symmetrical relative to the point  $z = 0$ . The denser and less dense phases are located on the positive and negative semi-axes. For adsorption, we have:

$$\Gamma = \int_{z_i}^{\infty} [n(z) - n_1] dz + \int_{-\infty}^{z_i} [n(z) - n_2] dz, \quad (32)$$

where  $z_i$  specifies the position of the arbitrary dividing surface. The integration of (32) with (31) gives:

$$\Gamma = z_i \Delta n. \quad (33)$$

For equimolecular surface and tension surface:

$$z_i = 0 \text{ and } z_i = z_s,$$

therefore, from (30) and (32) for the Tolman length, we find:

$$\delta = z_s, \quad (34)$$

where  $z_s$  is counted from the origin, i.e. from the middle of the profile. Formula (34) allows us to conclude that the sign of the Tolman length depends on the location of the tension surface. If the tension surface is near the dense phase (which, in our opinion, is the most natural), the Tolman length will be positive. Shifting the tension surface to a less dense phase relative to the equimolecular surface changes the sign of  $\delta$  to negative.

It should be noted that for certain thermodynamic systems the Tolman parameter can be considered negative, however, this case is not considered in this study.

For a small droplet with radius  $r$ , the stability condition has the form  $(\partial\sigma / \partial r)_{T,p} > 0$ . It follows that the function  $\sigma(r)$  must be increasing and the droplet must meet the condition  $\delta > 0$ .

## Conflict of interests

The author declares that they has no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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