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Surface Energy for Nanowires and Nanodroplets

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Abstract

The problems of nucleation of nanoparticles (nanodroplets and nanowires) are investigates. Systems of nonlinear differential equations describing the droplet profile or nanowires obtained. We consider formula that determines the surface energy in nanodroplets or nanowires. We have shown if the nanodroplets or nanowires parameters are compared the thickness of the surface layer dependence of the surface energy on thickness of the surface anisotropy is very important. An analytical solution of the simplest nonlinear equation is used to study the dimensional energy of surface tension for nanowires and nanodroplets.

Keywords: Nanodroplets, Nanowires, Gibbs-Tolman-Koenig-Buff Equation, Cahn-Hilliard Theory, Surface Energy.

Introduction

Studying the formation of nanodroplets and nanowires is a fundamental problem in modern nanotechnology. It has important implications for various technological processes in the chemical and glass industries, mechanical engineering, electronics, soil science, agriculture, and biology. There is a trend in modern technology towards miniaturization of sensors, especially if these sensors are to be used on board small-unmanned aerial vehicles.

Modern sensors in this area based on the use of the nanodrops or on the nanowires (nanoscale particles). To optimize these sensors the characteristics of the nanoscale particles need to be well known. Nanoscale particles are also a key component of important processes in the Earth's atmosphere and numerous technological applications.

Young's equation for microdroplets is determined by [1-7].

$$\sigma_1 = \sigma_2 + \sigma\cos\theta \quad . (1)$$

Parameters σ_1 is tension at the interface of the solid and liquid phases, σ_2 is tension at the interface of the solid and vapor phase, σ is tension at the interface of the liquid and vapor phases.

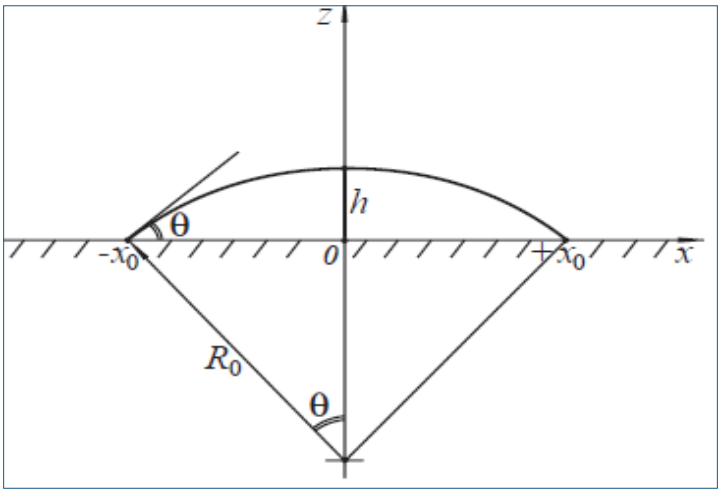


Figure 1: Model of Sessile Drops.

In this model, the angle θ play significant role (see Figure 1)

$$\tan\left(\theta/2\right) \sim (x_0/h)^{-1}. \quad (2)$$

The proposed theory does not contain size effects of surface tension.

Thermodynamic Approach

Let us consider 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 [6].

To determine the surface tension, let us apply the Gibbs equation that can be written in the form of

$$d\sigma = -\Gamma d\mu = -\delta\, d(\Delta p), \quad (3)$$

where Γ is the Gibbs adsorption, μ is the chemical potential, $\delta \geq 0$ is a non-negative parameter characterizing the thickness of the interfacial layer. The Tolman length is used as a parameter δ which is equal to the distance between the surface of tension and equimolar surface. The numerical values of parameter δ are in the range from 0.1 to 1 nm far from the critical boiling point. When writing the equation (3) we have taken into account that the differential for the chemical potential and the Gibbs adsorption are equal $d\mu = d(\Delta p)/\Delta n$ and $\Gamma = \delta \Delta n$, where Δn is the substance concentrations difference in interfacial phases. Equation (3) holds for any smooth interfacial phase irrespective of its geometrical shape. In what follows we assume that δ does not depend on the curvature radii. This assumption is considered acceptable if the curvature of the surface is not too large compared with 1/δ [1,2]; an analysis of the size dependence of the surface tension for the spherical surface show that such assumption is already acceptable when $|\kappa| < 0.1/\delta$. Substituting (2) into (3) we can obtain the equation

$$\frac{d\sigma}{\sigma} = -\frac{\delta}{1+\delta\kappa} d\kappa. \quad (4)$$

Having integrated (4) we can find

$$\sigma = \frac{\sigma^{(\infty)}}{1+\delta\kappa}, \quad (5)$$

where $\sigma^{(\infty)}$ is a flat surface tension as $\kappa \to 0$. For arbitrarily curved surface $\kappa = 1/r_1 + 1/r_2$, where r_1 and r_2 are the principal radii of curvature of the surface [9] therefore from (5) we finally obtain

$$\sigma = \frac{\sigma^{(\infty)}}{1+\delta\left(\frac{1}{r_1}+\frac{1}{r_2}\right)}. \quad (6)$$

When $r_1 = r_2$ from (6) the well-known Tolman formula is derived for small spherical droplets [3].

We also note that the above arguments are in accordance with the provision that at sufficiently high r_1 and r_2 in the thermodynamic equations for the spherical surface curvature can be replaced by medium (Euler) curvature.

In [6] a comparison of simple size dependency for spherical and cylindrical shaped surfaces resulted in the following interpolation formula

$$\sigma = \sigma^{(\infty)}\left[1-\delta\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right]. \quad (7)$$

It is easy to verify that formula (7) can be derived using expansion of (5) into series of in view of zero and consider first member only.

You can get equation (see monograph [6]):

.

$$\frac{d\,\text{h}\,\sigma}{d\,\text{h}\,R}=\frac{\frac{2\delta}{R}+\left(\frac{\delta}{R}\right)^2}{2+\frac{2\delta}{R}+\left(\frac{\delta}{R}\right)^2} \qquad (8)$$

Equation (8) is analogous to the well-known Gibbs-Tolman-Koenig-Buff equation for a cylindrical surface.
To solve equation (8), the dimensionless variable R/δ introduced. As a result,

$$\ln\frac{\sigma}{\sigma^{(\infty)}}=-\int_{R/\delta}^{\infty}\left(\frac{2x+1}{2x^3+2x^2+x}\right)dx\,. \qquad (9)$$

The integral in (9) is found by integrating rational functions (i.e. by expanding the integral function into partial fractions [6]). The result represented as (δ =const. [6]):
(Functions graphs see Figure 5)

$$\sigma=\frac{\sigma^{(\infty)}\,R}{\delta}\sqrt{\frac{2}{2(R/\delta)^2+2R/\delta+1}}\exp\left(-\text{arctg}\left(\frac{1}{1+2R/\delta}\right)\right). \qquad (10)$$

If $R>\ \delta$, (10) transformed into a well-known analogue of the Tolman formula:

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

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

If $R<<\delta$:

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

This is Russanov's formula [5, 6] for a cylindrical particle (see Figure 2).

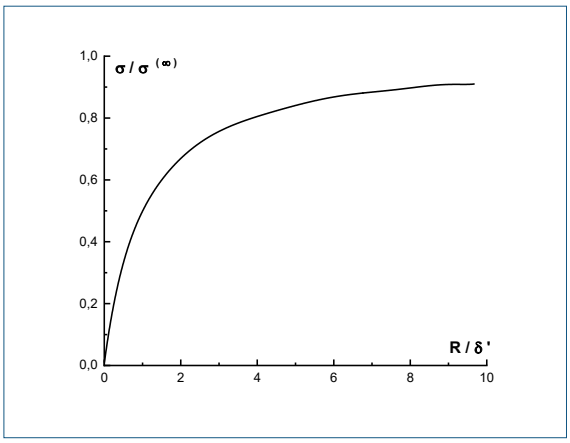


Figure 2: Functions Graphs of Solution (5) (see [6]).

In addition, we note that for a spherical nanoparticle, a formula was obtained (within the framework of the Gibbs-Tolman-Koenig-Buff theory [6]):

$$\ln\frac{\acute{o}}{\acute{o}_{\infty}}=-\frac{2+2^{\frac{1}{3}}-2^{\frac{2}{3}}}{6}\cdot\ln\left(\frac{2}{3}\frac{\ddot{a}^2}{R^2}+\frac{4-2^{2/3}}{3}\frac{\ddot{a}}{R}+\frac{1}{1+2^{-1/3}}\right)-$$

$$-\frac{\ddot{a}-2^{\frac{1}{3}}+2^{\frac{2}{3}}}{3}\cdot\ln\left(1+2^{-1/3}+\frac{}{R}\right)-$$

$$-\frac{2^{\frac{2}{3}}+2^{\frac{1}{3}}}{\sqrt{3}}\cdot\operatorname{arctg}\left(\frac{2^{4/3}-1}{\sqrt{3}}+\frac{2^{4/3}}{\sqrt{3}}\cdot\frac{}{R}\right)-$$

$$-\left(2^{-2/3}-2^{-1/3}\right)\cdot\ln\left(1+2^{-1/3}\right)+\frac{2^{\frac{2}{3}}+2^{\frac{1}{3}}}{\sqrt{3}}\operatorname{arctg}\left(\frac{2^{4/3}-1}{\sqrt{3}}\right),$$

When R → ∞ the formula leads to:

$$\frac{\acute{o}}{\acute{o}_{\infty}}=1-2,009774769\cdot\frac{\ddot{a}}{R},\ \text{(Tolman formula).}$$

If $R << \delta$:

$\sigma / \sigma^{(\infty)} \sim 0.304(R/\delta)$;
obtained Russanov's formula [5, 6] for a spherical nanoparticle.

Simple Linear Model

First, we will consider the linear theory proposed in [6], 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]:

$$n''+\frac{n'}{r}-\frac{1}{\delta^2}(n-1)=0, \qquad (11)$$

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/δ is introduced) is proportional to the volume density function, which we designate as N(x) (see below).
A particular physical solution (11) used, which has the form of [9]:

$$\mathrm{n(x)}=\mathrm{c}K_0(\mathrm{x}), \qquad (12)$$

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/δ). For it, the boundary conditions described as:

$$N(r/\delta)\to n(0)\equiv n(R)=1,$$
$$N\left(+\infty\right)\to n(+\infty)=0.$$

Using solution (12) and conditions (14a), we get:

$$N(r/\delta)=\begin{cases}1, & r\le R,\\ \dfrac{K_0(r/\delta)}{K_0(R/\delta)}, & r>R,\end{cases} \qquad (13)$$

Using (13), we derive the equation:

$$\frac{d\ln\sigma}{d\ln x}=\frac{1}{x\{K_0(x)/K_1(x_0)\}+1}. \qquad (14)$$

If x >> 1:

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

As a result,

$$\frac{d \ln \sigma}{d \ln x} = \frac{1}{x+1}$$, (15)

where follows the Tolman formula. When x << 1:

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

where γ = 1.781, and

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

As follows from the graph (Figure 3), it can assume that the emerging nanocylinder reaches thermodynamically equilibrium dimensions R ~ δ (with a relative volume density of its constituent fragments equal to one). This equilibrium dimension ~ δ in the Cahn-Hilliard-Hillert theory defined in [7-10]. Around the equilibrium dimension R ~ δ, there is an "atmosphere" of the volume density of the nanoparticle components (or discharged nanoparticle fragments), N(r/δ), which asymptotically approaches zero only within the r/δ→∞ 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 (see Figure 3). 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 δ, 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 [7-10] and, accordingly, with the classical theory of nucleation.

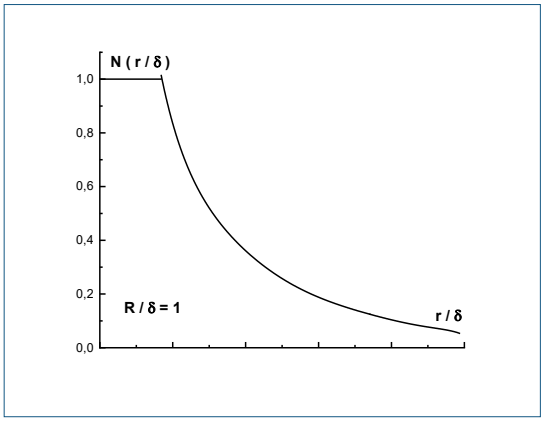


Figure 3: Volume Density Function, N(r/δ) (15).

Droplet Model

As the most important application of the above results from a practical point of view, let us consider the problem of the sessile droplet.

The assumptions made, in our opinion, are the most acceptable for liquid metals far from the evaporation phase ransition. Due to a high value of superficial tension, a small drop of typical liquid metal shall have the shape closer to spherical. For the same reason, for the metal at the boundary of" liquid−steam"separation the density distribution profile is approximately stepwise, the interphase region thickness tends to zero and dimensional dependencies of the superficial tension and contact angle can be ignored.

The equilibrium droplet profile is determined in terms of the constancy of the sum of hydrostatic and capillary pressure. In this case the Laplace equation is [7-10].

$$\sigma\left(\frac{1}{r_1}+\frac{1}{r_2}\right)=p_0+\Delta\rho\, g\, z\,,$$

$$\frac{1}{r_1}=\frac{d\varphi}{ds},\ \frac{1}{r_2}=\frac{\sin\varphi}{x},\ \varphi\in[0,\pi],\ (16)$$

where p_0 is the pressure of the droplet measured, φ is slope of the tangent at a point of the meridian, s is the arc length, x and z are the coordinates that define the droplet cross-section, $\Delta\rho = m\Delta n$ is the difference in density between the liquid and gaseous phases, g is the gravitational acceleration, m is the mass of a single particle (atom or molecule). In this case the surface tension depends on the local curvature of radii r_1 and r_2.

We will consider a special case of the equation [7-10].

$$\frac{d\phi}{ds}+\frac{\sin\phi}{x}=0\,,$$

$$\frac{dx}{ds}=\cos\varphi\,,\ \frac{dz}{ds}=\sin\varphi\,,\ \ x(s=0)=z(s=0)=\varphi(s=0)=0\,,$$

and

$$ds=adx$$

We can obtain asymptotic dependence

$$\tan\left(\varphi/2\right)\sim(x)^{-a}.$$

Below we obtain a similar formula for the nanocylinder. (Also see (1)).

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:

$$\mathrm{n_1}'' + \frac{1}{r}\mathrm{n_1}' + \frac{1}{\delta_1^{\,2}}\exp\{-\mathrm{n_1}\}=0\,, \qquad (17)$$

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

Choosing the function in the form of $\frac{1}{\delta_1^{\,2}}\exp\{-\mathrm{n_1}\}$ is undoubtedly an arbitrary decision when modeling an unknown functional.

However, if we expand the exponent $\frac{1}{\delta_1^{\,2}}\exp\{-\mathrm{n_1}\}$, we can obtain equation (7).

On the other hand, in our opinion, the function $\frac{1}{\delta_1^{\,2}}\exp\{-\mathrm{n_1}\}$ 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:

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

where (see below):

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

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 δ_1 is introduced through the normalization integral:

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

from which it was derived that

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

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:

$$N = 1 + 2\ln[1 - X_1^{\,2}] \quad . (18)$$

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 Figure 4.

The difference between solutions of the linear and nonlinear equations (Figures 3 and 4) is fundamental. In the first case, as we have 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 (6)), the growth of the nucleus is ultimately limited, which will be discussed below.

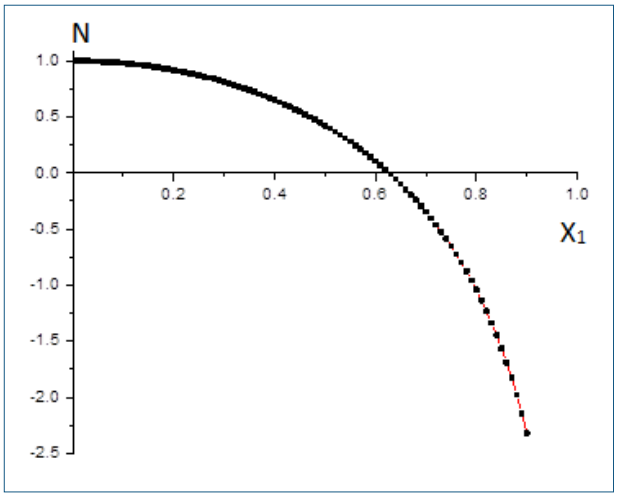


Figure 4: Plot of function (18) Obtained from Solution of Eq. (17). Only the Solution for N, When This Function Is Greater or Equal to Zero, Has A Physical Sense.

For a cylindrical particle, the limitation applies only to the cylinder's radial growth. The particle can grow in length.

Surface Energy for Nanowires and Nanodroplets

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, [7-10]. 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 [7-10] is represented by the angle function θ(ρ) 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 [7-10]:

$$H_{g,c} = \frac{A}{2}\left[\grave{e}'^2 + \frac{\grave{e}\sin^2}{r^2}\right], \quad (19)$$

where θ(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 (19) 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 [7-10]). It should also be noted that in our case these quasiparticles are topological compositions rather than dynamic particles. Therefore, in our case the kinetic energy means the virtual kinetic energy of the topological instanton.

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

$$\tilde{n} = \frac{r}{R_c},$$

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 $0 \le \rho \le 1$. The proposed continuum model of energy (19) 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 (19), it is simple to derive the Euler-Lagrange equation:

$$\grave{e}''(\tilde{n}) + \frac{\grave{e}'(\tilde{n})}{\tilde{n}} - \frac{\sin\grave{e}\cos\grave{e}}{\tilde{n}^2} = 0. \quad (20)$$

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

$$\grave{e}(\tilde{n}) = \begin{cases} \eth, & \tilde{n} = 0, \\ \frac{\eth}{2}\tilde{n} & \pm. \end{cases} \quad (21)$$

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

$$\tan\left(\frac{\grave{e}}{\tilde{n}}\right) = \frac{1}{-}, \quad (22)$$

which is convenient for further analysis.

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

$$\grave{e}_a''(\tilde{n}) + \frac{\grave{e}_a'(\tilde{n})}{\tilde{n}} - \frac{a^2\sin\grave{e}_a\cos\grave{e}_a}{\tilde{n}^2} = 0, \quad (23)$$

where a^2 is the ratio of anisotropy energy to exchange interaction constant A. Parameter a^2 was determined in [7-10]:

$$a^2 = \frac{B}{A} + 1, \quad (24)$$

The definition of the anisotropy function was also given there:

$$\frac{B\sin^2\theta_a}{2\rho^2}, \quad (25)$$

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 (23) is as follows:

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

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 Figure 5.

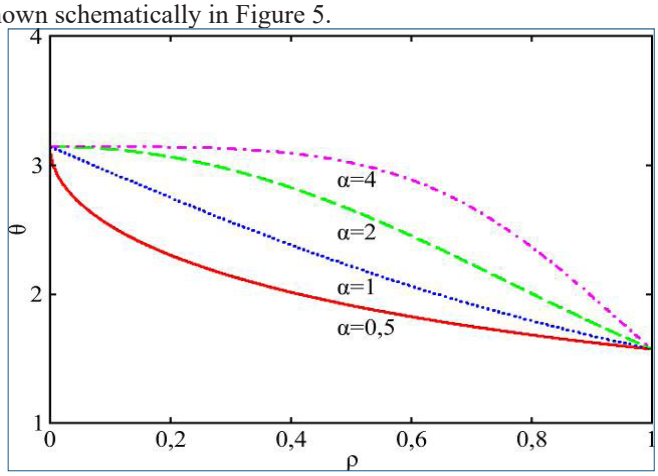


Figure 5: Diagrams of Solution (26) at Different Values of Parameter a.

It is easy to show that the function θ(ρ) 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 >> 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 Figure 5 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.

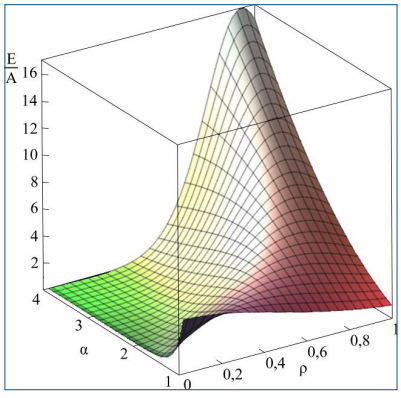
The change in the free energy from the center of the particle to its surface can be estimated. This estimation allows the physical interpretation of the introduced model parameters and their comparison with the conventional energy characteristics that are used to describe the nucleation process.

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(ρ) = T + U. Considering solution (27), 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:

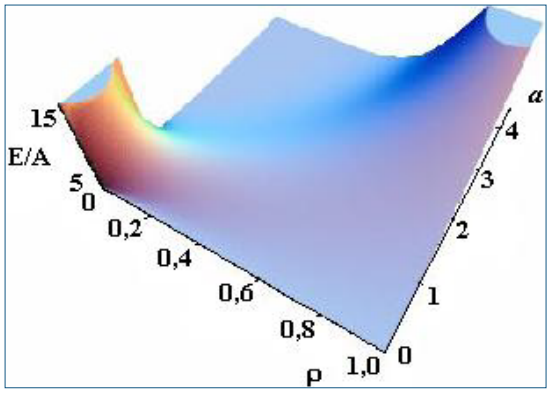
$$E(\rho) = T + U = 4A\left(\frac{a}{\rho}\right)^2 \frac{\rho^{2a}}{(1+\rho^{2a})^2}. \quad (27)$$

It follows from (27) that for a = 1 and $\rho \to 1$, the equality E(ρ) = 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 energy used in thermodynamic theories provided that these energies have different dimensions.

a)



b).



Figures 6 (a, b): Three-Dimensional Dependence of Energy on Parameters a and ρ.

A sharp increase in free energy (see Figure 6) 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(ρ) 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 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:

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

According to the Cahn–Hilliard theory, the energy of the activation barrier is proportional to the geometric average of two energy p arameters: $E_c \sim \sqrt{AB}$. Unlike the proposed theory, the Cahn–Hilliard theory is not scale invariant, and the quantity of B has a

dimension of J/m^3. 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.

Conclusion

The surface energy is the most important thermodynamic characteristic of the interface; it is the cause of almost all capillary phenomena. The value of surface energy, provided that all other conditions are equal, depends on the curvature of the interface. This relationship is commonly referred to as the size dependence. Physically, the dependence is due to a change in the interatomic or intermolecular interactions near the interface.

We have obtained results associated with the van der Waals gradient theory, which can be resumed in the following way. If in the formation of a nanoparticle there is only one energy form that plays the role of exchange interaction A, then, in the context of the proposed model, the additive separation of the system energy into the surface energy and the nanoparticle volume energy is incorrect. However, in this case, we can introduce the average energy of the whole nanoparticle and, from simple geometric considerations, derive the Rusanov linear formula for the surface energy. Typically, the Rusanov formula is assumed universally applicable. This fact is not confirmed when our model of the anisotropy energy is complicated.

Topological ideas, when applied, in particular, to field and elementary particle theory, and subsequently to the theory of magnetism, led to a number of fundamental results in statistical physics. One of these results, first obtained in this work, is the fundamental solution in the form of instanton waves, which are already used to describe the physical behavior of magnets and nematic liquid crystals.

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