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The character and direction of the physicochemical processes that occur at the interface between a solid and a liquid phase (adhesion interaction, wetting, spreading, etc.) are determined to a considerable extent by the

corresponding surface energies. For macrosystems these surface energies are known, which in most cases allows an a priori determination of the character and extent of interfacial interaction. At present much attention is devoted to systems with dispersed (10^3 – 10^5 nm) or highly dispersed (10–100 nm) phases whose physicochemical constants differ from similar properties of bulk materials [1, 2]. In particular, of considerable theoretical and experimental interest are the capillary properties of highly dispersed systems. According to the available theoretical and experimental data, the surface energy of objects 10–100 nm in size is different from the energy of bulk material. The literature data on surface energy and the pattern of its size dependence are ambiguous. In view of the practical importance of knowledge of the capillary properties of microobjects, we studied wetting in dispersed systems. We were particularly interested in getting data on the surface energy of small particles and ultrathin films.

The equilibrium conditions for a liquid drop on a solid substrate are determined by the surface energy of the contacting phases — the solid substrate, σ_s , the liquid drop, σ_l , and by the drop–substrate interfacial energy σ_{sl} , which are connected by Young's relation:

$$\cos \theta = (\sigma_s - \sigma_{sl}/\sigma_l), \quad (1)$$

where θ is the contact angle.

From formula (1) it follows that for highly dispersed systems (HDS) one can anticipate the occurrence of size effects upon wetting. These are due to the dependence of the surface energy of the dispersed phase (the solid and the liquid) on its characteristic size: the substrate thickness or the radius of liquid drops. In view of this, investigations of wetting as a function of the degree of dispersity of the contacting phases must yield information on the size dependence of the surface energy of the corresponding phase, which is very difficult to accomplish by other experimental techniques.

The present paper offers the results of an investigation of wetting as a function of the size of liquid drops and the thickness of film-substrates. In order to extract as general information as possible, we studied systems with different types of interfacial interaction.

The investigations were carried out on island metal films prepared by condensation in vacuo by the vapor-liquid mechanism. The degree of vacuum was varied in the range 10^{-5} – 10^{-7} Pa. The film preparation techniques and the procedures of determination of θ are described in detail in [3, 4].

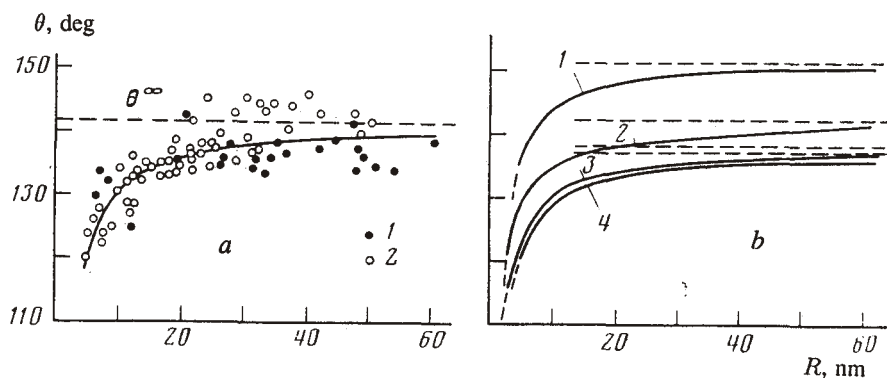


FIGURE 1. Dependence $\theta(R)$ for metal drop–amorphous substrate systems. (a) Pb–C system: (1) convolution data; (2) photometric data. (b): systems Sn–C (1), Bi–C (2), Au–C (3), and Pb–Si (4) [curves 1–4 correspond to an approximation of experimental points by relation (7)].

RESULTS AND DISCUSSION

Size Effects in Wetting for Chemically Inert Metal–Amorphous Carbon and Metal–Amorphous Silicon Systems

We studied wetting in metal (Sn, Bi, Pb, Au)–amorphous carbon and Pb–amorphous silicon film systems as a function of particle size and also in metal (In, Sn, Pb)–free carbon film systems and in the Sn–C–KCl system as a function of the carbon film thickness. It was found that with sizes $R > 10^2$ nm and a carbon film thickness $t > 20$ nm the laws of wetting and adhesion interaction, specific to the corresponding systems in the bulk state, are retained [5, 6]. With a particle size $R < 30$ nm and carbon film thickness $t < 10$ nm the degree of wetting is found to differ significantly from that of bulk specimens, this being a manifestation of the size effect on wetting.

Let us consider data on the size effect for systems with a highly dispersed liquid phase. For all the systems studied we found that with a particle size $R < 30$ nm the contact angle θ decreases with decreasing particle size, so that $\Delta\theta = 20^\circ$ at $R \simeq 4\text{--}5$ nm (here, $\Delta\theta = \theta_\infty - \theta$ and θ_∞ is the contact angle at $R \rightarrow \infty$). The experimental $\theta(R)$ curves for the systems under study are given in Figure 1.

The few data available in the literature on the $\theta(R)$ dependence are contradictory. For example, in [7] small drops of diffusion vacuum oil and titanium hexachloride were used to wet thin asbestos and vanadium

oxide filaments (both systems correspond to the case $\theta_\infty < 90^\circ$) and it was found that a decrease in the drop size and in the filament diameter leads to a decrease in θ . The effect was explained by the fact that with drop sizes comparable to the radius of action of the intermolecular forces in a liquid the interfacial interaction changes and this leads to a decrease θ . According to the data obtained later in [8], where the wetting in Au–C and Ag–C systems for a particle size of 5–10 nm was studied, the values for a particle size of 5–10 nm do not differ from the corresponding values for bulk material, i.e., the contact angle is found to be independent of R . Examination of the sample preparation technique and subsequent treatment used in [8] shows that this result is due most likely to the difference in the degree of shape equilibrium between particles of differing size because of their unfinished solid-phase coalescence. This conclusion is supported by micrographs of the particle profiles given in [8]. The works cited above are the only investigations of the size effect that have been published. At the same time, because of the increased interest in the properties of HDSs on the part of research workers and technologists, it becomes necessary to carry out detailed investigations of capillary phenomena at macrophase and microphase interfaces.

The size effect was first theoretically examined in [9], where the problem of the equilibrium shape of a small drop on a substrate was solved with consideration for the dependence of the surface energy of the liquid drop on its radius of curvature, and an expression for the contact angle of the drop was derived:

$$\cos \theta = \frac{\sigma_s - \sigma_{sl}^\infty}{\sigma_l^\infty (1 - 2\alpha/R)} \quad (2)$$

Here, σ_l^∞ and σ_{sl}^∞ are the surface energies of the drop and the drop–substrate interface at $R \rightarrow \infty$; and α is the parameter which determines the size dependence of the surface energy, so that, in accordance with [10]:

$$\sigma_l = \sigma_l^\infty (1 - \alpha/R). \quad (3)$$

At a microscopic level, the parameter α has the meaning of the radius of action of molecular forces (screening radius for metals). In the thermodynamics of surface phenomena [11], the quantity α is defined as the difference between the radius of an equimolecular surface R_{eq} and the radius of surface tension R_t . For formula (3) it follows that $\partial\sigma_l/\partial R = \alpha\sigma_l^\infty/R^2$, which is why the sign of the parameter α determines the character of the size dependence of the surface energy of small drops. There is no generally accepted opinion as to the sign of the parameter α for metals [10–17], but

an analysis given in [18] of experimental data on various properties of small particles (lattice period [19], melting [20], evaporation [21, 22], wetting [3, 18]) suggests a conclusion that the most probable result is $\alpha > 0$. The same conclusion has been drawn from an analysis of data on the size effect of compression and melting of small particles on the basis of the vacancy mechanism of the size effects in HDSs [23].

Thus, at $\alpha > 0$ it follows from relation (2) that the derivative $\partial\theta/\partial R$ has different signs for different systems, i.e., $\partial\theta/\partial R > 0$ at $\theta_\infty < 90^\circ$ and $\partial\theta/\partial R < 0$ at $\theta_\infty > 90^\circ$. This conclusion contradicts the data obtained for a number of systems in the present work. In [3] it has been demonstrated that the above-indicated contradictions can be eliminated if, in seeking an equilibrium shape for a small particle on a substrate, one takes into account the size dependence not only of the surface energy of the microparticle $\sigma_l(R)$ but also of the microparticle-substrate interface, σ_{sl} . The solution of the problem of minimization of the free surface energy of the microparticle-substrate system with consideration for the dependences $\sigma_l(R)$ and $\sigma_{sl}(R)$ makes it possible to derive an equation for the contact angle of a small drop on a bulk substrate of the form:

$$\cos \theta = \frac{\sigma_s - (\sigma_{sl} - R\partial\sigma_{sl}/\partial R)}{\sigma_l - R\partial\sigma_l/\partial R} \tag{4}$$

Taking account of formula (3) and assuming that the dependence of σ_{sl} on the size effect has the form [3]

$$\sigma_{sl} = \sigma_{sl}^\infty (1 - \beta/R) \tag{5}$$

(β is a parameter which has the meaning similar to that of α), we obtain from relation (4) an expression for $\theta(R)$ in an explicit form:

$$\cos \theta = \frac{\sigma_s - \sigma_{sl}^\infty (1 - 2\beta/R)}{\sigma_l (1 - 2\alpha/R)} \tag{6}$$

From formula (6) it follows that if the inequality $\beta > \alpha(1 - \sigma_s/\sigma_l^\infty > 0)$ is fulfilled, the size effect will manifest itself in an increase in the degree of wetting ($\partial\theta/\partial R < 0$) both for systems with $\theta_\infty > 90^\circ$ and $\theta_\infty < 90^\circ$

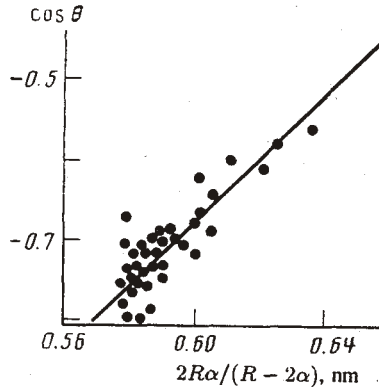


FIGURE 2. Dependence $\theta(R)$ for the Pb-C system.

TABLE I. Size Effect Data for Metal-Amorphous Carbon Systems

System	θ_{∞} , deg	σ_l^{∞} mJ/m ²	σ_{sl}^{∞} mJ/m ²	α , nm	β , nm
Sn-C	150.0	531	574	0.26	0.55
Bi-C	142.2	376	407	0.30	0.50
Pb-C	141.6	450	463	0.29	0.83
Au-C	138.4	1130	955	0.24	0.77

This conclusion is confirmed by the results of the present work and also by data from [7].

Relation (6) can be used to process data on the size effect obtained for metal-amorphous carbon systems. In particular, from the experimental dependences $\theta(R)$, using relation (6), we can obtain information on the parameters α and β for metals, i.e., we can find the size dependences of the surface energies σ_l and σ_{sl} . From formula (6) it follows that the dependence $\theta(R)$ in the coordinates $\cos \theta$ and $2R\alpha/(R - \alpha)$ must be linear, which is confirmed by the data presented in Figure 2 (the Pb-C system). The parameter α is determined from the empirical relationship $\alpha \approx 0.91(V_s/N_a)^{1/3}$ (where V_s is the atomic volume and N_a is Avogadro's number) [24]. Using relation (6) and the dependences $\theta(R)$ obtained, we found the parameters

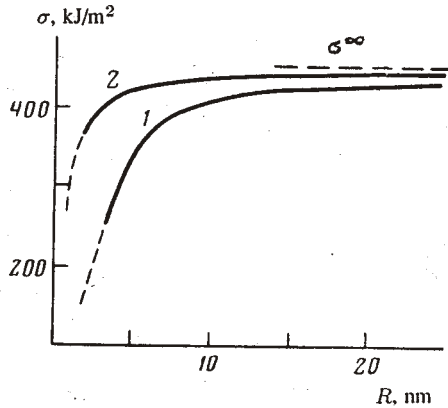


FIGURE 3. Dependence of the surface energy of a liquid drop on the particle size: (1) data on the size effect; (2) data on evaporation [22].

σ_{sl}^{∞} and β for various systems (Table I). It should be noted that the agreement between the value of the interface energy σ_{sl}^{∞} for the Au-C system and the data of [25], where σ_{sl}^{∞} was determined by an independent method through the use of the multiphase equilibrium technique, is quite satisfactory. Figure 1b shows the dependence $\theta(R)$ approximated by relation (6) with the corresponding parameters α and β obtained from the above-given analysis of experimental data.

Concluding the consideration of the size effect in systems of the metal-amorphous carbon type with a dispersed liquid phase, the following remarks should be made. First, for the metals studied the parameter α is close to the theoretical value ($\alpha = 0.3$ nm), which has been obtained within the framework of the electronic theory of the surface energy of metals [26]. Second, the estimates show that at $\alpha = 0.3$ nm the decrease of the surface energy is significant for a particle size of 1–2 nm, i.e., with the sizes indicated the ratio $\sigma/\sigma_{\infty} = 0.6$ nm. Figure 3 shows the dependence $\sigma_l(R)$ for Pb calculated from formula (4). It should be noted that the results on the dependence $\sigma(R)$ obtained in the present work from the data on the size effect are in good qualitative agreement with the data of experiments in evaporation of small particles [22] (curve 2 in Fig. 3).

Thus, from the data given above it follows that the contact angle decreases with decreasing size of liquid drops, this being a consequence of a decrease in the surface energy of small particles.

Of interest is the investigation of wetting in systems with a highly dispersed solid phase. An example of such a system is a ternary system of

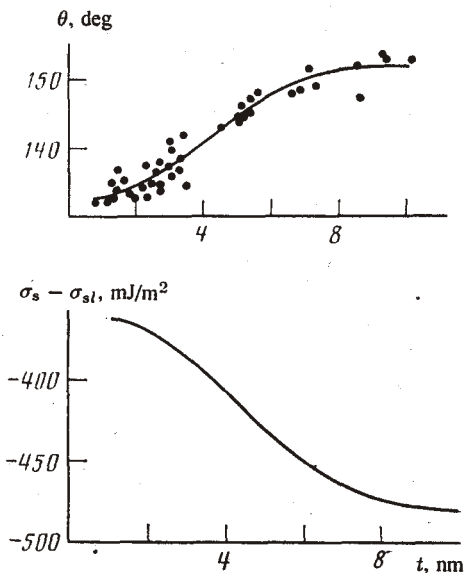


FIGURE 4. Dependence of the contact angle (a) and of the adhesion tension (b) on the carbon film thickness for the Sn-C-KCl system.

the metal-thin film-bulk substrate type. By varying the film thickness of the intermediate layer from minimal values that provide its continuity up to thicknesses when the film may be regarded as a bulk material, one can investigate the size effect associated with the possible variation in the surface energy of the thin film as the film thickness decreases. The dependence of the angle θ on the thickness of the intermediate layer has been earlier studied for a number of systems, and it has been found that the character of wetting largely depends on the thickness of the intermediate layer [26, 27]. This effect was explained by the authors of the works cited by the discontinuity of the sublayer film, so that the degree of heterogeneity of the substrate was dependent on the sublayer thickness. The solution to this problem, apart from the scientific aspects indicated, is undoubtedly of technological interest, since it makes it possible to control wetting processes in various contact systems in the desired manner.

In the present work we chose for experiments the Sn-C-KCl system, in which the carbon film thickness was varied within the range $2 \text{ nm} < t < 30 \text{ nm}$. Specimens were prepared by condensation in a vacuum of 10^{-6} Pa ; the geometry of the arrangement of the evaporators and the substrate was chosen such that it was possible to prepare specimens with substantially

different carbon film thicknesses in a single experiment. The angles were measured on crystallized drops more than 40 nm in size in order to avoid the dependence $\theta(R)$. It was found that with small carbon film thicknesses the angles θ tend to the values corresponding to the wetting of a clean substrate, i.e., $\theta(\text{Sn-C-KCl}) \rightarrow \theta(\text{Sn-KCl})$, with $t \rightarrow 0$, and that at large t the angle θ corresponds to the wetting of the film material by liquid metals, i.e., $\theta(\text{Sn-C-KCl}) \rightarrow \theta(\text{Sn-KCl})$ with $t \rightarrow \infty$ (Fig. 4). The range of carbon film thicknesses in which the angle θ varies within the extreme limits is $2.5 \text{ nm} < t < 7 \text{ nm}$. Electron-microscopic investigations of the structure of pure carbon films and also the literature data [28] point to the continuity of the carbon film up to a thickness of 1.5–2 nm. This suggests a conclusion that the dependence $\theta(t)$ is due, in accordance with formula (1), to the fact that the surface energy of carbon films varies as their thickness decreases. Since it is not only the surface energy of the film, σ_t , that varies with decreasing t , but also the film-particle interfacial energy σ_{sl} , it follows that the dependence $\theta(t)$ in the Sn-C-KCl system reflects, strictly speaking, the variation of the adhesion tension $\sigma_s - \sigma_{sl}$ with decreasing thickness of the carbon film residing on the KCl crystal. Figure 4 shows a plot of the adhesion tension versus the carbon film thickness for the Sn-C-KCl system calculated from data on $\theta(t)$. The increase in the adhesion tension with decreasing carbon film thickness is evidence of the decrease of the surface energy of the carbon film if it is assumed that the thin film-drop interface energy falls off with decreasing thickness, as is the case with the microparticle-substrate interface [3].

Because of the fact that in interpreting the wetting results for three-component liquid-thin film-bulk substrate systems it is difficult to separate the effect associated with the film thickness proper from the effect of the bulk substrate, it is useful to carry out investigations of wetting free thin films as a function of their thickness. We studied the wetting of free carbon thin films 3–30 nm thick with metals that are chemically inert to carbon (In, Sn, Pb). The carbon film thickness was determined directly from electron micrographs of the convolutions (Fig. 5a).

It was found that the contact angle diminishes with decreasing carbon film thickness (Fig. 6). The range of carbon film thicknesses in which the dependence $\theta(t)$ holds is 4–20 nm for all the systems studied, and at $t > 30$ nm the contact angle remains at a constant value θ_∞ corresponding to the wetting of a compact material. Analysis of microdrop profiles on free films of various thickness shows that the film is deformed by the drop (Fig. 5) and that the amount of deformation depends on the film thickness.

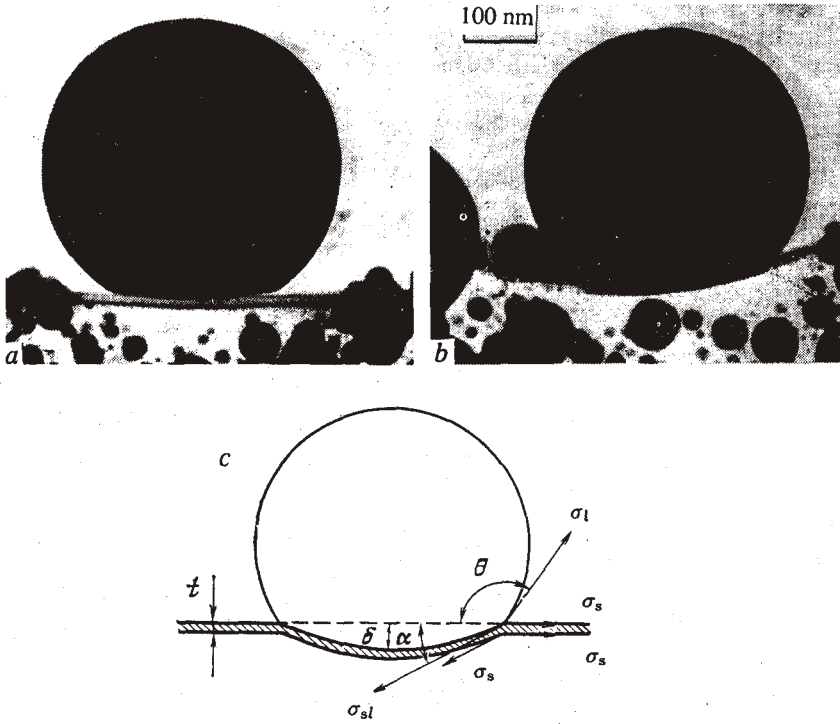


FIGURE 5. Micrographs of the profiles of crystallized drops of tin on carbon films of thickness 20 nm (a) and 10 nm (b) and a schematic representation of a liquid drop on a free thin film (c).

The interpretation of the results obtained should be based on a consideration of the equilibrium conditions for a drop. These can be obtained as follows. Part of the free energy due to the interaction of the drop with the film, is given by the following expression:

$$F = \sigma_l S_l + (\sigma_s + \sigma_{sl}) S_{sl} - 2\sigma_s S + f S_{sl}. \quad (7)$$

where S_l and S_{sl} are the surface areas of the drop; S is the cross-sectional area of the drop in the film plane; $f(t, \alpha)$ is the specific energy of deformation of the film. The equations of equilibrium for a drop on a deformed film can be derived from the conditions of the free energy minimum for the

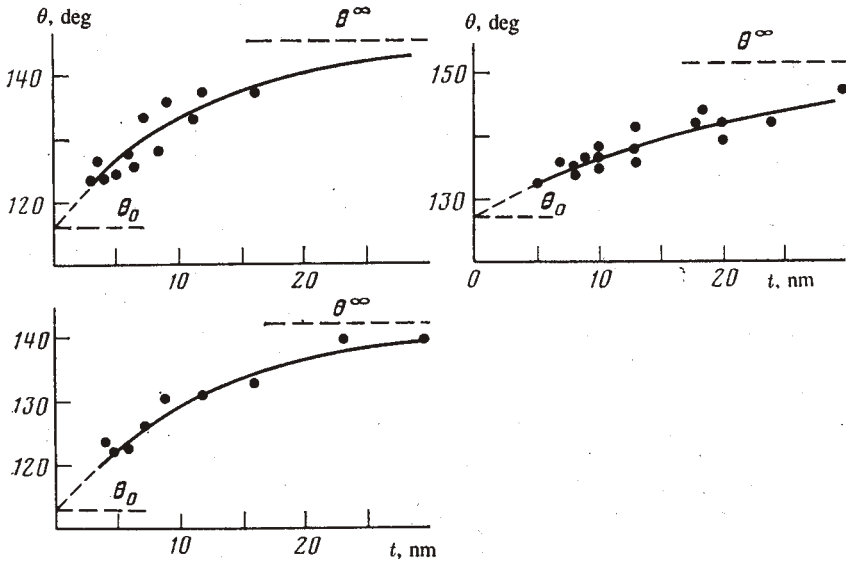


FIGURE 6. Dependence of the contact angle on the thickness of free carbon films for In (a), Sn (b), and Pb (c).

drop-film system ($\partial F/\partial \theta = 0, \partial F/\partial \alpha = 0$, where α is the deflection angle of the film (Fig. 5c):

$$\begin{aligned} \sigma_l \sin \theta &= (\sigma_s + \sigma_{sl}) \sin \alpha + \varphi(\alpha, t), \\ \sigma_l \cos \theta + (\sigma_s + \sigma_{sl}) \cos \alpha + \psi(\alpha, t) &= 2\sigma_s, \end{aligned} \tag{8}$$

where the terms $\varphi(\alpha, t)$ and $\psi(\alpha, t)$ take into account the deformation energy of the film.

Analysis shows that the solution of this problem in the general form is difficult, since, according to estimates and experimental data, the film deformation is not small, and therefore, there is no ground to believe that it is elastic. However, the problem can be simplified if one bears in mind that the binding energy per atom decreases with decreasing film thickness t [29] and that, according to estimates, at small thicknesses the terms φ and ψ can be neglected compared to the surface energy of the contacting phases. This supposition corresponds to the case of wetting by a drop of a liquid-like

TABLE II. Data on Wetting of Free Thin Films

System	θ_∞ , deg	θ_0 , deg	σ_l mJ/m ²	σ_s , mJ/m ²
In-C	145	116	559	121 ± 30
Sn-C	151	127	540	118 ± 30
Pb-C	142	113	450	113 ± 30

film, when the deformation occurs without loss of energy. Hence, instead of relations (8) we may write the following system of equations:

$$\begin{aligned}\sigma_l \sin \theta_0 &= (\sigma_s + \sigma_{sl}) \sin \alpha, \\ \sigma_l \cos \theta_0 + (\sigma_s + \sigma_{sl}) \cos \alpha &= 2\sigma_s, \\ \sigma_l \cos \theta_\infty &= \sigma_s - \sigma_{sl}\end{aligned}\quad (9)$$

Here, θ_0 corresponds to the wetting of a thin liquid-like film, i.e., $\theta_0 = \theta(t)$ for $t \rightarrow 0$. From relations (9) we obtain the expression for σ_s :

$$\sigma_s = \frac{\sigma_l \sin^2 \theta_\infty}{4(\cos \theta_0 - \cos \theta_\infty)}.\quad (10)$$

Thus, from the experimental dependence $\theta(t)$ for free films we can determine θ_0 and θ_∞ and, using the data on the substrate energy σ_l , it is possible to find the surface energy of the free film. In order to find θ_0 it is necessary to have an interpolation formula for the dependence $\theta(t)$, which can be obtained by the method of numerical treatment of the experimental data. Table II gives the surface energy values for thin carbon films obtained with the aid of formula (10) from the experimental data on $\theta(t)$ for the systems studied, which are in good agreement. The values of σ_s obtained refer to films 5–15 nm thick and are the upper limit of the surface energy values for carbon films, since the value of the deformation energy becomes, strictly speaking, negligibly small only with $t \rightarrow 0$, which cannot be realized experimentally. It should be noted that, according to indirect estimates based on various experimental data, the surface energy of graphite is 90–120 mJ/m² [30].

Analysis of the results shows that the theoretically predicted [31] dependence of the surface energy of a thin film on its thickness is a second-order effect as compared with the deformation of the film and that in order to find the dependence $\sigma(t)$ from data on the wetting of free thin films one has to know the particular form of the functions φ and ψ .

Thus, analysis of experimental data on the wetting of free thin films with consideration for their deformation allows one to estimate the surface energy of the thin film, which is difficult to do by means of other known methods.

Size Effects in Setting for Dispersed Systems of the Liquid Metal–Thin Metal Film Type

The investigation of the wetting in highly dispersed metal–metal systems as a function of the degree of dispersity of the liquid and solid phases is of theoretical and technological interest, since it enables one to study the effect of the geometric and physicochemical parameters on the contact interaction and allows one to control the wetting process for various systems. Among the factors that govern the wetting in dispersed metal–metal systems, apart from the size effects associated with the dependence of the surface energy on the phase size, we can distinguish the following: the discontinuity of the intermediate layer and the related heterogeneity of the substrate; the solubility of the components and the formation of chemical compounds at the solid–liquid interface; the oxidation of the metal film, which will depend on the physicochemical parameters of sample preparation. For polycrystalline films one should expect the dependence of wetting on the ratio of the characteristic sizes of liquid drops and crystal grains in the substrate film.

Thus, the process of wetting in highly dispersed systems depends on a number of parameters, which are very difficult to separate. To solve this problem we carried out investigations of wetting in Sn–Al–KCl, Bi–Fe–KCl, Pb–Ni–NaCl, and Pb–Ni–Si systems as a function of the metal film thickness ($5 \text{ nm} < t < 200 \text{ nm}$) and of the liquid drop size ($5 \text{ nm} < R < 10^4 \text{ nm}$). The choice of the system and of the ranges of variation of the parameters t and R was dictated by the need to obtain as generalized data as possible. According to [32], the systems indicated differ significantly in the nature of the interaction: complete insolubility in the solid and liquid states for Bi–Fe; solubility $\approx 0.5 \text{ wt.}\%$ of Al in Sn for Sn–Al; and solubility up to 4 wt.% of Ni in Pb for Pb–Ni.

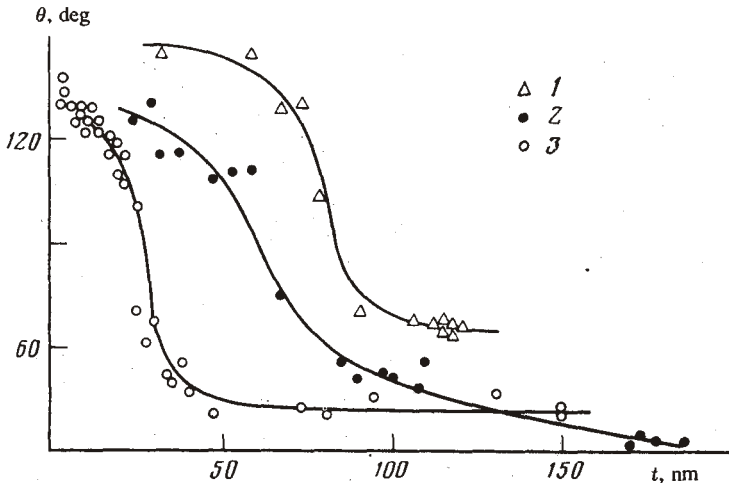


FIGURE 7. Dependence $\theta(t)$ for the following systems: (1) Bi-Fe; (2) Sn-Al; (3) Pb-Ni.

The specimens used for our investigations were prepared as follows. A metal film of variable thickness (Al, Fe, Ni) was condensed on KCl (or NaCl) single crystals in a vacuum of 10^{-5} – 10^{-6} Pa; then the metal to be studied (Sn, Bi, Pb) was condensed on the metal film by the vapor-liquid mechanism without upsetting the vacuum. After cooling in a vacuum the films with crystallized drops were examined using electron and optical microscopy. It was found that the contact angle θ depends on both the film thickness and the particle size at constant thickness.

Figure 7 presents the dependence of the angle θ on the film thickness t for the systems studied. The degree of wetting depends to a substantial extent on the film thickness, but the range of thicknesses in which θ varies is found to be different for different systems. Analysis of the data obtained shows that the dependence $\theta(t)$ for different systems is due to different mechanisms. We will now consider the results in more detail.

In the Pb-Ni-NaCl system in the range of nickel film thicknesses $5 \text{ nm} < t < 40 \text{ nm}$, θ varies in the range $\theta(\text{Pb-Ni-NaCl}) \rightarrow \theta(\text{Pb-NaCl})$ at $t < 5 \text{ nm}$ and $\theta(\text{Pb-Ni-NaCl}) \rightarrow \theta(\text{Pb-Ni})$ at $t > 40 \text{ nm}$, i.e., at small film thicknesses θ tends toward the value corresponding to the wetting of a clean NaCl substrate, while at large t the angle θ corresponds to the wetting of an Ni film in the bulk state by a liquid metal. Electron-microscopy and electron-diffraction data show that the dependence $\theta(t)$ is mainly due to the

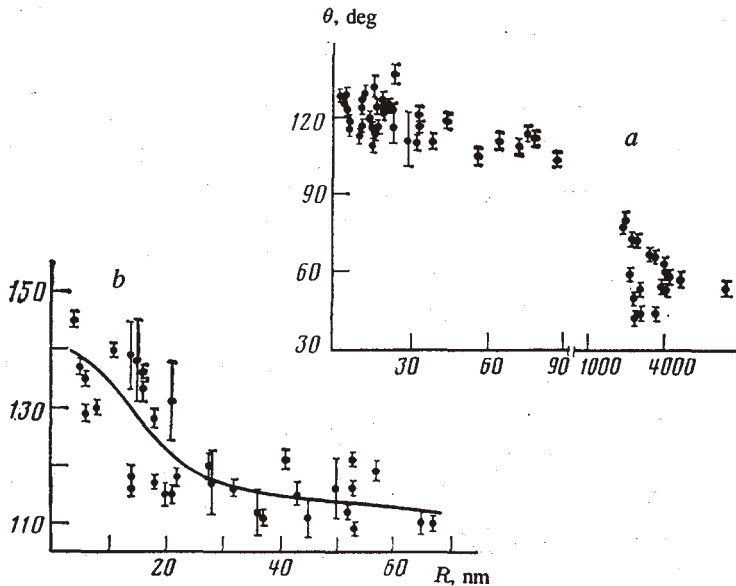


FIGURE 8. Dependence $\theta(R)$ in the Sn-Al-KCl system for Al films of thickness 110 nm (a) and 40 nm (b).

dissolution of Ni in Pb, which leads to a discontinuity of the Ni film, i.e., with certain film thicknesses the substrate becomes heterogeneous. Since the solubility in the Pb-Ni system is limited, it follows that the degree of heterogeneity of the substrate will depend on the Ni film thickness, which is what accounts for the observed dependence $\theta(t)$.

For the Bi-Fe-KCl system, which is characterized by the complete solubility of the components in the solid and liquid states, the dependence $\theta(t)$ is also observed but with much thicker Fe films than for the Pb-Ni-NaCl system. From the data presented in Figure 7 it follows that with Fe film thicknesses $t < 60$ nm the angle $\theta \approx 145^\circ$, i.e., it substantially exceeds the value for the Bi-KCl system ($\theta \approx 120^\circ$). This means that the upper limit of wetting in the Bi-Fe-KCl system cannot be accounted for by the Fe film discontinuity. In accordance with the electron-microscopy data and with the results of qualitative electron-diffraction analysis, the dependence $\theta(t)$ in the given system is due to the oxidation of Fe films, which may occur by the mechanism of oxidation of the metal-alkali-halide crystal interface [33], and also due to the supply of oxygen from the residual atmosphere of the vacuum chamber. Because of this, thin films may have an oxide layer

of a larger thickness and, hence, for them the interfacial interaction at the drop-substrate interface will be weaker. This must lead to an increase in the contact angle with a decrease in the Fe film thickness in the Bi-Fe-KCl system.

The Sn-Al-KCl system is characterized by a low solubility of Al in Sn and in this respect it is intermediate between the systems considered above. The results obtained on $\theta(t)$ for this system show that the variation of the angle θ occurs within a wider range of Al film thicknesses (30–150 nm). Electron-microscopy studies of bilayer Sn-Al films and electron-diffraction data on the structure of Al films of various thicknesses indicate that the dependence $\theta(t)$ is due to two mechanisms: the dissolution of Al in Sn drops and the oxidation of films with the formation of the oxide Al_2O_3 .

In the present work, we studied the wetting of the Sn-Al-KCl system as a function of the size of liquid drops with fixed thicknesses of the sublayer films. It was found that θ increases with decreasing particle size. Figure 8 gives the dependence $\theta(R)$ for Al films 110 and 40 nm thick. On the Al film ($t = 110$ nm) the angle θ varies from 50° for drops with a size of several microns to 110° for drops with a radius of 3–40 nm. At $t = 40$ nm, drops 25–40 nm in size have approximately the same contact angle. For Sn particles with $R < 20$ nm there is an increase in θ with decreasing drop radius, in distinction to the metal-carbon systems. An analogous increase in the angle θ with decreasing particle size was also found for Bi-Fe-KCl systems.

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