SURFACE TENSION PROBLEM FOR MICRO- AND NANOWIRES

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Abstract

An analytical solution for the Gibbs–Tolman–Koenig–Buff equation for microwire and nanowire surfaces has been obtained. Analysis has been performed for a cylindrical surface in terms of the linear and nonlinear Van der Waals theory.

Keywords: Gibbs–Tolman–Koenig–Buff theory, Tolman length, Van der Waals theory

Rezumat

A fost obținută soluția analitică a ecuației Gibbs–Tolman–Koenig–Buff pentru suprafața microfirelor și nanofirelor. Analiza a fost efectuată pentru suprafața cilidrică în cadrul teoriei liniare și neliniare Van der Waals.

Cuvinte cheie: teoria Gibbs–Tolman–Koenig–Buff, lungimea Tolman, teoria Van der Waals

1. Introduction

In this paper, the surface tension in microwires prepared by the Taylor–Ulitovsky method is studied. Surface tension is a fundamental thermodynamic parameter that significantly affects the formation of micro- and nanowires.

The chemical and physical properties of interphase boundaries in micro- and nanowires, as well as for micro- and nanoparticles, have been studied by many authors (see fundamental monographs [1–5], papers [6–20], and reports of S.A. Baranov [21–24]). The following theoretical approaches should be mentioned: the Gibbs–Tolman–Koenig–Buff equation method and the linear and nonlinear Van der Waals theory [22–27].

The study aims at derivation and detailed analysis of expressions for the surface tension of microwires in thermodynamic equilibrium in terms of the Gibbs–Tolman–Koenig–Buff equation method and the Van der Waals theory.

The given theory can find application in microwire production technology.

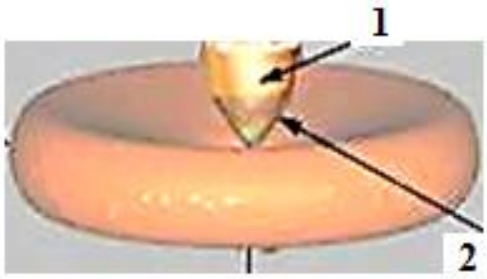

Fig. 1. Process of casting glass-coated amorphous magnetic micro- and nanowires: (*1*) the cylindrical zone and (*2*) the cone zone.

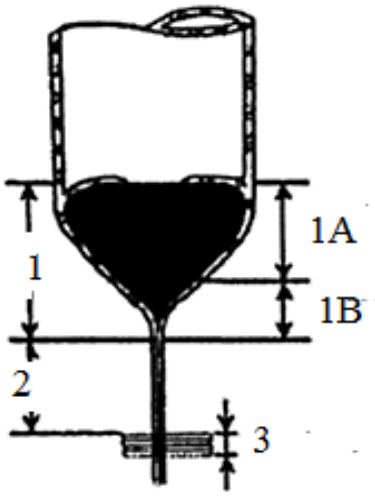

Fig. 2. Schematic micro- and nanowire formation process by the Taylor–Ulitovsky method: (*1*) the microbath: (1A) the primary cone of the microbath and (1B) the secondary cone of the microbath; (*2*) the extension zone; and (*3*) the crystallizer.

It is evident from the figures that cylindrical and conical surfaces should be studied.

2. Modeling of Surface Energy for Microwires in Terms of the Gibbs–Tolman–Konig–Buff Theory

The Gibbs–Tolman–Koenig–Buff differential equation (for a cylinder) [2–6] will be used to describe the surface tensions (σ_i) of micro- and nanowires [1]:

$$\frac{d\ln\sigma_i}{d\ln R_i}=\frac{\frac{2\delta_i}{R_i}+\left(\frac{\delta_i}{R_i}\right)^2}{2+\frac{2\delta_i}{R_i}+\left(\frac{\delta_i}{R_i}\right)^2}, \tag{1}$$

where R_i are the radii of micro- and nanowires (metallic kernel radius R_m or the total radius of glass R_g).

Non-negative parameters (δ_i) characterize the thickness of the interfacial layer (for example, between the glass and the metal).

In surface thermodynamics, Tolman length is used as a parameter that is equal to the distance between the surface of tension and the equimolar surface. The numerical values of the parameter—"Tolman length" analog—for micro and nanowires lie in a range of 0.1–1 μm.

The integral in (1) (if δ_i = const) can be taken exactly. The final result is as follows [11]:

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

The well-known Tolman`s formula (for a cylinder) is in a special case of $R >> \delta$ for formula (2):

$$\sigma/\sigma^{(\infty)}\sim\frac{1}{1+\frac{\delta}{R}}. \tag{3a}$$

In the case of $R << \delta$:

$$\sigma/\sigma^{(\infty)}\sim 0.645(R/\delta). \tag{3b}$$

We get the Rusanov`s linear formula (3b) for the cylindrical surface (see [5, 11]).

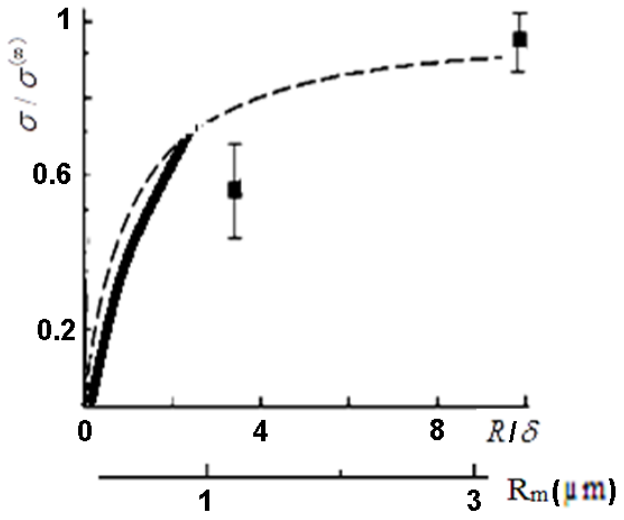

Fig. 3. Function graphs of (dashed line) solutions (3) and (bold line) solutions (10)–(14). Experimental data for the surface tension of metal–glass as a function of metallic kernel radius R_m.

3. Modeling of Surface Energy for Micro- and Nanowires

The basic equation of the linear Van der Waals theory of an inhomogeneous medium (see [1–3, 11, 27] for details) can be written as follows:

$$n'' + \frac{n'}{r} - \frac{1}{\delta^2}(n - n_{1,2}) = 0\,, \tag{4}$$

where n (x) is the function proportional to the volume density $N(x)$ ($x = r/\delta$, n_o = const)**,** r is the radial variable measured from the center of a nanoparticle, and δ is the Tolman length [1–3, 11, 27].

The general solution to Eq. (4) has the form

$$n(r) = n_{1,2} + A I_0(r/\delta) + B K_0(r/\delta)\,, \tag{5}$$

where $I_0(r/\delta), K_0(r/\delta)$ are modified Bessel and Hankel functions.

$$n(0) = n(R) = n_1\,, \quad n(+\infty) = n_2\,. \tag{6}$$

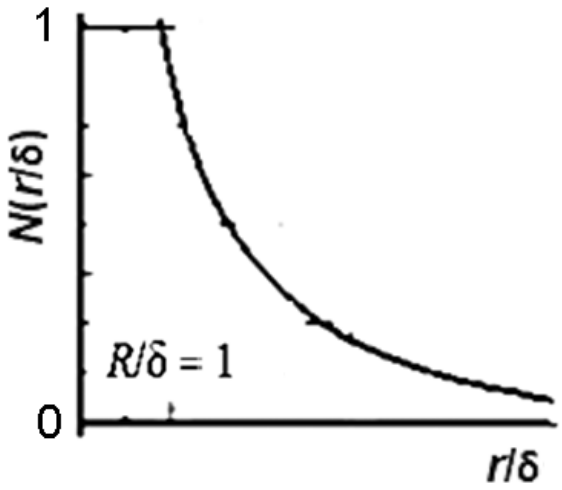

Fig. 4. Function graph of volume density function $N(r/\delta)$ [11, 27].

We will accept for the volume density function $N(r/\delta)$:

$$N(r/\delta) \to n(0) \equiv n(R) = 1\,,\ N\left(+\infty\right) \to n(+\infty) = 0\,. \tag{7}$$

Substituting solution (5) into expression (7) and integrating, we obtain [11, 27]:

$$N(r/\delta)=\begin{cases}1, & r\le R,\\ \dfrac{K_0(r/\delta)}{K_0(R/\delta)}, & r>R,\end{cases} \tag{8}$$

Solution (8) can be used for calculating adsorption, which is defined as the excess number of atoms or molecules in the surface layer of the nanoparticle per unit area:

$$\Gamma \to \delta\,\frac{K_1(x)}{K_0(x_0)}, \tag{9}$$

($x = r/\delta$, $x_0 = R/\delta$).

Taking into account adsorption (9), we obtain the differential equation [11, 27]

$$\frac{d\,\ln\sigma}{d\,\ln x}=\frac{1}{x\{K_0(x)/K_1(x_0)\}+1}. \tag{10}$$

At $x >> 1$

$$\frac{K_0(x)}{K_1(x_0)}\to 1, \tag{11}$$

we obtain

$$\frac{d\,\ln\sigma}{d\,\ln x}=\frac{1}{x+1}, \tag{12}$$

(see Eqs. (2) and (3a));

At $x << 1$

$$\frac{K_0(x)}{K_1(x)}\approx x\ln\frac{2}{\gamma x}, \tag{13}$$

where $\gamma = 1.781$ is the Euler constant, we obtain

$$\frac{d\,\ln\sigma}{d\,\ln x}=\frac{1}{x\ln\dfrac{2}{\gamma x}+1}. \tag{14}$$

This equation is integrated numerically.

4. Modeling of Surface Energy for Micro- and Nanowires in Terms of the Nonlinear Theory

The nonlinear equation can be written as follows [27]:

$$n_1'' + \frac{1}{r}n_1' + \frac{1}{\delta_1^{\,2}}\exp\{-n_1\}=0, \tag{15}$$

Simple volume density function N can be determined as follows [27]:

$$N_1 = 1 + 2\ln[1 - X_1^{\,2}]\,, \tag{16}$$

$$X_1 = \mathrm{r}/(2\sqrt{2}\delta_1)\,. \tag{17}$$

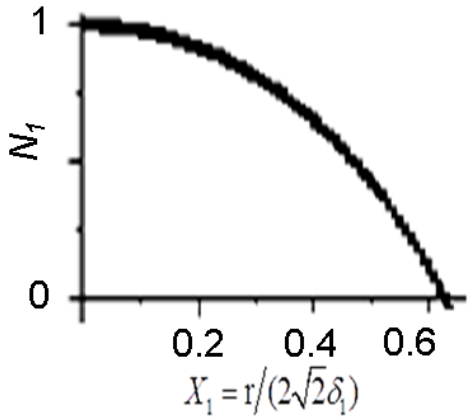

Fig. 5. Function graph of solution (16) [27].

The results obtained have a physical meaning only as long as function N_1 is positive.

The resulting density profile (see Fig. 5 and (16), (17)) significantly differs from the results of the linear theory (see Fig. 4 and (8)) and, therefore, the Gibbs–Tolman–Koenig–Buff theory (see (2), (3a), (3b)).

Micro- and nanowires will be produced with a limited metallic kernel R_{m} [27].

5. Modeling of Surface Energy of Micro- and Nanowires for a Particular Case of the Theory

The equation can be written (for a particular case of the theory) as follows

$$\mathrm{n}_2'' + \frac{1}{r}\mathrm{n}_2' = 0\,. \tag{18}$$

A particular solution to Eq. (18) can have the form

$$n_2 = c\ln(\mathrm{R}/\delta)\,. \tag{19}$$

We will accept the initial values

$$\mathrm{N}_{2,0} = 1\,, \tag{20}$$

and obtain

$$N_2 = 1 + \ln(\mathrm{R}/\delta)\,. \tag{20a}$$

The function graph of N_2 is shown in Fig. 6.

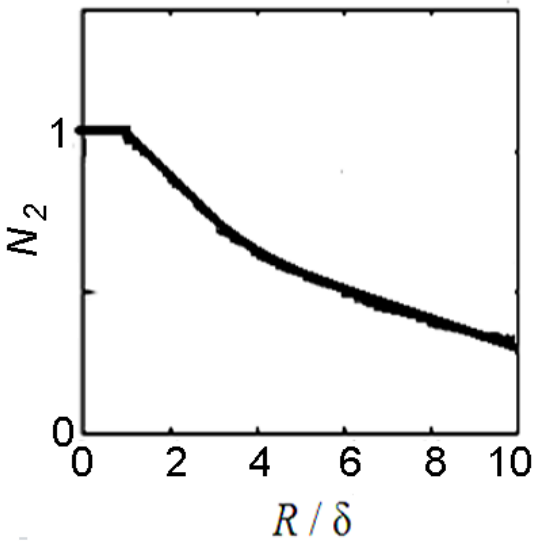

Fig. 6. Function graph of solutions (20) and (20a).

6. Conclusions

A feature of micro- and nanowires is that these objects consist of an amorphous alloy core (metal conductor) with a diameter of 0.1–50 μm, which is covered with a Pyrex-like coating with a thickness of 0.5–20 μm. Therefore, the main technological parameter for the preparation of glass-isolated micro- and nanowires is the surface tension of micro- and nanowires.

According to the previous analysis [1], the geometry of this microwire is most significantly affected by the glass properties. Microwire radius R_g (outer radius of the glass shell) is estimated as follows [1]:

$$Rg \sim \frac{\eta^{2-k}}{V_d^k \sigma_s^{1-k}} \tag{21}$$

where k is a parameter dependent on a casting rate ($0 < k < 1$), V_d is the casting rate, and σ_s is the surface tension.

The metallic radius R_m can be estimated approximately:

$$R_m \sim \frac{\sigma_{sm}}{V_d^{2-k_m}} \tag{22}$$

σ_{sm} is the surface tension of metal–glass($0 < k_m < 1$).

Thus, it has been confirmed that surface tension, which is defined as excess free energy per unit surface area, determines the radius of micro- and nanowires.

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