Methods of Determination of Wetting in Highly Dispersed Systems

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Kharkov State University, Kharkov

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Procedures are described for studying the wetting of solid substrates by island vacuum condensates. The proposed methods are based on the application of optical and electron microscopy and may be used to find the angles of contact over a wide range of particle sizes ($3-10^5$ nm).

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 determines the capil-
lary properties of the systems under consideration is the
corresponding surface energy (the intrinsic surface energy
for isolated objects or the interfacial energy of the con-
tacting 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 θ shows that the conventional methods, a
detailed review of which is given in [1-4], have a very lim-
ited 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 lim-
ited to the case $\theta < 90°$. 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 in-
teraction (i.e., they can be applied both for $\theta > 90°$ and
$\theta < 90°$) with the characteristic size of the phases varying
within $3-10^5$ 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 con-
densation.

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 for-
mation 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 in-
vestigate 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 con-
dense 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 micro-
scope 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 θ, 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).
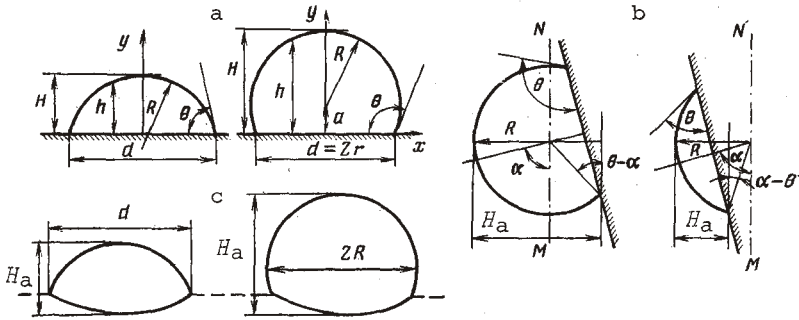
N. T. GLADKIKH *et al.*

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 θ 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°. 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 θ 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 θ is given by the following relation:

$$\theta = 2\tan^{-1}\frac{2H}{d} = \cos^{-1}\left(1 - \frac{H}{R}\right) = \begin{cases} \sin^{-1}\dfrac{d}{2R}, & \theta < 90°, \\[3mm] & \qquad (1) \\[1mm] 180° - \sin^{-1}\dfrac{d}{2R}, & \theta > 90° \end{cases}$$

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 θ, 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
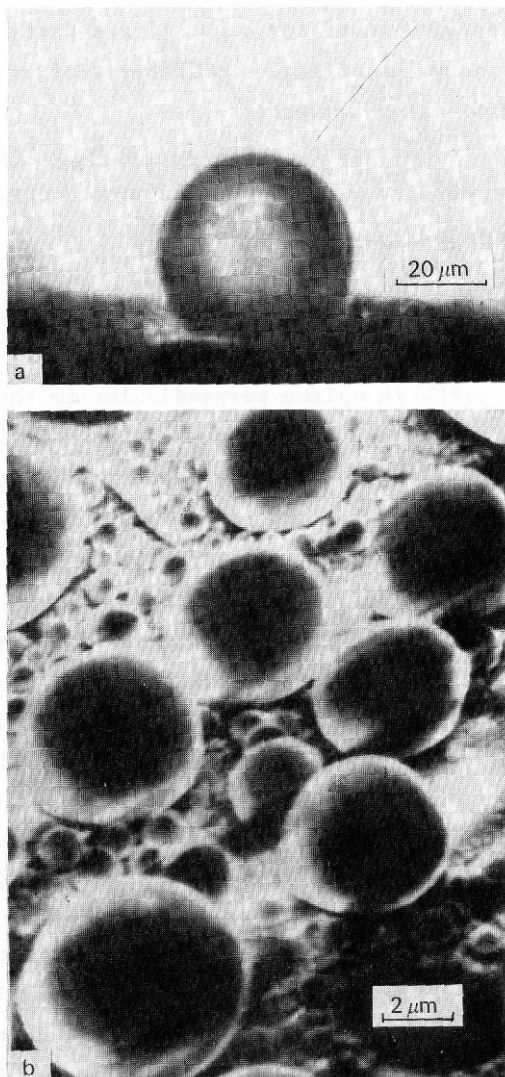
Figs. 2a,b

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).
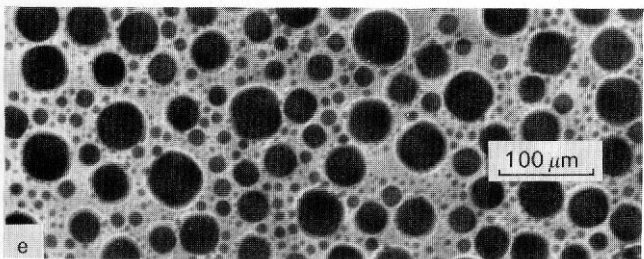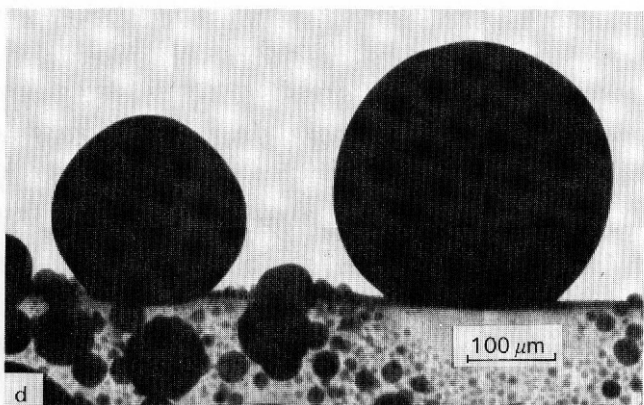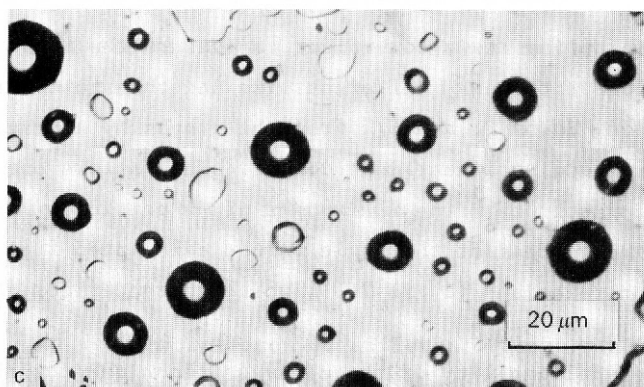
Figs. 2c,d,e

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 $R \geqslant (3-5) \times 10^3$ 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 ($\theta > 90°$).

THE OBLIQUE TECHNIQUE

This method of determination of the angles is also based on the measurements of the parameters of drop profiles, but in contast to the cleavage method, the substrate normal is inclined at an angle α 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 θ it is necessary to measure the "apparent height" of the particle H_a and its radius of curvature R (d for $\theta < 90°$). The angle θ is re-

lated with the quantities R, H_a, and α measured by the fol-
lowing relations:

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

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

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 $\theta < 90°$ a method of θ determination has been
developed which does not require the study of the particle
profile. The angle θ is determined in terms of d and R: d
is the base diameter of the drop on the substrate in the op-
tical 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 fol-
lows that the radius of curvature of the spherical surface
R can be determined from the distance to the object, S, and
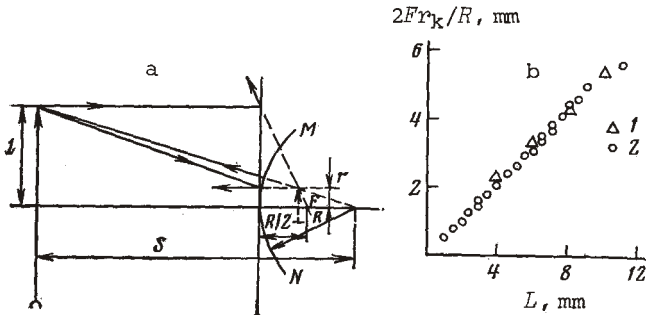its size $2l$ as follows:

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 aper-
ture diaphragm L.   The values of F are: (1) 8.4
mm;   (2) 4.3 mm.

$$R = 2Sr_k/l \quad (\text{at } S \gg R) \tag{3}$$

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 θ
from relation (1).   The method can be used to find θ 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 measure-
ment of the angles of contact for transparent liquid drops
on a transparent substrate.

The use of the metallographic microscope makes it possible
to determine θ for metal drops on opaque substrates (the re-
mote object may be the aperture diaphragm of the microscope).
It can be shown that in this case the following relation is
fulfilled:

$$R = 2r_k F/(AL). \tag{4}$$

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

$$\theta = \sin^{-1}\left(\frac{d}{2r_k} \frac{AL}{F}\right). \tag{5}$$

Since L and F are known, it follows that, knowing A and measuring d and r_k, we can determine θ. To find the constant A, we measured R and r_k for particles at $\theta > 90°$ (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 $40° < \theta < 70°$. The lower θ 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 θ approaches $90°$.

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 $R \geqslant 10^2$ nm. Since for smaller particles the relative
error of measurements increases considerably, for the study
of wetting in systems with $R \lesssim 10$ nm a method was developed
of the photometric analysis of the electron-microscopic image
of particles.

PHOTOMETRIC MEASUREMENTS

The angle of contact θ 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 photo-
metric 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 par-
ticle 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 δ from the edge to the nth maximum is given by

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

Here Δf 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;
λ 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 $\delta =$
$(\Delta f\lambda)^{\frac{1}{2}}$. The defocusing distance Δf is determined experi-

mentally with the aid of a goniometer stage, derived from
the angle of inclination of the test object, which is a col-
lodion film with holes of diameter $\approx 10^3$ nm. The angle of
inclination of the test object ϕ_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 lin-
ear 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.
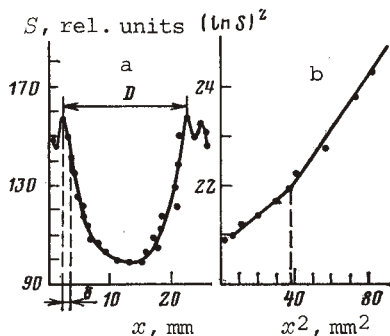

FIGURE 4. (a) Dependence of the darkening S on the
running coordinate x. (b) Dependence $S(x)$ in the
$(\ln S)^2$ vs x^2 coordinates.

Thus, the radius of curvature of the particle is deter-
mined from its image by the relation:

$$R = \tfrac{1}{2}(D - 2\delta), \tag{7}$$

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 satis-
fied:

$$S = kI\tau, \tag{8}$$

where k is a coefficient which takes into account the indi-
vidual properties of the photoemulsion and the conditions of
its treatment; I is the incident radiation intensity; τ 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:

$$I = I_0 \exp (-\mu h), \tag{9}$$

where I_0 is the intensity of the primary electron beam and
μ 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.,

$$h(x) = \begin{cases} a + (R^2 - x^2)^{\frac{1}{2}} & \text{at} \quad x < r; \\ 2(R^2 - x^2)^{\frac{1}{2}} & \text{at} \quad r < x < R. \end{cases} \tag{10}$$

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 deter-
mine the quantities R and r for microparticles on the sub-
strate from the dependence $S(x)$. The angle θ is calculated
from relation (1).

The method described above enables one to find θ for
both crystallized and liquid particles with $\theta > 90°$ 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 $\theta < 90°$.
Indeed, for a particle having the shape of a spherical seg-
ment with the radius of curvature R and height H (Fig. 1a)
the dependence $h(x)$ has the form

$$h(x) = H - R + (R^2 - x^2)^{\frac{1}{2}}. \tag{11}$$

If the diameter of the particle beam is less than the ex-
tinction 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

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

where S_0 is the darkening corresponding to the background.
In order to determine θ, 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 μ
is unknown, the angle θ can be found by solving a system of
n conditional equations (n is the number of experimental points)
with the unknowns μ, H, and R. The solutions can be found
using the least-squares method by determining the formerly
approximate values of μ_0, H_0, and R_0 and by expanding ex-
pression (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
$\Delta\mu$, ΔH, and ΔR:

$$Y_i = \Delta H + \Delta R X_i + M Z_i, \quad i = 1, 2, \ldots, n, \tag{13}$$

where

$$Y_i = y_i/\mu_0; \quad X_1 = R_0/(R_0^2 - X_1^2)^{\frac{1}{2}} - 1;$$
$$Z_1 = H_0 - R_0 + (R_0^2 - x_1^2)^{\frac{1}{2}}; \quad M = \Delta\mu/\mu_0 + 1.$$

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

ESTIMATION OF θ 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

$$m = \rho \int_{R_{\min}}^{R_{\max}} V(R,\theta)n(R)dR, \tag{14}$$

where ρ is the substance density; $V(R,\theta) = \frac{4}{3}\pi R^3\Phi(\theta)$ is the volume of the particle; $n(R)$ is the distribution function for particle sizes. Assuming θ 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 $\Phi(\theta)$ for an island film:

$$\Phi(\theta) = \frac{3m}{4\pi\rho} \int_{R_{\min}}^{R_{\max}} R^3 n(R)dR, \tag{15}$$

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

$$\frac{\Phi(\theta)}{\sin\theta} = \frac{3m}{4\pi\rho} \int_{r_{\min}}^{r_{\max}} r^3 n(r)dr. \tag{16}$$

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 θ 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.

REFERENCES

1. Yu.V. Naĭdich, *Kontaktnye yavleniya v metallicheskikh rasplavakh* (Contact phenomena in molten metals) (Kiev: Naukova Dumka, 1972) (in Russian).
2. A.D. Zimon, *Adgeziya zhidkosti i smachivanie* (Adhesion of liquids and the wetting) (Moscow: Khimiya, 1974) (in Russian).
3. A.W. Adamson, *Physical Chemistry of Surfaces* (New York: Interscience Publ., 1967).
4. L.M. Shcherbakov, A.R. Novoselov, and V.P. Chestyunin, *Adgeziya rasplavov i paĭka materialov* (Adhesion of melts and soldering of materials) (Kiev: Naukova Dumka, 1978) Iss. 3:13 (in Russian).
5. L.S. Palatnik, N.T. Gladkikh, M.N. Naboka, and N.K. Mishneva, *Zavod. Lab.* *39*:1098 (1973) (in Russian).
6. N.T. Gladkikh, V.I. Larin, and O.V. Usatenko, *Fiz. i Khim. Obrab. Mater.* No. 2:96 (1979) (in Russian).
7. A.I. Ankilov and A.I. Borodulin, *Kolloid. Zhurn.* 40:195 (1978) (in Russian).
8. R. Heidenreich, *Fundamentals of Transmission Electron Microscopy* (New York, 1964).