Modelless X-Ray Scattering Study of a Silica Hydrosol Surface

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Abstract

The structure of the adsorbed layer of alkali ions on the surface of colloidal silica solutions with a particle size of 27 nm has been studied by reflectometry and diffuse scattering of synchrotron radiation with a photon energy of about 71 keV. Electron density profiles in the direction perpendicular to the surface have been reconstructed from experimental data and spectra of the correlation function of heights in the surface plane have been obtained. The revealed deviation of the integral and frequency characteristics of the roughness spectra of the silica sol surface from predictions of the capillary-wave theory is of a fundamental character. This deviation is due to the contribution from roughnesses with low spatial frequencies $\nu < 10^{-4}$ nm$^{-1}$ and to the interference of diffuse scattering from different layer interfaces of the surface structure.

The surface of a colloidal solution of SiO$_2$ nanoparticles stabilized by alkali metal hydroxide is strongly polarized because of the difference between the potentials of electric image forces for univalent metal cations and particles with a large negative charge (macroions) \cite{1}. It was reported in \cite{2} that heavy Cs$^+$ ions are selectively collected at the hydrosol-air interface, removing light Na$^+$ ions. The dependence of the electrostatic free energy of a charged sphere at the water-air interface between two dielectric media on its radius $r$ obtained in \cite{3,4} makes it possible to explain the substitution of Cs$^+$ cations with a larger radius $r \approx 1.8$ Å for Na$^+$ ions with a smaller radius $r \approx 1.2$ Å \cite{5}.

In this work, we report new experimental data on diffuse scattering under the conditions of total external reflection and synchrotron radiation reflectometry with a photon energy of about 71 keV for the surfaces of both NaOH-stabilized and CsOH-enriched silica sols. In contrast to the previous studies, the data are analyzed within a self-consistent approach that makes it possible to reconstruct both the electron density profiles perpendicular to the hydrosol surface and spectra of the height-height correlation function in the surface plane without any prior information on the surface structure \cite{6,7}.

Figure 1 shows a qualitative four-layer model of the structure of the hydrosol-air interface proposed in \cite{2,8}. This model is based on the structural parameters extracted from synchrotron radiation X-ray reflectometry data with a photon energy of about 15 keV. This model involves a standard model approach (see, e.g., \cite{9-11}) with plotting electron density profiles based on the error function used in the capillary-wave theory developed by Buff, Lovett, and Stillinger \cite{12}. The total width of the surface transition layer is about the Debye screening length in the solution (> 200 Å at pH $\approx$ 10). The first layer (∼8 Å thick) is a layer of suspended metal ions with an estimated surface density of ∼4 · 10$^{18}$ m$^{-2}$. The second layer (∼13 Å thick) is a layer of the spatial charge of hydrated Na$^+$ ions with the estimated surface density of sodium ions of ∼8 · 10$^{18}$ m$^{-2}$, which is independent of the presence of heavy ions in the bulk of hydrosol.

The silica sol samples were prepared and studied in an airtight cell with X-ray-transparent windows according to the method described in \cite{8}. The initial concentrated monodisperse Ludox TM-50 sol stabilized by sodium hydroxide was purchased from...
the Grace Davison Co. (pH = 9, 50 wt % SiO₂ and 0.2 wt % Na). Further, the sol was either diluted by deionized water (ELGA, PURELAB Option-Q) or enriched by mixing in a vessel (shaken and then placed in a Bandelin ultrasonic bath) with a solution of cesium hydroxide in deionized water to a solution (shaken and then placed in a Bandelin ultrasonic bath) with a concentration of Na⁺ ions in the solutions was ~ 0.06 mol/L (pH = 9) and the concentration of Cs⁺ ions in the enriched solution was ~ 0.6 mol/L (pH = 12). Solid hydrate CsOH · x(H₂O) (99.9 wt % metal and 1520 wt % H₂O) was purchased from the Alfa Aesar Co.

According to the small-angle scattering data, the initial Ludox TM-50 suspension contains homogeneous amorphous silica particles with a characteristic diameter of ~ 27 nm [14]. Adding CsOH to the initial hydrosol stabilized by NaOH (pH ~ 9), one can obtain a solution with a high volume concentration of Cs⁺ (pH ≈ 12), which remains liquid in the airtight cell at room temperature at least for a month [15, 16]. At a very high concentration of cesium hydroxide (pH ~ 12.5), Ludox sols usually become opaque and are solidified into a gel in about a week. In this process, the size distribution of SiO₂ particles hardly changes [17].

The reflectivity R and intensity of surface diffuse X-ray scattering I₅₄ at the hydrosol-air interface were measured under normal conditions on the ID31 beamline of the ESRF synchrotron [18]. In the experiments, the intensity of the focused monochromatic photon beam with a wavelength of λ = 0.1747±0.0003 Å (photon energy of ≈ 71 keV) was ~ 10⁻¹⁰ photons/s at transverse dimensions of ~ 10 μm in height and ~ 250 μm in the horizontal plane. We already used reflectometry and diffuse scattering data jointly to determine the structures of the liquidair and liquidliquid interfaces but within the model approach [19-21].

It is convenient to describe the kinematics of grazing scattering at the macroscopically flat interface oriented by the gravitational force in the coordinate system with the origin O at the center of the illuminated region. The xy plane coincides with the interface between the monolayer and water, the axis Oz is perpendicular to the beam direction, and the axis Oy is perpendicular to the surface and is opposite to the gravitational force (see the inset of Fig. 2). Let kᵢ₅ and kₛₑₑ be the wave vectors with the amplitude kₒ = 2π/λ of the incident and scattered beams in the direction to

the observation point, respectively; α be the glancing angle in the yz plane; β be the scattering angle such that α, β << 1; and φ be the angle between the incident beam and scattering direction in the xy plane. Thus, the components of the scattering vector q = kᵢ₅ − kₛₑₑ in the interface plane are qₓ = kₒ cos β sin φ and qₜ = kₒ (cos β cos φ − cos α) and the projection on the axis Oz is qₜ = kₒ (sin α + sin β).

The surface samples were prepared and studied at T = 298 K in a Teflon dish with a diameter of 100 mm placed in an airtight single-stage thermostat. The total external reflection angle αₑ ≈ 2λ√(e₀ ρ₀/π) ≈ 3 × 10⁻⁴ rad (where rₑ = 2.814 · 10⁻⁸ Å is the classical radius of the electron) for the solarair interfaces is determined by the bulk electron density ρₑ ≈ 1.2 ρₐ in solutions, where ρₐ = 0.333 e⁻/Å³ is the electron density in water under normal conditions.

At specular reflection (α = β, φ = 0), the scattering vector q is directed along the Oy axis, i.e., q = q₀ ≈ 2kₒα. Figure 2 shows curves R(qₑ) for the surface of (1) NaOH-stabilized and (2) CsOH-enriched sols. At qₑ < q₀ = (4π/λ)αₑ ≈ 0.025 Å⁻¹, the incident beam undergoes total external reflection; i.e., R ≈ 1.

Figure 3 shows the two-dimensional map of the surface scattering intensity for hydrosol stabilized by NaOH as a function of the angles β and φ at the glancing angle α ≈ 2.1 × 10⁻⁴ rad (≈ 0.012°). Figure 4 shows the data for the surface diffuse (non-specular) scattering intensity Iₑ(β) for the surface of (1) NaOH-stabilized and (2) CsOH-enriched sols at the same α value and φ = 0 (see the inset of Fig. 4). The most intense peak on these curves corresponds to the specular reflection at β ≈ 0.7αₑ.

In this work, scattering and reflectometry data were jointly analyzed within an iterative approach described in detail in [7]. Specular reflectivity curves were analyzed within a model-independent method based on the extrapolation of the asymptotic angular dependence of the specular reflectivity R(qₑ) to the region of large qₑ values without any prior assumptions on the structure of the sample surface. The polarizability profile δ(z) thus obtained unambiguously specifies the electron density distribution along the Oz axis ρ(z) ≈ 2πδ(z)/(rₒ λ²) [22]. Using this approach, we previously studied the structure and formation kinetics of macroscopically flat lipid membranes on the hydrosol surface [23-25].

Diffuse scattering was analyzed within perturbation theory in the function ζ(x, y) describing the surface relief (roughness) at the mediumair interface. For conformal roughnesses (the function ζ(x, y) is independent of the distribution of polarizability over the Oz axis and ζ(x, y) = 0), the two-dimensional distribution of the scattering intensity from the surface (scattering
Formal roughnesses, this contribution is given by the Nevot-Croce expression:

\[ I_d(k_{\text{in}}, k_{\text{sc}}) = \frac{k_0^4}{(4\pi)^2 \sin \alpha} \times \left| \int \psi(z, k_{\text{in}}) \psi(z, k_{\text{sc}}) \frac{d\epsilon}{dz} \right|^2 \bar{C}(\nu). \]  

(1)

Here, \( \bar{C}(\nu) \) is the power spectral density function, which is the Fourier transform of the relief autocorrelation function (height-height correlation function) and depends on the length of the spatial frequency vector \( \nu = q_0/(2\pi) \). \( \epsilon(z) \approx 1 - \delta(z) \) is the distribution of the relative permittivity near the surface, and \( \psi(z, k) \) is the distribution of the complex amplitude of the wave in the sample, which is numerically found as the solution of the one-dimensional wave equation with the profile \( \epsilon(z) \).

On one hand, since the liquid surface is isotropic, the calculation of the function \( \bar{C}(\nu) \) requires only the indicatrix in the plane of reflection \( \phi = 0 \). Any prior assumptions on the statistics of its height distribution are not necessary for this calculation. The required information on the distribution \( \delta(z) \) can be obtained from the analysis of the angular dependence of the reflectivity curve \( R(q_s) \).

On the other hand, the experimental reflectivity also includes the contribution from diffuse scattering on roughnesses; for conformal roughnesses, this contribution is given by the Nevot-Croce formula [28]

\[ R(q_s) = R_0(q_s) \cdot \exp \left( -\alpha^2 q^2 \sqrt{q^2 - k_0^2 \delta} \right) \]  

(2)

Here, \( \delta \approx 1.1 \cdot 10^{-7} \) for \( \lambda = 0.1747 \) Å, \( R_0(q_s) \) is the reflectivity from the surface with the profile \( \rho(z) \) in the absence of roughness (i.e., \( \zeta(x, y) \equiv 0 \) at any points \( (x, y) \)), and

\[ \sigma^2 = \int_0^\infty \bar{C}(\nu) d\nu \]  

(3)

is the rms height of roughnesses. Thus, within the used approach, in each iteration step, the surface polarizability profile \( \delta(z) \) was first reconstructed with the roughness parameters found at the preceding step and the roughness spectrum \( \bar{C}(\nu) \) was then calculated with this found profile.

Figures 5 and 6 show the reconstructed electron density profiles \( \rho(z) \) normalized to the electron density in water \( \rho_w = 0.333 e^-/\text{Å}^3 \) and roughness spectra \( \bar{C}(\nu) \) for the surfaces of (1) NaOH-stabilized and (2) CsOH-enriched sols of 27-nm particles. It is noteworthy that three iterations appear to be enough to reach a stable solution in which the next iterations for the polarizability profile and roughness spectrum coincide with the preceding iterations for the respective quantities.

Both electron density profiles (see Fig. 5) include a peak with the thickness \( d = 15 - 20 \) Å near the surface; this peak corresponds to the layer of adsorbed ions. The surface density of Na\(^+\) ions \( \Theta = \int_0^L \rho(z) dz/n_e (n_e = 10 \) is the number of electrons in the Na\(^+\) ion) is estimated as \( \Theta = (7 \pm 1) \cdot 10^{18} \text{m}^{-2} \). The electron density in the surface layer of the sol enriched with cesium hydroxide is increased to a value corresponding to the surface density of Cs\(^+\) ions \( n_e = 54 \) \( \delta \Theta = (5 \pm 1) \cdot 10^{18} \text{m}^{-2} \). These values are in agreement with the values previously obtained within capillary wave models [2,8,13].

In turn, the effective roughness \( \sigma \) calculated from the functions \( \bar{C}(\nu) \) in the experimentally available range of spatial frequencies \( \nu = 10^{-5} - 10^{-2} \text{nm}^{-1} \) (Fig. 6) was \( \sigma = (5.7 \pm 0.3) \) Å and \( \sigma = (2.8 \pm 0.3) \) Å for the surfaces of the NaOH-stabilized and Cs-enriched sols, respectively. It is noteworthy that the calculated roughness caused by capillary waves on the silica sol surface is \( (2.8 \pm 0.2) \) Å and hardly depends on the ionic composition of the solution [8]. The experimentally available \( \nu \) range is limited by the width of the direct beam and maximum \( \beta \) value that allows separating surface scattering from scattering in the bulk.

The integral characteristic \( \sigma \) of the roughness spectrum of the Cs-enriched sol is in good agreement with the theoretical prediction, whereas this characteristic for the NaOH-stabilized solution is significantly larger than the theoretical prediction. The comparison of the experimental spectrum (dashed line in Fig. 6) with the calculation within the capillary-wave theory [29] (dash-dotted straight line in Fig. 6) shows that the function \( \bar{C}(\nu) \) for the NaOH-stabilized solution at low spatial frequencies...
served translational correlation length between Na
ability of appearance of a longrange order on the free surface of the
than the density of alkali ions on the silica sol surface. The possi-
classical electrons suspended over the surface of some cryogenic
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\( \approx 5 - 6 \, \text{Å} \), which is smaller than the Bjerrum length for univalent
ions in the aqueous medium \( \approx 7 \, \text{Å} \). Many authors believe that
ions adsorbed with such a high density, e.g., on the surface of
charged particles (macroions) in a colloidal solution, constitute a
strongly correlated two-dimensional liquid, where the short-range
order is close to a Wigner crystal [32-38].

Alkali metal ions on the silica sol surface can be considered
as a heavy, very dense analog of the twodimensional system of
classical electrons suspended over the surface of some cryogenic
insulators (liquid \(^{3}\text{He}, \, ^{4}\text{He}, \) and liquid and solid hydrogen) by
electric image forces and external electric field [39]. A solid phase of
two-dimensional electrons (Wigner crystal) was previously ob-
served on the surface of liquid helium [40,41]. The temperature
in those experiments was much lower than room temperature
\( \approx 0.5 \, \text{K} \), but the experimentally achievable density of the elec-
tron gas on the liquid helium surface is a factor of \( \approx 10^4 \) lower
than the density of alkali ions on the silica sol surface. The possi-
bility of appearance of a longrange order on the free surface of the
colloidal solution is still incompletely clear because, e.g., the ob-
served translational correlation length between Na\(^+\) ions on the

\[ 10^{-4} \, \text{nm}^{-1} \] is much larger than capillary wave values. This
is possible if the sol surface has two-dimensional spatial inho-
genities with correlation lengths of 10 – 100 \( \mu \text{m} \), which are not
described within the capillary wave formalism, and their distribu-
tion deviates from a normal law.

In addition, both dependences \( \bar{C}(\nu) \) exhibit oscillations indic-
ating the interference of diffuse scattering from different layer
interfaces of the surface structure [30]. Since the layer of ad-
sorbed ions on the surface has a thickness of \( \approx 20 \, \text{Å} \) smaller than
the characteristic radiation penetration depth in the region of
total external reflection \( \approx \lambda/2\pi\alpha_c \approx 80 \, \text{Å} \) (e.g., see [31]), the
observed oscillations in roughness spectra are assuming due to
diffuse scattering at the inner interface between layer 2 and de-
plicated layer 3. To obtain information on the roughness of these
hidden interfaces, an additional analysis using an extended pro-
cedure described in [7] is necessary, which is beyond the scope of
this work.

The mean distance between Na\(^+\) cations in layers 1 and 2 is
\( \approx 5 - 6 \, \text{Å} \), which is smaller than the Bjerrum length for univalent
ions in the aqueous medium \( \approx 7 \, \text{Å} \). Many authors believe that
ions adsorbed with such a high density, e.g., on the surface of
charged particles (macroions) in a colloidal solution, constitute a
strongly correlated two-dimensional liquid, where the short-range
order is close to a Wigner crystal [32-38].

\begin{align*}
\text{Figure 6. } & \text{Roughness spectra } \bar{C}(\nu) \text{ according to diffuse scattering data for the surfaces of the (solid line 1) NaOH-stabilized and (dashed line 2) CsOH-enriched sols of 27-nm particles. The dash-
dotted line is the theoretical spectrum of the correlation function of capillary wave heights [29].}
\end{align*}

surface of the NaOH-stabilized sol is smaller than \( \approx 30 \, \text{Å} [13] \).

To summarize, we have demonstrated the possibility of us-
ing diffuse scattering data measured under the conditions of to-
tal external reflection to obtain information on the statistical
properties of the surface of liquid without any prior information
on its structure. Electron density profiles and spectra of the
height-height correlation function have been reconstructed from
experimental data. According to this analysis, the density of
suspended Cs\(^+\) cations on the surface of the CsOH-enriched sol is
\( (5 \pm 1) \cdot 10^{18} \, \text{m}^{-2} \), which is in good agreement with the data
reported in [8]. The revealed deviation from the integral and fre-
quency characteristics of the roughness spectrum of the hydrosol
surface from predictions of the capillary-wave theory is of a fun-
damental character. This deviation is due to the contribution
from roughnesses with low spatial frequencies \( \nu < 10^{-4} \, \text{nm}^{-1} \)
and to the interference of diffuse scattering from different layer
interfaces of the surface structure. The deviation of the integral
characteristic \( \sigma \) of the spectrum \( \bar{C}(\nu) \) from the values calculated
within the capillary-wave theory was previously reported, e.g.,
for oilwater interfaces in [42,43]. Usually, the spectral features of
\( \bar{C}(\nu) \) responsible for this deviation were not indicated in the cited
works, where the interpretation was reduced to the assumption
of the existence of a certain intrinsic structure.

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