

## INTERPHASE ENERGY AT A THIN METAL THREAD–DIELECTRIC MEDIUM INTERFACE

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*Within the framework of the method of electron-density functionals, the influence of the dielectric medium on the interphase energy of alkaline-metal threads has been studied. It is shown that the interphase energy increases with decrease in the thread radius.*

Thermodynamic analysis of interphase phenomena at a thin metal thread–dielectric medium interface has been carried out in [1–4]. Here, in order to evaluate the interphase energy, one applied, as a rule, the Gibbs–Tolman–König–Baff equation obtained for free spherical drops and not for threads and containing no characteristics of the dielectric medium. At the same time, knowledge of the interphase characteristics at the thin metal thread–dielectric medium interface is needed for designing capillary energy-storage devices, capillary electric motors [3, 4], and tunnel and atomic-force microscopes and for developing new composite materials produced by the method of impregnation [5, 6] and the technology of production of nanowires [7].

We are familiar only with one work ([8]) where in the stabilized-jelly approximation the surface energy is evaluated for cylindrical nanowires of elementary Al, Na, and Cs metals at  $T=0$  K. It is shown that the mean values of the surface energy increase with decrease in the thread radius  $R$ , while for  $R < (9-10)a_0$  they oscillate. However, in [8], the influence of the dielectric medium on the surface energy has not been studied.

In the present work, within the framework of the method of electron-density functionals, we study the influence of the dielectric medium with a permittivity  $\epsilon$  on the interphase energy of alkaline-metal threads.

Usually, in simulating metallic systems, when the jelly approximation is used, no account is taken of the relaxation and reconstruction of a surface, which are considerable in ionic and semiconductor crystals. In the case of metals, as is shown in [9], account for the relaxation leads to an insignificant decrease in the surface energy for close-packed faces and to a maximum decrease of 3–7% in the surface energy for the loosest faces. Therefore, the density of the positive charge inside the thread can be assigned in the form of the step function  $n_+(r)$ :

$$n_+(r) = \begin{cases} n_0, & 0 < r < R_0, \\ 0, & r > R_0. \end{cases} \quad (1)$$

We assign the electron-charge distribution in the thread by the trial function

$$n_-(r) = n_0 \begin{cases} 1 - \exp(-\beta R_G) \cosh \beta r, & r < R_G, \\ \sinh \beta R_G \exp(-\beta r), & r > R_G. \end{cases} \quad (2)$$

in which  $\beta$  and  $R_G$  are found from the condition of conservation of the thread charge:

$$2\pi q_s R_0 + \pi n_0 R_0^2 = \pi n_0 R_G^2 + \frac{2\pi n_0}{\beta^2} [1 - \exp(-\beta R_G)]. \quad (3)$$

The electrostatic-potential distribution in the thread is determined from a Poisson equation written in a cylindrical coordinate system with account for the boundary conditions  $\phi'(0) = \phi'(\infty) = 0$  and the continuity conditions  $\phi(r)$  and  $\phi'(r)$  at the interface  $r = R_0$ :

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$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \varphi}{\partial r} \right) = - \frac{4\pi [n_-(r) - n_+(r)]}{\varepsilon \theta (r - R_0) + \theta (R_0 - r)}. \quad (4)$$

From Eq. (4) with Eqs. (1) and (2) taken into account we obtain the following expressions for the electrostatic potential distribution at the thread–dielectric medium interface:

for  $R_G < R_0$

$$\varphi(r) = \frac{4\pi n_0}{\beta^2} \begin{cases} \exp(-\beta R_G) (\cosh \beta r - I_1(r)) + C_{11}, & 0 < r < R_G, \\ -\sinh \beta R_G \exp(-\beta r) + (\beta r)^2/4 - \beta^2 (q_s R_0/n_0 + R_0^2/2) \ln \beta r + C_{21}, & R_G < r < R_0, \\ -\sinh \beta R_G \exp(-\beta r)/\varepsilon, & R_0 < r; \end{cases} \quad (5)$$

for  $R_G > R_0$

$$\varphi(r) = \frac{4\pi n_0}{\beta^2} \begin{cases} \exp(-\beta R_G) (\cosh \beta r - I_1(r)) + C_{12}, & 0 < r < R_0, \\ [\exp(-\beta R_G) \cosh \beta r - (\beta r)^2 + (1 + 0.5 (\beta R_G)^2) \ln \beta r]/\varepsilon + C_{22}, & R_0 < r < R_G, \\ -\sinh \beta R_G \exp(-\beta r)/\varepsilon, & R_G < r, \end{cases} \quad (6)$$

where

$$I_1(r) = \sum_{k=1}^{\infty} \frac{(\beta r)^{2k}}{(2k) \cdot (2k)!}; \quad I_2(r) = \sum_{k=1}^{\infty} \frac{(-\beta r)^k}{k \cdot k!}; \quad (7)$$

$$C_{1k} = I_1(R_G) - 1 + (\beta R_G)^2/4 - (\beta^2 q_s R_0 + 0.5 (\beta R_0)^2) \ln \beta R_G + C_2, \quad k = 1, 2;$$

$$C_{21} = \sinh \beta R_G \exp(-\beta R_0) (1 - 1/\varepsilon) - (\beta R_0)^2/4 + (\beta^2 q_s R_0/n_0 + 0.5 (\beta R_0)^2) \ln \beta R_0; \quad (8)$$

$$C_{22} = -\frac{1}{\varepsilon} + \frac{1}{\varepsilon} \exp(-\beta R_G) I_1(R_G) + \frac{(\beta R_G)^2}{4\varepsilon} - \frac{1}{\varepsilon} (\exp(-\beta R_G) \cosh \beta R_G + 0.5 (\beta R_G)^2) \ln \beta R_G.$$

The interphase energy with account for Eqs. (1) and (2) in the homogeneous-background approximation can be calculated by using the known relation [10] written in cylindrical coordinates:

$$\sigma_j(\beta, \varepsilon) = \frac{1}{2R_0} \int_0^{\infty} \varphi(r) [n_-(r) - n_+(r)] r dr + \frac{1}{R_0} \int_0^{\infty} \{w[n_-(r), \varepsilon] - w[n_+(r), \varepsilon]\} r dr, \quad (9)$$

where

$$w[n(r), \varepsilon] = 0.3 (3\pi^2)^{2/3} n^{5/3}(r) + \frac{1}{72} \frac{|\nabla n(r)|^2}{n(r)} - 0.75 \left(\frac{3}{\pi}\right)^{1/3} n^{4/3}(r) - 0.056 \frac{n^{4/3}(r)}{0.079 + n^{1/3}(r)} + C_{\text{ex}}(r_c) \frac{|\nabla n(r)|^2}{n^{4/3}(r)}. \quad (10)$$

As an example, we present the results of calculations of the surface energy for threads made of pure Na, K, and Cs with  $q_s = 0$  and  $\varepsilon = 1$  and of the interphase energy at the thread–dielectric medium interface with  $\varepsilon = 1.9$  and 81: a) at fixed values of the thread radius  $R_0$  and at assigned values of  $\varepsilon$  the values of  $\beta$  changed from 0.4 to 1.4

TABLE 1. Values of the Variational Parameters  $\beta$  and  $R_G$  for Sodium and Potassium at the Interface with the Dielectric Medium ( $\epsilon = 81$ )

Sodium			Potassium		
$R_0$ , AU	$R_G$ , AU	$\beta_{\min}$ , AU $^{-1}$	$R_0$ , AU.	$R_G$ , AU	$\beta_{\min}$ , AU $^{-1}$
10.82	10.71	0.94	13.48	13.39	0.92
11.50	11.40	0.95	14.32	14.24	0.93
12.39	12.30	0.95	15.43	15.35	0.93
13.16	13.08	0.95	16.40	16.32	0.93
13.63	13.55	0.96	16.98	16.91	0.94
14.07	13.99	0.95	17.53	17.46	0.93
14.68	14.61	0.96	18.29	18.23	0.94
15.25	15.18	0.95	19.00	18.94	0.94
15.60	15.53	0.95	19.44	19.38	0.94
15.94	15.87	0.95	19.86	19.80	0.94
16.43	16.36	0.95	20.46	20.41	0.94
16.88	16.82	0.96	21.03	20.98	0.94
17.17	17.11	0.95	21.40	21.34	0.93
17.46	17.40	0.97	21.75	21.69	0.93
17.86	17.80	0.96	22.25	22.20	0.93
18.25	18.19	0.96	22.74	22.69	0.93
18.50	18.44	0.96	23.05	23.00	0.95
21.18	21.13	0.96	26.38	26.34	0.96
23.31	23.26	0.96	29.04	29.00	0.96

with a step of 0.01; b) from the array of data on interphase energy we selected the smallest value of  $\sigma_j = \min_{\beta} \sigma_j(\beta)$  (these values of  $\sigma_j$  and  $\beta$  were taken to be true); c) similarly we found the values of  $\sigma_j$  for the new radius  $R_0$ , etc. The accuracy of calculation of  $\sigma_j$  was 0.1 mJ/m $^2$ .

The values of  $\beta$  corresponding to the minimum of the interphase energy and the values of  $R_G$  identical to them for the Na and K threads are given in Table 1, from which it is evident that the Gibbs coordinate  $R_G$  is less than  $R_0$ .

The results of calculations of  $\sigma_j$  are presented in Fig. 1 and in Tables 2 and 3.

For the sodium threads of dimension  $R_0 \geq (13-15)a_0$  our data are about 20 mJ/m $^2$  higher than the data of [8]; here the surface energy of the threads increases with decrease in  $R_0$ .

The dimensional dependences  $\sigma_j(R_0)$  given in Fig. 1 are satisfactorily approximated by the formula

$$\sigma_j/\sigma_{\infty} = \exp(2\delta/R_0). \quad (11)$$

The coefficients  $\sigma_{\infty}$  and  $\delta$  in formula (11) found by the method of least squares and the correlation coefficients  $k$  close to 1 are contained in Table 2.

The dimensional dependences  $\sigma_j(R_0)$  are also satisfactorily approximated by the polynomials

$$\sigma_j/\sigma_{\infty} = 1 + a/R_0 + b/R_0^2. \quad (12)$$

As is seen from Table 3, for  $R_0 > 10a_0$  in formula (12) the third term can be neglected, which gives the Tolman-type formula  $\sigma_j/\sigma_{\infty} = 1 + 2\delta/R_0$ , where  $\delta \approx a/2$ . In [3], it is noted that for many metals the values of  $\delta$  change from 0.2 to 0.3 Å; in this case their range is  $(0.32-0.40)a_0$  or  $(0.17-0.21)$  Å, which is close to that of [3] in order of magnitude. From Tables 2 and 3 and Fig. 1 it is evident that the dielectric medium leads to a decrease in the surface

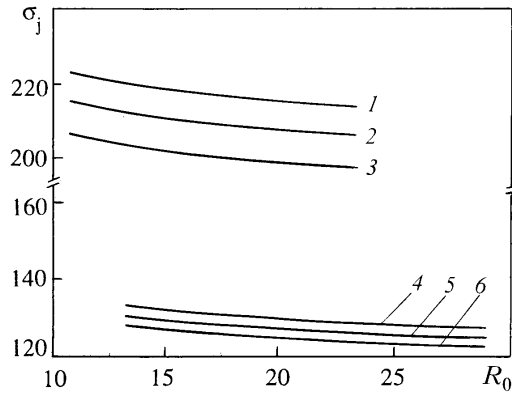


Fig. 1. Dependence of the surface energy  $\sigma_j$  on the thread dimension: 1) sodium–vacuum; 2) sodium in benzene; 3) sodium in water; 4) potassium–vacuum; 5) potassium in benzene; 6) potassium in water.  $\sigma_j$ ,  $\text{mJ/m}^2$ ;  $R_0$ , AU.

TABLE 2. Values of the Coefficients  $\sigma_\infty$  and  $\delta$  in Eq. (11)

Metal	$\epsilon$	$\sigma_\infty$ , $\text{mJ/m}^2$	$\delta$ , AU	$k$
Sodium	1.9	200	0.3886	0.9979
	81	191	0.3994	0.9983
Potassium	1.9	123	0.3547	0.9977
	81	121	0.3456	0.9975
Cesium	1.9	89	0.3262	0.9918
	81	88	0.3180	0.9940

TABLE 3. Values of the Coefficients of the Approximation Polynomials in Eq. (12)

Metal	$\epsilon$	$\sigma_\infty$ , $\text{mJ/m}^2$	$a$ , AU	$b$ , $\text{AU}^2$	$k$
Sodium	1.9	199	0.9643	-1.2910	0.9988
	81	191	0.8925	-0.4746	0.9985
Potassium	1.9	123	0.8085	-0.8071	0.9980
	81	121	0.7660	-0.5603	0.9977
Cesium	1.9	89	0.3689	3.6806	0.9950
	81	88	0.4306	2.7153	0.9958

energy of the nanowires and the greater, the higher the values of the permittivity of the medium  $\epsilon$ . Just as in [3], the evaluations obtained by us point to the growth in the interphase energy with decrease in the thread radius. The similar dimensional dependence does not contradict the results of certain works in which the surface energy for free liquid spherical drops decreases with decrease in their radius [11], since in this case one evaluates the free surface energy  $f = \sigma - TS^\omega$  at  $T \neq 0$  K and not the surface energy  $\sigma$ . In this connection, the behavior of the dimensional dependence  $f(R_0)$  can change because of the dimensional dependence of the surface entropy  $S^\omega(R_0)$ . The results of [12] also point to the difference in the dimensional dependences of the surface tension for solid and liquid drops.

## NOTATION

$\sigma_\infty$ , surface energy of the macroscopic metal,  $\text{mJ/m}^2$ ;  $\sigma_j$ , surface energy of the metal thread,  $\text{mJ/m}^2$ ;  $a_0$ , Bohr radius;  $R_0$ , thread radius, AU of the length or Bohr radii;  $\epsilon$ , permittivity of the medium;  $n_+(r)$ , function characterizing the density distribution of the positive charge;  $r$ , coordinate perpendicular to the thread axis;  $n_0$ , density of the positive thread charge;  $r_c$ , radius of the Wigner–Seitz cell;  $n_-(r)$ , function characterizing the electron-charge distribution;  $\beta$ , variational parameter minimizing the interphase energy,  $\text{AU}^{-1}$ ;  $R_G$ , radius of the Gibbs separating surface, AU of the length or Bohr radii;  $\theta$ , Heaviside function;  $q_s$ , surface density of the charge at the thread–dielectric medium interface,

$C/m^2$ ;  $w[n(r), \epsilon]$ , density of the energy of the inhomogeneous electron gas involving the kinetic and exchange-correlation energies with gradient corrections;  $\delta$ , Tolman constant analog, AU of the length or angstroms;  $f$ , free surface energy,  $mJ/m^2$ ;  $S^0$ , surface entropy of the medium;  $\varphi(r)$ , function characterizing the electrostatic-potential distribution at the thread-dielectric medium interface;  $a$  and  $b$ , coefficients in the approximation polynomial;  $C_{ex}(r_c) = 2.702 - 1.74r_c$ , coefficient in the correction to the exchange-correlation interaction taken in the Heldart-Razolt approximation. Subscripts: s, surface; min, minimum; j, jelly; ex, exchange-correlation interaction; G, Gibbs surface radius; c, cell.

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