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## More about the Size Dependence of the Surface Energy of Charged Metal Clusters. Liquid Drop Model

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The problem of the sign of the size correction to the surface energy per unite area of a single charged metal nanocluster within the liquid-drop model (LDM) is considered. Within the stabilized jelly model detailing the LDM, the effective radii of the electron cloud for Cs, Na, Mg and Al clusters are estimated from the asymptotic behaviour of the electrical capacitance calculated by the Kohn–Sham method. The uncertainty of the cluster boundary associated with the atomic-scale roughness and nonsphericity of the surface, with taking into account the effective radius of the electron cloud of the cluster, can lead to an inversion of the sign of the size correction for surface tension. The distribution function of Cs clusters by charge and number of atoms in dense vapour on the saturation line is estimated. The fact that the surface energy of a metal depends on the dielectric constant  $\tilde{\epsilon}$  as weighted average over the area of contact with the external environment is discussed. A metal droplet on a dielectric substrate and a droplet in its own dense vapour are discussed as appropriate contacts. The dependence of surface tension on  $\tilde{\epsilon}$  for Cs, Na, Mg, Pb, Au and Al is calculated. Contact of a droplet with a dielectric substrate always leads to a decrease in surface energy.

**Key words:** surface energy, metal nanocluster, electron-cloud radius, stabilized jelly model.

Розглянуто проблему знаку розмірної поправки до питомої поверхневої енергії відокремленого зарядженого металевого нанокластера в крапельному моделі. У моделі стабільного желе, що деталізує краплинний модель, з асимптотичної поведінки електричної місткості, розрахованої методом

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Кона–Шема, оцінено ефективні радіуси електронної хмари для кластерів Cs, Na, Mg й Al. Невизначеність межі кластера, яка пов'язана з шерсткістю атомарного масштабу та несферичністю поверхні, а також ефективного радіуса електронної хмари кластера можуть приводити до інверсії знаку розмірної поправки поверхневого натягу. Оцінено функцію розподілу кластерів Cs за зарядом і числом атомів у них у густих парах на лінії насити. Обговорюється той факт, що поверхнева енергія металу залежить від середньозваженої по площі контакту із зовнішнім середовищем діелектричної константи  $\epsilon$ . Як доречний контакт обговорюється металева крапелька на діелектричній підкладці та крапля в густому власному парі. Розраховано залежність поверхневого натягу від  $\epsilon$  для Cs, Na, Mg, Pb, Au й Al. Контакт завжди приводить до зменшення поверхневої енергії.

**Ключові слова:** поверхнева енергія, металевий нанокластер, радіус електронної хмари, модель стабільного желе.

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## 1. INTRODUCTION

The role of surface effects in the processes of condensation, melting, evaporation and emission of charged particles increases with decreasing cluster sizes. Moreover, the characteristics of these effects, such as the melting temperature, surface tension, electron and ion work functions, the heat of atom evaporation, and the vacancy formation energy themselves begin to depend on the size of the clusters.

The free energy per unite area of the spherical surface between two phases can be represented in the asymptotic form as

$$\gamma(R) = \gamma_0 \pm \frac{\gamma_1}{R} + O\left(\frac{1}{R^2}\right) \equiv \gamma_0(1 + k\delta), \quad (1)$$

where  $\gamma_0$  is the energy of flat surface,  $\delta = \gamma_1/\gamma_0$ , and  $k = \pm 1/R$  is a signed curvature.

The problem of the dependence of the surface tension of vapour bubbles and liquid droplets on the radius of curvature of the equimolecular surface is the subject of numerous theoretical and experimental studies for simple and polar liquids [1–8].

The diversity of approaches and methods has not yet led to a unity of views even on the qualitative nature of such dependence. Experimental data for nucleation in simple liquids indicate that at temperatures close to critical, the surface tension of vapour bubbles is less than at a flat boundary [5].

Within the framework of the Gibbs separating surface method, Tolman, Kirkwood and Buff [1, 2] formulated a visual definition of  $\delta$  as twice the distance between positions of the Gibbs ‘tension’ surface and the equimolecular one,  $R$ . The Kirkwood–Buff statistical calcula-

tion leads to a decrease in the surface tension of the drop (the ‘tension’ surface position for  $k = +1/R$  is closer to the condensed phase than to the vapour). However, numerical calculations for  $\gamma(R)$  within the framework of the van der Waals model for a bubble in a superheated liquid indicate the sensitivity of the magnitude and sign of the parameter  $\delta$  to the choice of model and calculation method.

In [10], crystalline Ar clusters of ‘almost spherical’ shape were studied. In the nearest-neighbour approximation, the total surface energy and parameter  $\delta$  were calculated for a spherical particle. Then attention is drawn to the fact that a ‘real’ close-packed cluster is not a sphere, but a polyhedron. In this case, it is proposed to take the radius of a spherical surface described around a polyhedron as an equimolecular surface. This radius is larger than the previous one by approximately the average distance between atoms, *i.e.*, the renormalized quantity  $\delta' \approx \delta - 2r_0 < 0$  is introduced. In review [11], this technique is recommended for calculating the specific surface energy of solid clusters.

Relatively little attention has been paid to the size dependence of the surface tension  $\gamma(R)$  of metal droplets, which is apparently due, firstly, to the complexity of a consistent description of the surface of a liquid metal plasma, and, secondly, to the lack of reliable experimental data. From an analysis of the evaporation rate of microdroplets deposited on a carbon substrate, the value of  $\delta \cong -11.4$  and  $-10.4a_0$  ( $a_0$  is the Bohr radius) was estimated for Pb and Au, respectively [12, 13]. In [14], the size dependence of the wetting angle of Pb nanodroplets on a carbon substrate was measured, which leads to the value  $\delta \cong -2.5a_0$ . These results confirm the conclusions of thermodynamics [3, 7] about the presence of a negative size correction to the surface tension of a flat surface, thereby indicating the existence of a general nature of the dependence for microscopic droplets of a simple liquid with short-range interaction forces between atoms, and for metal clusters (the Coulomb systems).

In one of the first works [15], using the Kohn–Sham method in the model of ordinary jelly at zero temperature, a noticeable size dependence of surface energy  $\sigma(R)$  of solid Na clusters was not detected at all. Then, in [16], using the same model and the Ritz method, the value  $\delta$  for alkali metal clusters ( $\delta > 0$ ) was calculated for the first time. In [17], the quantity was ‘extracted’ from the vacancy formation energy

$$\varepsilon^{\text{vac}} = 4\pi r_0^2 \sigma_0 (1 + k^{\text{vac}} \delta), \quad k^{\text{vac}} = -1 / r_0. \quad (2)$$

Using these magnitudes of  $\delta$ , it turned out to be possible to obtain good values for the atomic cohesion energy

$$\varepsilon^{\text{coh}} = 4\pi r_0^2 \sigma_0 (1 + k^{\text{coh}} \delta), \quad k^{\text{coh}} = +1 / r_0. \quad (3)$$

In Ref. [18], these results were tested in two ways: by the numerical

solution of the Euler–Lagrange equation in the gradient expansion of the electron density functional and using the Kohn–Sham method. As a result,  $\delta = 1.76$  and  $2.76a_0$  were found for Na and Cs, respectively. The authors of [18, 19] concluded that  $\delta > 0$  for all metal clusters.

In the two-component model of a liquid metal plasma [20, 21], the Fisher–Wortis formula for  $\delta$  [4] was generalized to the case of the Coulomb liquids and obtained for an ideally smooth convex spherical surface.

For  $\sigma(R)$  at low temperatures, using the semi-empirical Frenkel–Langmuir rule, it was found that  $\delta/r_0 \cong 1/2$  for metals and inert gases [21]. It follows that the surface area of the radius  $r_0$  is well described the experimental data in LDM, however, the radius of a many-atomic cluster apparently needs to be renormalized.

Modern data on the melting of small metal clusters [22–24] confirm and complement the analytical results of Pavlov [25]: as the cluster size decreases, firstly, the melting temperature decreases, and secondly, only at cluster radii  $R \leq 1$  nm (at which already quantum size effects are significant) the size dependence of the melting temperature becomes noticeable. As noted in [22], the process of melting a cluster consisting of hundreds of atoms, firstly, corresponds to an uncertainty in the melting temperature—a pre-melting stage, extended in temperature by 10–15 K, which creates uncertainty in the atomic density and cluster size; secondly, the diffusion of surface vacancies into the bulk is more favourable for clusters with unfilled electron shells than for magic clusters. These key observations indicate the complexity of the problem, the complex physics, and are useful for a comprehensive analysis of the semi-classical size dependence of surface energy. The value  $R = 1$  nm corresponds to the numbers of atoms in cluster  $N \cong 38, 106, 181$  and  $254$  for Cs, Na, Mg and Al, respectively.

As follows from the above, microscopic calculations for droplets of metals and simple liquids, as well as semi-empirical estimates, give opposite size dependences  $\gamma(R)$  and  $\sigma(R)$ , which makes its study relevant in the future.

## 2. BASIS OF CONSIDERATION

The total energy of a droplet, with ideal sphericity of its surface (*i.e.*, ‘point-likeness’ of atoms), is represented as the sum of the energy of the volume and surface:

$$E = E^{\text{bulk}} + E^{\text{surf}}, E^{\text{bulk}} \propto R^3, E^{\text{surf}} \propto R^2. \quad (4)$$

In fact, (4) is an expansion of the total energy in powers of  $R^{-1}$ , implying a well-defined quantity  $R$ . However, the atomic-scale surface roughness does not allow one to determine accurately the cluster

boundary. Therefore, for example, the scattering of conduction electrons on the surface of nanoclusters is predominantly diffuse, which is important when calculating the optical characteristics of mono- and bimetallic nanospheres [26].

The value  $E$  of a cluster consisting of  $N$  atoms can be calculated in any model and then represented as an expansion in powers of  $N^{-1/3}$ , not  $R^{-1}$ . For example, within the framework of *ab initio* calculations, a many-particle potential is first formed, and then, by sorting through atomic configurations, the total force from all atoms on a selected atom is equal to zero, *etc.* As a result, the equilibrium shape of the cluster in vacuum, temperature  $T=0$  and distances between atoms correspond to zero pressure [20, 21, 27–30], which can be considered as a mechanical analogue of thermodynamics (criticism of the thermodynamic approach for clusters in a rarefied atmosphere was given in [13]). The resulting cluster shape is never spherical.

In fact, the cluster can be conditionally represented as a sphere (see Fig. 1 in [10]) only for such numbers as  $N_n = 13, 55, 147, 309, \dots$ , which correspond to numbers  $n = 1, 2, 3, 4, \dots$  of coordination spheres of atoms. Only clusters with such  $N_n$  are polyhedra, close-packed atoms (balls of radius  $r_0$ ) Representing the total number of atoms in a cluster as a sum  $N_n = N_n^{\text{bulk}} + N_n^{\text{surf}}$ , we can introduce the corresponding radii in the form

$$\mathcal{R} = r_0(n + \xi). \quad (5)$$

The coefficient  $\xi = 0$  corresponds to the surface passing through the centres of the corner atoms of the polyhedron, and  $\xi = 0.66$  and  $2^{-1/2}$  corresponds to the equimolecular surface of the icosahedron and cub-octahedron, respectively [10].

In Gibbs theory, the total surface energy of a cluster does not depend on the choice of the radius of the dividing surface:

$$E^{\text{surf}} = \sigma(R)S(R) = \sigma(\mathcal{R})S(\mathcal{R}). \quad (6)$$

Then

$$\sigma(\mathcal{R}) = \frac{S(R)}{S(\mathcal{R})} \sigma_0 \left( 1 + \frac{\delta}{\mathcal{R}} \right) = \sigma_0 \left( 1 + \frac{\delta - 2r_0}{\mathcal{R}} \right) + O\left( \frac{\delta^2}{\mathcal{R}^2} \right), \quad (7)$$

which, taking into account (5), leads to the expression

$$\frac{\sigma(\mathcal{R})}{\sigma_0} = 1 + \frac{\tilde{\delta} - 2\xi}{n} + O\left( \frac{1}{n^2} \right), \quad \tilde{\delta} \equiv \frac{\delta}{r_0}, \quad (8)$$

provided that the second term in r.h.s of (8) is much less than 1.

### 3. CALCULATION RESULTS AND DISCUSSION

In LDM, which has proven itself well in nuclear physics and the physics of metal clusters [31–36], a unique correspondence is established between the radius of the cluster (ion core) and  $N$

$$R = N^{1/3} r_0. \quad (9)$$

In classical electrostatics, the capacitance of a conducting sphere is determined by its radius  $R$ . In LDM, the boundary of a positively charged (ionic) core is always determined by the coordinate  $r = R$ . However, the electron liquid spill-out beyond this boundary. Renormalization of the surface area can be carried out taking into account the effective radius of the electron cloud [34], which determines the electrical capacitance.

In Refs. [36, 37], we studied the energy characteristics of charged solid metal clusters and clusters containing a single vacancy in the stabilized jelly model detailing the LDM for  $N \leq 270$ , using the Kohn–Sham method taking into account the quantization of the electron spectrum. Let us use these results.

All energy characteristics, in particular, the ionization potential of the cluster  $IP_N$  and the energy of electron affinity  $EA_N$ , have a strong oscillatory dependence due to the spherical electron shell structure. According to Koopmans' theorem

$$IP_N = -\varepsilon_N^{\text{HO}} + \frac{(+e)^2}{2C_N^+}, \quad EA_N = -\varepsilon_N^{\text{LU}} + \frac{(-e)^2}{2C_N^-}, \quad (10)$$

where  $\varepsilon_N^{\text{HO}}$ ,  $\varepsilon_N^{\text{LU}}$  and  $C_N^\pm$  are the energies of the upper occupied and lower unoccupied orbitals, and electrical capacitances of positively and negatively charged clusters, respectively.

Independent calculation of self-consistent quantities  $IP_N$ ,  $EA_N$ ,  $\varepsilon_N^{\text{HO}}$  and  $\varepsilon_N^{\text{LU}}$  allows one to calculate the capacitances of charged

$$C_N^Z = \frac{e^2}{2(IP_N + \varepsilon_N^{\text{HO}})} \quad (Z = +1), \quad C_N^Z = \frac{e^2}{2(EA_N + \varepsilon_N^{\text{LU}})} \quad (Z = -1), \quad (11)$$

as well as neutral

$$C_N^Z = \frac{e^2}{IP_N + \varepsilon_N^{\text{HO}} - EA_N - \varepsilon_N^{\text{LU}}} \quad (Z = 0) \quad (12)$$

clusters ( $e$  is elementary positive charge). For large spheres in the Hartree units ( $e = m = \hbar = 1$ )

$$C_N^Z \rightarrow r_0(n + \xi_C^Z) = \mathcal{R}. \quad (13)$$

**TABLE 1.** The results of calculations in LDM for  $T = 0$  K.

Metal	$r_0/a_0$	$\tilde{\delta}$	$\xi_C^Z$		
			$Z = -1$	$Z = 0$	$Z = +1$
Cs	5.63	0.26	0.40	0.36	0.33
Na	3.99	0.32	0.42	0.32	0.32
Mg	3.39	0.54	0.37	0.54	0.46
Al	2.99	0.57	0.44	0.57	0.57

In fact, this is the effective radius of the electron cloud. Next, from asymptotic behaviour of the cohesion energy (Fig. 8 in [36]) and electrical capacitance (Fig. 6 in [36]) for the magic numbers of atoms, the values of  $\tilde{\delta}$  and  $\xi_C^Z$  were found (Table 1).

The value  $\xi_C^0$ , for example, for Na, exceeds by approximately 10% the similar value calculated in a different way in [34], and the values  $\xi_C^{-1} > \xi_C^0 > \xi_C^{+1}$  differ too by approximately 10% from each other. It should still be noted that the magic numbers of atoms in LDM [36], as a rule, do not coincide with  $n$  those in formula (13).

Let us recall that the value  $\xi_C^Z$  must refer to expression (8) for clusters whose shape is close to spherical. In the future, for estimates with arbitrary  $N$ , we will use a hybrid approach and the formula

$$\frac{\sigma^Z(\mathcal{R})}{\sigma_0} = 1 + \frac{\tilde{\delta} - 2\xi_C^Z}{N^{1/3}} + O\left(\frac{1}{N^{2/3}}\right) \quad (14)$$

(on the issue of redefining the cluster radius, see also Ref. [38]).

Effects associated with the curvature of the surface of atomic clusters and the temperature dependence of surface properties can determine the energetically favourable formation of cluster components in plasma and their ability to accumulate an electric charge.

It is possible to estimate the distribution function of Cs clusters by charge and number of atoms in them in dense vapour on the saturation line using LDM in a similar way to how we did it earlier when calculating the ionization equilibrium in plasma (see details in [39] and [40]). Caesium was chosen due to relatively low temperatures and the availability of reliable data for calculations. The dependence of the density and pressure of caesium vapour on the temperature at the saturation line is well known (unknown, however, is the temperature behaviour of surface tension at temperatures above the melting point).

Therefore, having made a replacement  $\sigma \rightarrow \gamma(T)$  in (14), we then used a decreasing linear temperature dependence  $\gamma_0(T)$  from the melting point to the critical point, at which it is precisely known that  $\gamma_0 = 0$ ; from Table 1 the values  $\tilde{\delta}$  and  $\xi_C^Z$ , were taken, calculated at  $T = 0$  K (in the two-component model [20] near the melting point for alkali metals,

the calculated dependence  $\delta(T)$  turned out to be weak).

In the theory of nucleation, it is believed that droplets containing more than a dozen particles are macroscopic. Such droplets are considered when describing heterogeneous nucleation in supersaturated vapour. For estimations on the saturation line, we used the expression:

$$n_N^Z(T) \propto \frac{1}{\lambda_T^3} N^4 \exp \left\{ -\frac{1}{T} \left[ \sigma^Z(\mathcal{R}, T) + \frac{Z^2}{2\varepsilon_\nu C_N^Z} \right] \right\}, \quad (15)$$

where  $\lambda_T$  is the thermal wavelength of the atom in the vapour,  $\varepsilon(T)$  is the dielectric constant of the vapour [39, 40].

In Figure 1, *a* for caesium, the normalized distributions of clusters by the number of atoms in them are shown. The applicability of LDM is determined mainly by the half-width of the cluster concentration distribution  $n_N^Z(T)$  (Fig. 1, *a*) and values  $N^*(T)$  (Fig. 1, *b*). For  $N = N^*(T)$  the functions  $n_N^Z(T)$  have maxima in Fig. 1, *a*. With increasing temperature, the maxima  $n_N^Z(T)$  shift towards higher  $N$ . The half-width of the distribution is quite large, so in the problem when averaging with a function  $n_N^Z(T)$ , the main contribution will come from large clusters. For comparison, Fig. 1, *b* shows the result of the calculation for which the size dependence of the surface energy in (14) is completely absent. The negative sign of the correction in (14) indicates favourable formation of heavier clusters in the metal–vapour–plasma, and Fig. 1, *b* demonstrates the sensitivity of the LDM applicability to the description of critical phenomena.

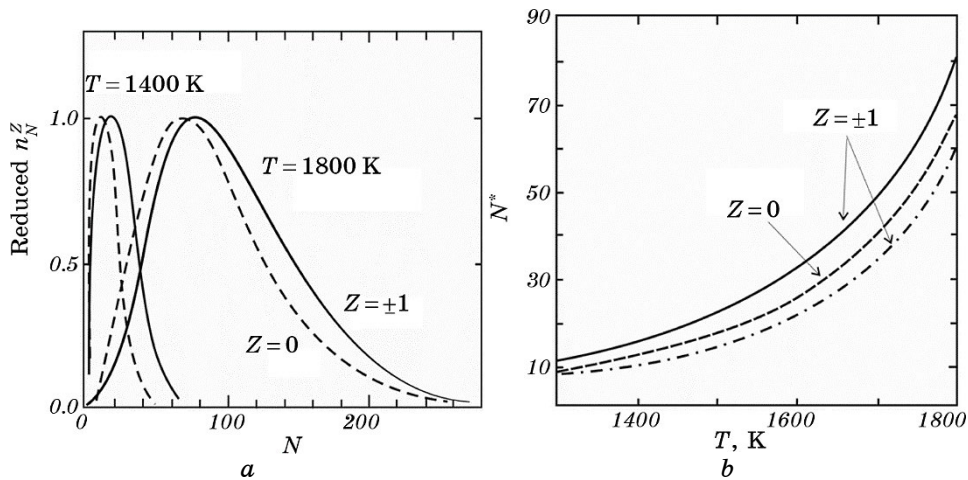


Fig. 1. Calculated dependences  $n_N^Z(T)$  and  $N^*(T)$  on the saturation line for Cs vapour. The dash-dotted curve indicates the dependence  $N^*(T)$  calculated under the assumption  $\sigma^Z(N)/\sigma_0 = 1$  in (14).



In conclusion, let us pay attention to the possible refinement of experimental data on the surface tension of liquid metal nanodroplets obtained by measuring the size dependence of the Young contact angle [12, 14].

It is known that in the statistical description of a metal drop, the pressure tensor, including  $T = 0$  K, contains the Maxwell stress tensor, which depends on the dielectric constant of the environment [20, 41, 42]. Recent works [41–43] have developed an approach to the problem of a metal surface with a non-uniform dielectric coating. Attention is drawn to the fact that the work function of the metal depends on the dielectric constant  $\tilde{\varepsilon}$  weighted average over the contact area.

If a metal droplet of area  $S$  is in the vapour phase with a constant  $\varepsilon_v$ , but touches a dielectric substrate with a constant  $\varepsilon$  (contact area  $\alpha S$ ,  $\alpha < 1$ ), then the effective influence of the substrate and vapour, as follows from the Gauss theorem [43], is reduced to calculating the work function of the droplet in a homogeneous fictitious dielectric medium with constant

$$\tilde{\varepsilon} = \alpha\varepsilon + (1 - \alpha)\varepsilon_v. \quad (16)$$

A comparison of the results of fully self-consistent calculations in [44, 45] and partially self-consistent calculations in [41, 42] indicates that the results obtained for the surface energy in [41, 42] can be taken approximately as an ‘upper’ estimate. The calculation involves integration over the entire space, taking into account the complex behaviour of electron density and potential profiles, which the Ritz method is not capable of reproducing.

Taking into account the dielectric coating leads to a decrease in surface energy compared to a drop in a vacuum. For a drop suspended in a vapour,  $\alpha = 0$ , and the vapour constant  $\varepsilon_v$  can be estimated using the Clausius–Mossotti formula. Therefore, the surface tension of a droplet in a vacuum, a droplet on a dielectric substrate, and a droplet in dense vapour are different from each for  $\sigma_0$ .

Using the calculation scheme of the Ritz method and the trial function [41, 42], the values  $\sigma_0(\tilde{\varepsilon})$  for Cs, Na, Mg, Pb, Au and Al were calculated (see Table 2).

Example: a drop of Pb on a substrate of amorphous carbon, for which  $\varepsilon = 10$ , and  $\varepsilon_v = 1$  for vapour. Let the fraction of the surface touching the substrate is  $\alpha = 1/10$ . What is its surface energy now? Using (16), we obtain

$$\tilde{\varepsilon} = \frac{1}{10}10 + \left(1 - \frac{1}{10}\right)1 = 1.9,$$

and, based on Table 2, we are guessing that  $\sigma_0 \approx 614$  erg/cm<sup>2</sup>. Compared to  $\tilde{\varepsilon} = 1$  the decrease in surface energy was 14%. Apparently, such a significant decrease is weakly dependent on the capillary effect.

**TABLE 2.** The results of calculations  $\sigma_0(\tilde{\epsilon})$  (in erg/cm<sup>2</sup>) for  $\alpha = 1$ .

$\tilde{\epsilon}$	1	2	3	4	5	10
Cs (1)	66/79	63	62	62	62	61
Na (1)	178/191	167	163	161	159	157
Mg (2)	520/569	460	436	424	417	401
Pb (4)	714/465	603	560	537	523	493
Au (3)	858/1134	690	625	590	568	523
Al (3)	872/1160	698	630	593	570	522

Let us recall that such an estimate gives a somewhat overestimated effect of the dielectric coating.

Now consider a drop of Cs suspended in dense vapour ( $\alpha = 0$ ) on the saturation line at  $T = 1400$  K, when the vapour can still be considered as an ideal gas. Then, formula (16) gives  $\tilde{\epsilon} = \epsilon_v$ , and the Clausius–Mossotti formula gives  $\epsilon_v = 1.064$ . Moreover, although the exact surface tension at such a temperature is unknown, calculations at  $T = 0$  and such a value of  $\tilde{\epsilon}$  indicate an insignificant effect for this temperature.

#### 4. CONCLUSIONS

In this work, the effective radii of the electron cloud for Cs, Na, Mg and Al were calculated using the stabilized jelly model from the asymptotic behaviour of the electric capacitance. The calculation results were used to analyse the size dependence of the surface tension of charged metal clusters. To comply with thermodynamic theory, in which atoms are points, it is obvious to refine the surface area of the cluster taking into account the finite sizes of atoms (their non-pointiness). The uncertainty of the boundary associated with the roughness of the atomic scale, as well as taking into account the effective radius of the electron cloud of the cluster, can lead to an inversion of the sign of the correction.

Contradictions arise not only when choosing a calculation method, but also in determining the area of the real surface and its local curvature, which may indicate that the accuracy of the model is exceeded in the absence of reliable experimental data. Therefore, in asymptotic, representing the total cluster energy in the form of an expansion in powers of  $N^{-1/3}$ , and not  $R^{-1}$  at least reduces the overall modelling error.

The influence of the environment on the surface energy of the droplet is estimated. Particular attention is paid to the influence of the dielectric substrate: the surface energy of the metal depends on the dielectric constant weighted average over the area of contact with the exter-

nal environment. Calculations were performed for Cs, Na, Mg, Pb, Au and Al. Contact of a drop with a dielectric substrate can lead to a significant decrease in surface energy.

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