Methods of Determination of Wetting
in Highly Dispersed Systems

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The study of the properties of small-size objects--highly dispersed systems (HDS)--which are receiving much attention at present, is of interest primarily because highly dispersed systems frequently display differences in their physicochemical, structural, thermodynamic, and kinetic characteristics from the respective bulk values. The capillary properties of HDSs, which should be expected to exhibit effects of the dependence of the surface characteristics on the object size, have been studied little.
The most important parameters that determine the capillary properties of the systems under consideration is the corresponding surface energy (the intrinsic surface energy for isolated objects or the interfacial energy of the contacting phases). The information on this energy can be obtained in studies of wetting in two-phase systems of the solid-liquid type. Analysis of the known methods of determination of the angles of contact $\theta$ shows that the conventional methods, a detailed review of which is given in [1-4], have a very limited use for studying wetting in highly dispersed systems: most of the known methods require considerable amounts of liquid, while the drop-on-the-thin-filament method is limited to the case $\theta < 90^\circ$. In view of this, new methods are required that would enable one to study wetting and contact interaction in HDSs, both in those containing a dispersed liquid phase and those with a dispersed solid phase. Since HDSs should be expected to display size effects, the methods must be applicable over a wide size range.

The present work describes methods which make it possible to study wetting in HDSs with different types of contact interaction (i.e., they can be applied both for $\theta > 90^\circ$ and $\theta < 90^\circ$) with the characteristic size of the phases varying within $3 \times 10^5$ nm.

The samples studied were island films of various metals condensed in vacuum onto solid substrates by the vapor-liquid mechanism. The substrates were also prepared by vacuum condensation.

The use of the method of vacuum condensation for the preparation of samples made it possible to prepare very clean contacting surfaces and to reduce to a minimum the effects of the interfering physicochemical factors on wetting: the formation of adsorbed layers, oxide films, etc. The method of
vacuum condensation also allows one to exclude the effect of geometric factors (surface roughness and porosity of the substrate, etc.), since the prepared substrate surface can be smooth and "clean" at the atomic level if use is made of surfaces cleaved under vacuum and layers freshly deposited under ultrahigh-vacuum conditions. And, finally, the method of vacuum condensation enables one to control the dispersity of the droplet-substrate system as desired and thus to investigate the dimensional effect on wetting.

In order to prepare samples, we used an oil-free vacuum system, which made it possible to prepare films at $10^{-8}$-$10^{-7}$ Pa. The sample preparation technique was as follows. The substrates were deposited in vacuum onto NaCl cleavages at temperatures which permitted the metal under study to condense into a liquid phase. Then the metal was deposited onto this surface by the vapor-liquid mechanism. The film thickness was determined by means of a quartz detector and also control glasses by the method of equal-chromatic-order lines or using the data on the optical density of the sample. The films prepared were cooled in vacuum to room temperature and then the crystallized particles were examined by optical, scanning, and transmission electron microscopy. To measure the angles of contact we used an MIM-8 metallographic microscope and EM-200, EMV-100BR, and REM-200 electron microscopes.

In cases when gravitation may be neglected, small droplets have the shape of a spherical segment (estimates show that for metals this is valid for particles smaller than $10^5$ nm in size). In order to find the angle $\theta$, it is sufficient to measure any two of the three characteristics of the drop on the substrate: the radius of curvature of the drop surface, $R$, the diameter of its base, $d$, or the height $H$ (Fig. 1a).
FIGURE 1. Schematic representation of a liquid drop on a solid substrate (a), the cross section (b), and view (c) of drops during oblique observation of the sample.

In the methods described below the above parameters were usually measured on crystallized droplets, which is why we had to estimate the error due to the change in the volume of the droplet upon its solidification on the substrate. Since the heat transfer upon cooling of droplets in vacuum occurs predominantly across the boundary between the drop and the substrate, upon crystallization of drops the area of contact is not changed. In this case, it is easy to show that the error in the determination of $\theta$ will be given by

$$\Delta \theta = \frac{1}{3} (2 + \cos \theta) \sin \theta \frac{\Delta \rho}{\rho_s},$$

where $\Delta \rho/\rho_s$ is the relative density change of the metal upon crystallization. One can see that at $\Delta \rho/\rho_s = 0.05$ (a typical value for metals) the value of $\Delta \theta$ does not exceed $2^\circ$. This is confirmed by experimental data [5, 6], demonstrating that on crystallization of particles the angle of contact does not vary within experimental error. Thus, the variation in the angle of contact during droplet crystallization can be neglected.
and the values of $\theta$ found for crystallized particles can be referred to the value of angles of contact of liquid drops at the solidification temperature.

In order to measure the wetting angles of particles with a size of $10^3$-$10^5$ nm, we used optical microscopy.

**THE METHOD OF CLEAVAGE**

The cleavage method is based on the measurement of the parameters of the drop profile in a plane perpendicular to the substrate surface (the cleavage plane of the substrates, Figs. 1a and 2a). In this case one can easily measure all the three parameters $R$, $d$, and $H$; the angle $\theta$ is given by the following relation:

$$\theta = 2 \tan^{-1} \left( \frac{2H}{d} \right) = \begin{cases} \sin^{-1} \frac{d}{2R}, & \theta < 90^\circ, \\ 180^\circ - \sin^{-1} \frac{d}{2R}, & \theta > 90^\circ \end{cases}$$

Since in vacuum condensation the particles formed vary in size, in the cleavage plane there always is a sufficient number of particles suitable for measurements but greatly differing in size. To obtain reliable values of the angle $\theta$, the quantities $R$, $d$, and $H$ should be measured for particles that lie exactly in the cleavage plane. Because of the small depth of focus in optical microscopy, the criterion for selection of particles is a sharp image of both the particle base and the edge of the cleaved surface of the substrate crystal. It should be noted that since in the method under consideration the substrate plane is always perpendicular to the focal plane of the objective lens, slight displacements of the particles relative
FIGURE 2. Micrographs illustrating the measurement of angles of contact by different methods: (a) the cleavage method (Sn–NaCl; X800); (b) the method of oblique observation, scanning electron microscopy (Sn–C; X6000); (c) the method of specular reflection (Pb–Ni; X800); (d) the convolution method (Pb–Si; X150000); (e) the photometric measurement method (Sn–C; X150000).
to the cleavage plane do not give substantial errors in the $R$, $d$, and $H$ values.
In practice it is convenient to measure the $R$, $d$, and $H$ values for particles of different size and then to determine the ratios $H/d$, $d/R$, and $H/R$ from the graphs by averaging of the corresponding linear dependences. This allows one to minimize the errors in the measurement of the particle parameters. The maximum spread of the angle values calculated from the different relations (1) is 2-3°, which characterizes the accuracy of the method.

The applicability of the cleavage technique for the study of wetting in dispersed systems is limited by the particle size $R \geq (3-5) \times 10^3$ nm because of the limited resolving power of the optical microscope. The cleavage method also imposes restrictions on possible substrate materials, since the substrate should be such that one could break or cleave it without damaging the microparticles it carries. Analysis shows that the study of the profile of particles gives reliable results for systems with a limited degree of wetting ($\theta > 90^\circ$).

**THE OBLIQUE TECHNIQUE**

This method of determination of the angles is also based on the measurements of the parameters of drop profiles, but in contrast to the cleavage method, the substrate normal is inclined at an angle $\alpha$ to the optical axis of the microscope. This makes it possible to considerably extend the range of measured angles and types of substrates, since in this method any smooth surface may be used as the substrate. The outline of the drop on the substrate with oblique observation is shown in Figure 1. In order to find $\theta$ it is necessary to measure the "apparent height" of the particle $H_\text{a}$ and its radius of curvature $R$ ($d$ for $\theta < 90^\circ$). The angle $\theta$ is re-
lated with the quantities $R$, $H_a$, and $\alpha$ measured by the following relations:

$$H_a = R(1 + \sin(\theta - \alpha)) = \frac{d}{2 \sin \theta} (1 + \sin(\theta - \alpha)).$$  \hspace{1cm} (2)

The explicit representation of $\theta$ in terms of $d$, $H_a$, and $\alpha$ is cumbersome, therefore the angle $\theta$ at $\theta < 90^\circ$ can be easily taken from a nomogram on which a family of curves are plotted in the $H_a/d$ vs $\theta$ coordinates at different values of $\alpha$. The advantages of the method of oblique observation are the presence of a large number of particles suitable for measurements and also the fact that it works equally well for both $\theta < 90^\circ$ and $\theta > 90^\circ$ cases. For accurate measurements it is necessary that the difference between $\alpha$ and $|\theta - 90^\circ|$ would not be less than $20^\circ$.

The cleavage and oblique observation methods can also be realized with scanning electron microscopy (Fig. 2b), the application of which substantially extends the range of usable particle sizes for the study of wetting in HDSs.

THE METHOD OF SPECULAR REFLECTION

For systems with $\theta < 90^\circ$ a method of $\theta$ determination has been developed which does not require the study of the particle profile. The angle $\theta$ is determined in terms of $d$ and $R$: $d$ is the base diameter of the drop on the substrate in the optical microscope, and the radius of curvature $R$ is determined by the method of specular reflection [7] from the dimensions of the image of a remote object given by the spherical surface of the drop (Figs. 2c and 3a). From geometric optics it follows that the radius of curvature of the spherical surface $R$ can be determined from the distance to the object, $S$, and its size $2l$ as follows:
FIGURE 3. Method of specular reflection: (a) the path of rays during the determination of the spherical surface curvature radius; (b) dependence of the quantity $2rF/R$ on the diameter of the aperture diaphragm $L$. The values of $F$ are: (1) 8.4 mm; (2) 4.3 mm.

\[ R = \frac{2Sr_k}{l} \]  \hspace{1cm} (at $S \gg R$) \hspace{1cm} (3)

where $2r_k$ is the size of the image of the remote object. If we regard the drop surface as a spherical mirror we can find the radius of its curvature $R$ from formula (3) by measuring $r_k$, with the known values of $S$ and $l$, and then determine $\theta$ from relation (1). The method can be used to find $\theta$ for both transparent substrates in the transmitted and reflected light and opaque substrates in the reflected light. A particular variant of this method has been used in [7] for the measurement of the angles of contact for transparent liquid drops on a transparent substrate.

The use of the metallographic microscope makes it possible to determine $\theta$ for metal drops on opaque substrates (the remote object may be the aperture diaphragm of the microscope). It can be shown that in this case the following relation is fulfilled:
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\[ R = 2r_k F/(AL). \]  

(4)

where \( F \) is the focal length of the objective lens; \( L \) is the diameter of the aperture diaphragm; \( A \) is a characteristic constant of the illuminating system of the microscope. From relations (1) and (4) it follows that the angle of contact is equal to

\[ \theta = \sin^{-1}\left( \frac{d}{2r_k} \frac{AL}{F} \right). \]  

(5)

Since \( L \) and \( F \) are known, it follows that, knowing \( A \) and measuring \( d \) and \( r_k \), we can determine \( \theta \). To find the constant \( A \), we measured \( R \) and \( r_k \) for particles at \( \theta > 90^\circ \) (in this case \( 2R = d \)) at different fixed values of \( L \) and \( F \). The results are presented in Figure 3b in the coordinates of \( 2r_k F/R \) vs \( L \). The slope of the straight line gives the value of the constant \( A = 0.53 \).

The method works for droplets \( 10^3-10^5 \) nm in size and for the angle range \( 40^\circ < \theta < 70^\circ \). The lower \( \theta \) limit is due to the nonspherical shape of drops owing to good wetting, and the upper limit is due to an increase in the error as \( \theta \) approaches \( 90^\circ \).

The measurements of the angles of contact for particles with a size less than \( 10^4 \) nm were made using the electron microscopy methods: the convolution method and the method of photometric analysis of electron micrographs of drops.

THE CONVOLUTION METHOD

The method is based on measurements of the profile parameters of microparticles \( (R, d, H) \) on the electron micrographs taken with a plane of the substrate parallel to the incident beam (Fig. 2d). The method can be applied to particles with a
size $R \geq 10^2$ nm. Since for smaller particles the relative error of measurements increases considerably, for the study of wetting in systems with $R \leq 10$ nm a method was developed of the photometric analysis of the electron-microscopic image of particles.

PHOTOMETRIC MEASUREMENTS

The angle of contact $\theta$ is determined through the parameters $R$ and $r$, which are found by photometric analysis of particle micrographs taken with the substrate plane perpendicular to the beam (Fig. 2e). Figure 4 shows the dependence of the darkening $S$ on the running coordinate $x$ obtained by photometric measurement on the particle image along its diameter. The parameters $R$ and $r$ can be determined from the dependence $S(x)$ as follows.

Electron micrographs show intensity maxima near the particle edge which are due to the diffraction effects corresponding to the maxima of Fresnel diffraction. According to [8], the position of the Fresnel maxima relative to the image of the object edge depends on the focusing conditions, so that the distance $\delta$ from the edge to the $n$th maximum is given by

$$\delta = \left[ \Delta f^c(2n - 1)\lambda \right]^{\frac{1}{2}}. \quad (6)$$

Here $\Delta f^c$ is the defocusing distance of the objective lens, which is equal to the distance between the focal plane of the objective lens and the plane in which the object lies; $\lambda$ is the wavelength of electrons. When the object is in the focal plane of the objective, $\delta = 0$ and no edge fringes are observed. In electron microscopy usually $n = 1$, therefore $\delta = (\Delta f^c \lambda)^{\frac{1}{2}}$. The defocusing distance $\Delta f^c$ is determined experi-
mentally with the aid of a goniometer stage, derived from the angle of inclination of the test object, which is a colloid film with holes of diameter \( \approx 10^3 \) nm. The angle of inclination of the test object \( \phi_0 \) is found from the conditions when a Fresnel edge fringe appears upon inclination of the specimen. In this case \( \Delta f = (L/2) \tan \phi_0 \), where \( L \) is the linear size of the test object. Estimates show that with an accelerating voltage of 100 kV (\( \lambda = 3.7 \times 10^{-3} \) nm) and the defocusing distance \( \Delta f = 10^2 \) nm the value of \( \delta = 0.6 \) nm.

\[
S, \text{ rel. units } (\ln S)^2
\]

\[
\begin{array}{c}
170 \\
130 \\
90 \\
\end{array}
\begin{array}{c}
a \\
D \\
24 \\
\end{array}
\begin{array}{c}
10 \\
20 \\
40 \\
80 \\
\end{array}
\begin{array}{c}
x, \text{ mm} \\
\ln S \\
\end{array}
\begin{array}{c}
b \\
22 \\
\end{array}
\begin{array}{c}
x^2, \text{ mm}^2 \\
\end{array}
\]

FIGURE 4. (a) Dependence of the darkening \( S \) on the running coordinate \( x \). (b) Dependence \( S(x) \) in the \((\ln S)^2\) vs \( x^2 \) coordinates.

Thus, the radius of curvature of the particle is determined from its image by the relation:

\[
R = \frac{1}{2}(D - 2\delta),
\]  

(7)

where \( D \) is the diameter of the first Fresnel fringe, which is found by photometry from the dependence \( S(x) \) (Fig. 4).

The radius of the base of the particle, \( r \), can also be determined from the dependence \( S(x) \). On the linear portion
of the characteristic curve the following relation is satisfied:

\[ S = \kappa I \tau, \]  

(8)

where \( \kappa \) is a coefficient which takes into account the individual properties of the photoemulsion and the conditions of its treatment; \( I \) is the incident radiation intensity; \( \tau \) is the exposure time. If an exponential law of energy absorption is fulfilled within the particle, then for the intensity of electron beam that has passed through the specimen we may use the following relation:

\[ I = I_0 \exp (-\mu h), \]  

(9)

where \( I_0 \) is the intensity of the primary electron beam and \( \mu \) is the absorption coefficient. For particles having the shape of a spherical segment (Fig. 1a) the dependence \( h(x) \) differs substantially in the two regions, i.e.,

\[ h(x) = \begin{cases} 
\alpha + (R^2 - x^2)^{1/2} & \text{at } x < r; \\
2(R^2 - x^2)^{1/2} & \text{at } r < x < R.
\end{cases} \]  

(10)

From relations (8), (9), and (10) it follows that \( \ln S \sim h(x) \), which is why the dependence \( S(x) \) in the coordinates of \( (\ln S)^2 \) vs \( x^2 \) has a kink at \( x = r \) (Fig. 4). Thus, on the basis of the photometric data of particle micrographs we can determine the quantities \( R \) and \( r \) for microparticles on the substrate from the dependence \( S(x) \). The angle \( \Theta \) is calculated from relation (1).

The method described above enables one to find \( \Theta \) for both crystallized and liquid particles with \( \Theta > 90^\circ \) in the size range of 3 nm < \( R < 70 \) nm. The lower limit of the size is determined by the sensitivity of the microphotometer and
the upper limit is related to the ultimate thickness of the
object that is still transparent for electrons.

The use of the method may be extended to the case \( \theta < 90^\circ \).
Indeed, for a particle having the shape of a spherical segment with the radius of curvature \( R \) and height \( H \) (Fig. 1a) the dependence \( h(x) \) has the form

\[
h(x) = H - R + (R^2 - x^2)^{1/2}. \tag{11}
\]

If the diameter of the particle beam is less than the extinction length (the condition of the absence of thickness fringes on the electron micrographs of a particle), then the image contrast is governed only by the thickness of the absorbing layer, \( h \). Using formulae (8), (9), and (11), we get

\[
\ln S(x) = \ln S_0 - \mu[H - R + (R^2 - x^2)^{1/2}], \tag{12}
\]

where \( S_0 \) is the darkening corresponding to the background.

In order to determine \( \theta \), it is necessary to find \( H \) and \( R \)
from equation (12) by using the experimental data of \( x_i \) and
\( y_i = \ln S_0 - \ln S(x_i) \).

In the general case where the absorption coefficient \( \mu \)
is unknown, the angle \( \theta \) can be found by solving a system of \( n \) conditional equations (\( n \) is the number of experimental points) with the unknowns \( \mu, H, \) and \( R \). The solutions can be found using the least-squares method by determining the formerly approximate values of \( \mu_0, H_0, \) and \( R_0 \) and by expanding expression (12) into a power series \( \Delta \mu = \mu - \mu_0, \Delta H = H - H_0, \) and \( \Delta R = R - R_0 \). Neglecting terms of the order higher than first order, we obtain a system of equations for the corrections \( \Delta \mu, \Delta H, \) and \( \Delta R \):

\[
y_i = \Delta H + \Delta R x_i + M z_i, \quad i = 1, 2, \ldots, n, \tag{13}
\]
where

\[ y_1 = y_i/\mu_0; \quad x_1 = R_0/(R_0^2 - x_1^2)^{\frac{1}{2}} - 1; \]

\[ z_1 = R_0 - R_0 + (R_0^2 - x_1^2)^{\frac{1}{2}}; \quad M = \Delta \mu/\mu_0 + 1. \]

The solution of the system of equations (13) for the unknowns \( M, \Delta H, \) and \( \Delta R \) can be obtained by the least squares method. In the above method of treatment of the experimental data for the determination of the angle \( \theta \) at \( \theta < 90^\circ \) we assumed that the absorption coefficient of electrons, \( \mu \), is unknown. The method of photometric measurement allows one to use an independent method for the determination of the coefficient \( \mu \). Indeed, from (12) it follows that, knowing the dependence \( h(x) \) and representing the photometric measurement data in the coordinates of \( \ln S \) vs \( h \), we can determine \( \mu \). For this purpose, it is convenient to use the results on the particles with \( \theta > 90^\circ \), since in such cases the absorption of electrons in the substrate is excluded. For particles with \( \theta > 90^\circ \) the thickness of the absorbing layer is \( h(x) = 2(R^2 - x^2)^{\frac{1}{2}} \). Having determined the coefficient \( \mu \) for the metal under study, we can simplify considerably the analysis of the dependence for finding the angle of contact in systems with \( \theta < 90^\circ \).

ESTIMATION OF \( \theta \) FROM HISTOGRAMS

This method makes it possible to determine the averaged value of the angle of contact for an assembly of particles that compose an island film. Let the island film consist of particles which are similar spherical segments with a radius of curvature in the range \( R_{\min} < R < R_{\max} \). The value of \( R_{\min} \) is determined by the resolution of the instrument and \( R_{\max} \) by the amount of the condensed substance. The mass of the unit
area of such a film is equal to

\[ m = \rho \int_{R_{\text{min}}}^{R_{\text{max}}} V(R, \theta) n(R) dR, \]  

(14)

where \( \rho \) is the substance density; \( V(R, \theta) = \frac{4}{3} \pi R^3 \varphi(\theta) \) is the volume of the particle; \( n(R) \) is the distribution function for particle sizes. Assuming \( \theta \) to be independent of \( R \) (this condition is satisfied for particles with \( R > 20-30 \) nm) and having determined \( m \) and \( n(R) \), we can find the function \( \varphi(\theta) \) for an island film:

\[ \varphi(\theta) = \frac{3m}{4\pi \rho} \int_{R_{\text{min}}}^{R_{\text{max}}} R^3 n(R) dR, \]  

(15)

where \( \varphi(\theta) = \frac{1}{4} (2 + \cos \theta)(1 - \cos \theta)^2 \). In the case of \( \theta < 90^\circ \) we measure the radius of the base of the segment \( r = R \sin \theta \) and relation (15) transforms to

\[ \frac{\varphi(\theta)}{\sin \theta} = \frac{3m}{4\pi \rho} \int_{r_{\text{min}}}^{r_{\text{max}}} r^3 n(r) dr. \]  

(16)

Hence, knowing the mass of the condensed substance and having constructed the histogram from the micrograph of the island film prepared by condensation by the vapor-liquid mechanism, we can determine the averaged value of \( \theta \) for an assembly of particles.

Thus, the entire set of experimental methods developed enables one to study the wetting of solid surfaces by small metallic particles with the size of the latter varying within the range 3-10^5 nm.
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