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SURFACE MORPHOLOGY OF ARACHIDIC ACID – Cd ARACHIDATE LB-FILMS STUDIED WITH SFM

V. R. NOVAK*, V. V. ZHIZHIMONTOV,
A. V. BELYAYEV and V. A. BYKOV

*State Research Institute of Physical Problems, Zelenograd,
103460 Moscow, Russia*

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Atomic force microscopy was used to study surface morphology and structure of mixed multilayers of cadmium arachidate/arachidic acid obtained at three different pH values (5.3, 5.6 and 5.8). One-dimensional auto-correlation functions and statistical parameters of the studied surfaces were determined from the AFM topography images. There was found a correspondence between optical waveguide loss factor and statistical parameters (rms roughness and correlation length). A streaky structure of the surface of multilayers built up at pH = 5.3 was observed. The streaky domains have an average width of 10–20 nm and different length from less than a hundred nm to several hundred nm.

Keywords: Langmuir-Blodgett films; AFM microscopy; optical properties

1. INTRODUCTION

Langmuir-Blodgett (LB) films of cadmium arachidate/arachidic acid and cadmium stearate/stearic acid are among the most well studied LB systems. They were widely used in different optical, electrical, photo-electrical and other physical experiments [1–7].

Composition of LB films of fatty acids and their salts with two valent metals is determined by the pH value and ionic composition of water subphase [1]. The pH ranges for formation of acid, salt and mixed films are characteristic of each metal ion. In the case of Cd ion

*Corresponding author.

the dependence of composition of fatty acid films on pH value was studied in [1, 8–15].

According to published data for multilayers of cadmium arachidate/arachidic acid the mixed films were deposited at pH between 4.4 and 6.6, acid films at pH below 4.4 and salt films at pH above 6.6. A successful deposition of the Y-type multilayers (with an up and down transfer ratio equal to unity and a high deposition speed) takes place just for the mixed films at pH = 4.8–5.8 and Cd ion concentration of water subphase in the range of 1–0.1 mM [1, 8–10, 16, 17]. The best optical quality is revealed by the multilayers obtained at pH = 5.5–5.7 [1, 4, 17].

During the past few years the scanning (atomic) force microscopy (SFM) has been widely used for LB films analysis [18–20]. Using SFM allows a study of surface topography with nanometer lateral resolution and sub-nanometer normal one without any additional sample pretreatment. In the present work, SFM was used to study surface morphology and structure of the mixed LB films of cadmium arachidate/arachidic acid (CdA-A) obtained at three different pH values and having therefore different salt-acid composition: (1) films with equal amount of salt and acid (pH 5.6); (2) films containing more acid than salt (pH 5.3) and (3) films containing more salt than acid (pH 5.8).

2. EXPERIMENTAL

LB films of CdA-A were prepared using a MDT-LB5 Langmuir trough. Multilayers were deposited onto fused quartz substrates by Langmuir-Blodgett method. The deposition conditions were as those described in [17]. The substrates were pretreated by dimethyldichlorsilane to make their surfaces hydrophobic [8]. The monolayers were spread from a benzene-hexane solution of arachidic acid (concentration 0.5 mg/ml) over the water subphase. The latter contained $4 * 10^{-4}$ M $CdCl_2$. The subphase pH was maintained with acetate buffer. The transfer pressure used was 23 mN/m. The substrate speed was 10 mm/min. The transfer ratio was unity. Figure 1 shows an example of P-A isotherm of CdA-A monolayer on water surface (pH 5.3) and

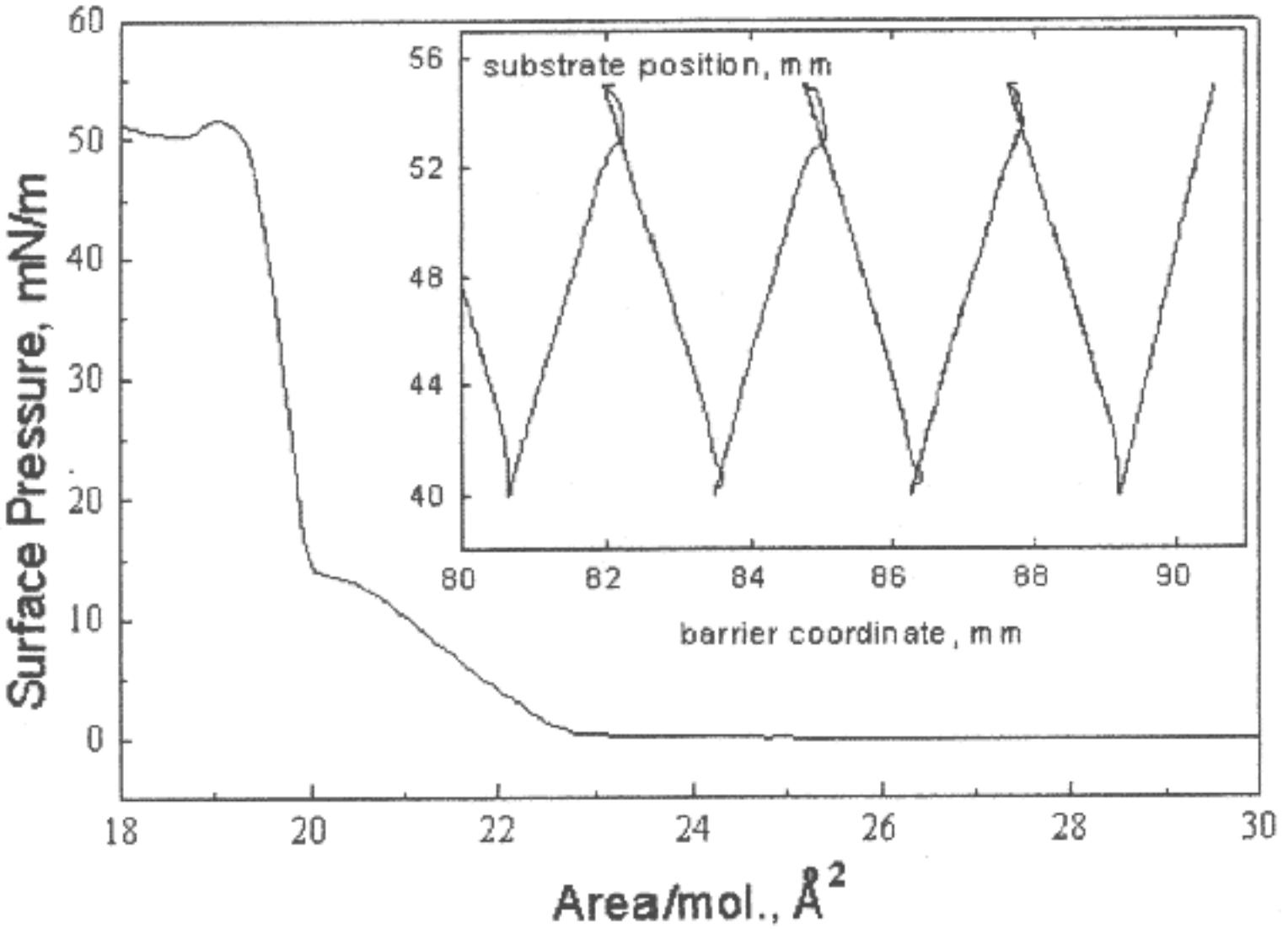

FIGURE 1 Surface pressure–molecular area isotherm of mixed CdA-A monolayer on water surface (pH = 5.3) and dependence of substrate position on barrier coordinate (insert).

dependence of substrate position on the barrier coordinate, that characterizes the deposition process.

SFM investigation was done with a scanning probe microscope Solver P47 [21] and Ultrasharp cantilevers [21] with resonant frequency 550–552 kHz and tip curvature radius less than 10 nm. All the samples were studied in the semicontact mode (tapping) [22] which provided nondestructive scanning of a soft surface.

3. RESULTS AND DISCUSSION

AFM images of three samples of CdA-A films are shown in Figures 2–4. These samples were built up at three different pH values of water subphase and, as a result, had different salt-acid composition. Figures 2–4 correspond to pH = 5.3, 5.6 and 5.8, respectively. All the samples have the same thickness equal to 120 monolayers. AFM images have the same size of about 600×600 nm. Evidently, the sample corresponding to pH = 5.3 reveals a profile with lager features both the in-plane and normal direction.

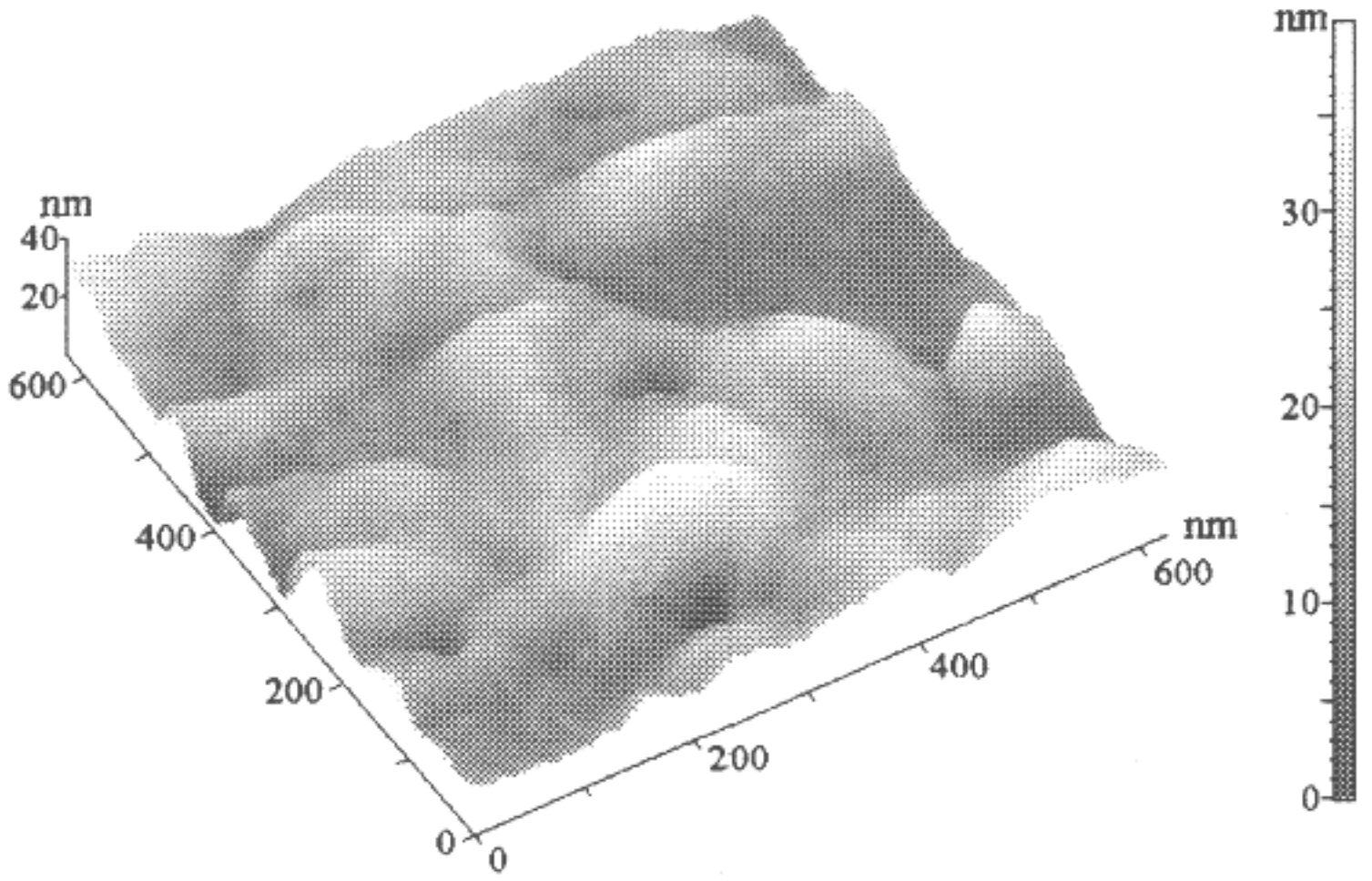

FIGURE 2 AFM image of topography of CdA-A LB-film, built up at pH 5.3. The thickness of the film 120 monolayers.

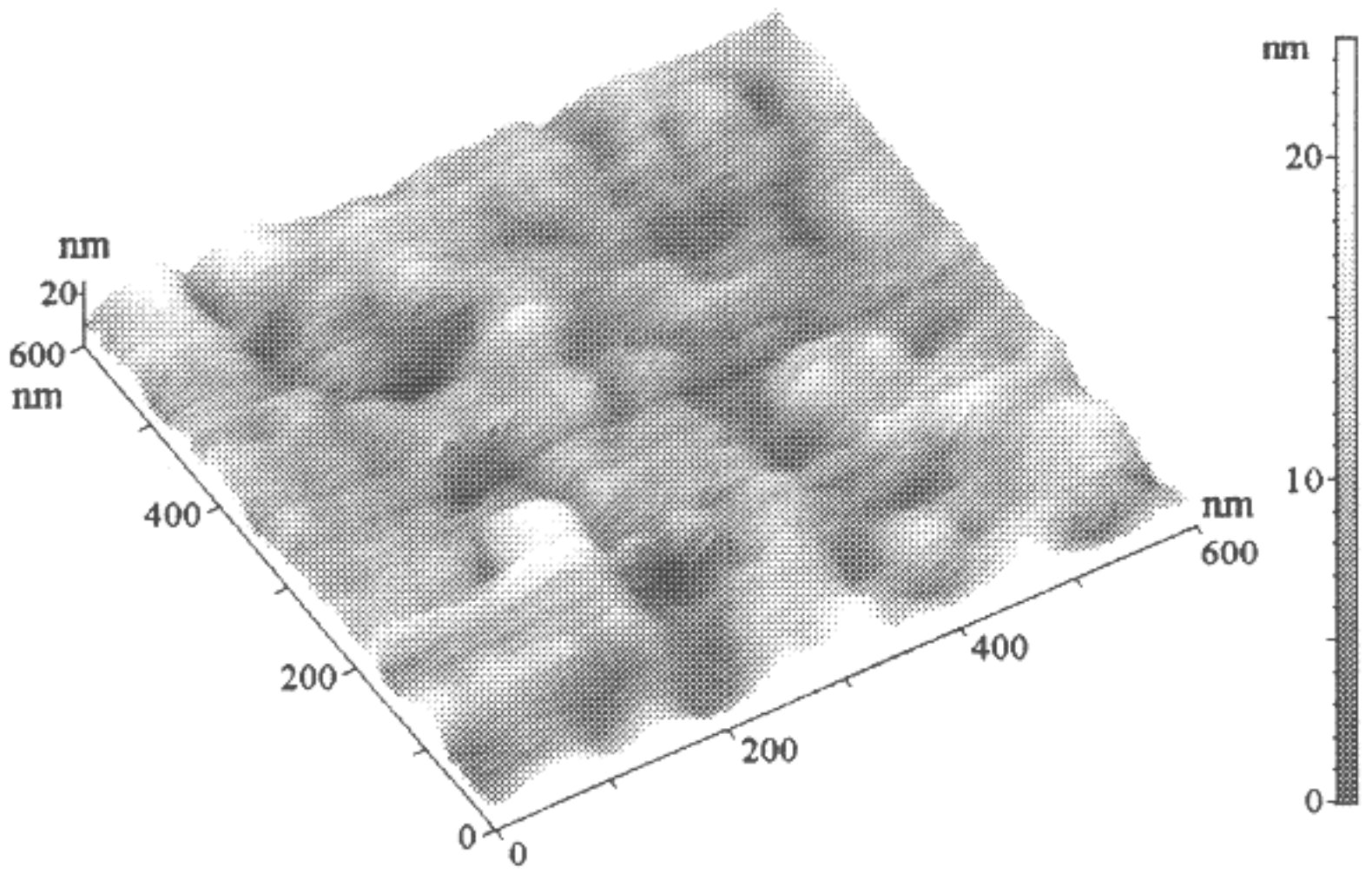

FIGURE 3 AFM image of topography of CdA-A LB-film, built up at pH 5.6. The thickness of the film 120 monolayers.

For mathematical description of a rough surface, the relief height variations *versus* the in-plane coordinates are treated as a random process using the probability theory [23–25]. Let $z_i = h(x_i, y_i) = h(\vec{r}_i)$

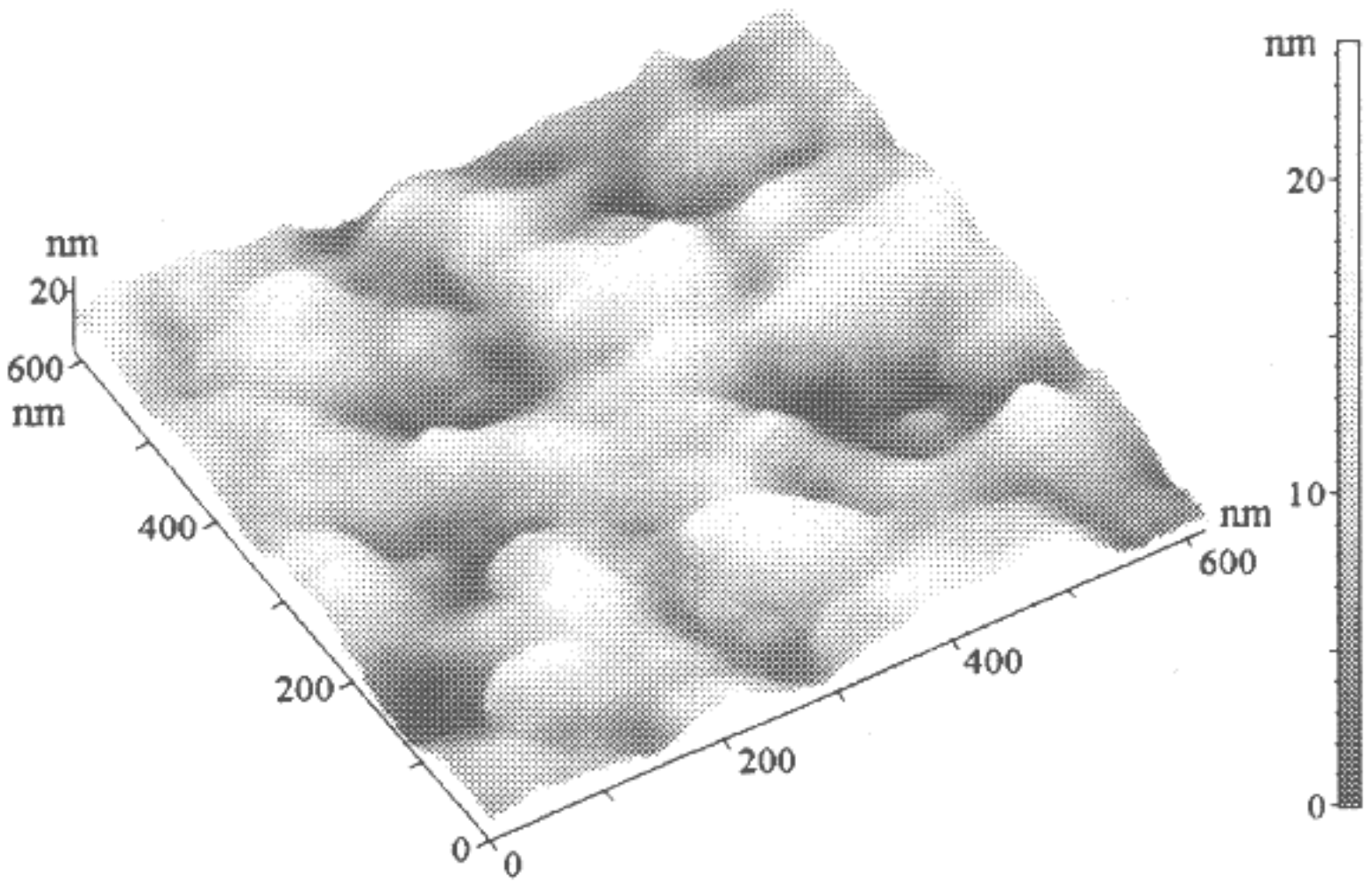

FIGURE 4 AFM image of topography of CdA-A LB-film, built up at pH 5.8. The thickness of the film 120 monolayers.

be a function of a surface profile, where $\vec{r}_i$ is a radius-vector of any of N points within some area of the plane. The value of function z_i is measured along the normal to the average plane, which is defined by the condition:

$$\langle z_i \rangle = \frac{1}{N} \sum_{i=1}^{N} z_i = 0.$$

The arithmetic mean of absolute height deviation (R_a) or the root-mean-square (rms) deviation of height (R_q or σ) are used as parameters for quantitative characterization of a rough surface [23–25]:

$$R_a = \frac{1}{N} \sum_{i=1}^{N} |z_i - \langle z_i \rangle|, \quad R_q \equiv \sigma = \left(\frac{1}{N} \sum_{i=1}^{N} (z_i - \langle z_i \rangle)^2 \right)^{\frac{1}{2}}$$

Autocorrelation function $G(\vec{r})$ is a fundamental physical characteristic of a surface that may be defined as an average of relief height products for all pairs of points separated by a radius vector $\vec{r}$ over a sufficiently large area [23–25]:

$$G(\vec{r}) = \langle h(\vec{r}\,')h(\vec{r}\,' - \vec{r}) \rangle$$

For statistically isotropic surfaces $G(\vec{r})$ depends only on a scalar distance r (parameter of shift). In the case of a simple surface an initial part of $G(r)$ is a descending function of r and is characterized by two main parameters: rms height deviation σ and correlation length (correlation interval) Λ. The correlation length limits a distance of statistical coherence of a process and is defined as a value of argument corresponding to a decrease of $G(r)$ by a factor of 1/e. The $G(r)$ value at $r = 0$ corresponds to the sum of the squares of the rms and the arithmetic deviation of height from the reference level. If the heights are measured from the average level, then $\langle z_i \rangle = 0$ and $G(0) = \sigma^2$.

One-dimensional autocorrelation functions $G(x)$ were calculated for each of three AFM images shown above (see Fig. 5). In $G(x)$ an argument x is a parameter of shift along one axis. Table I represents the values of statistical parameters of the studied surfaces for samples obtained for three pH values of water subphase and which, as a consequence, have different composition.

According to [24], the optical characteristics of a rough surface are functions of its statistical parameters σ and Λ. These parameters define an intensity of reflected and scattered light and its space distribution. The dependence of light wave losses in light-guiding LB films of CdA-A on the composition of films was studied earlier [17]. Those data on the loss factor (α) are presented in Table I. It is of interest to compare the statistical parameters of our surfaces with the loss factor data from [17].

In the case of a flat thin film waveguide both bulk losses due to absorbing and scattering and losses caused by surfaces roughness can give some contribution to the loss factor. According to [26], the contribution to the loss factor connected with the scattering on the roughness of upper surface depends on the statistical parameters of the surface as $\sim(\sigma/\lambda)^2$, and $\sim(\Lambda/\lambda)^2$, where λ is a wavelength of light. As can be seen from Table I, the films built up at pH = 5.3 have the maximum values of σ and Λ (5.3 nm and 67 nm). They also have the maximum loss factor ($\alpha = 7\,\mathrm{cm}^{-1}$). The films built up at pH = 5.6 have the minimum values of σ and Λ (2.9 nm and 26 nm) and the minimum loss factor ($\alpha = 2.5\,\mathrm{cm}^{-1}$). So there is a general correlation between the roughness parameters and corresponding loss factors. The lack of direct proportionality of the loss factor to $(\sigma * \Lambda)^2$

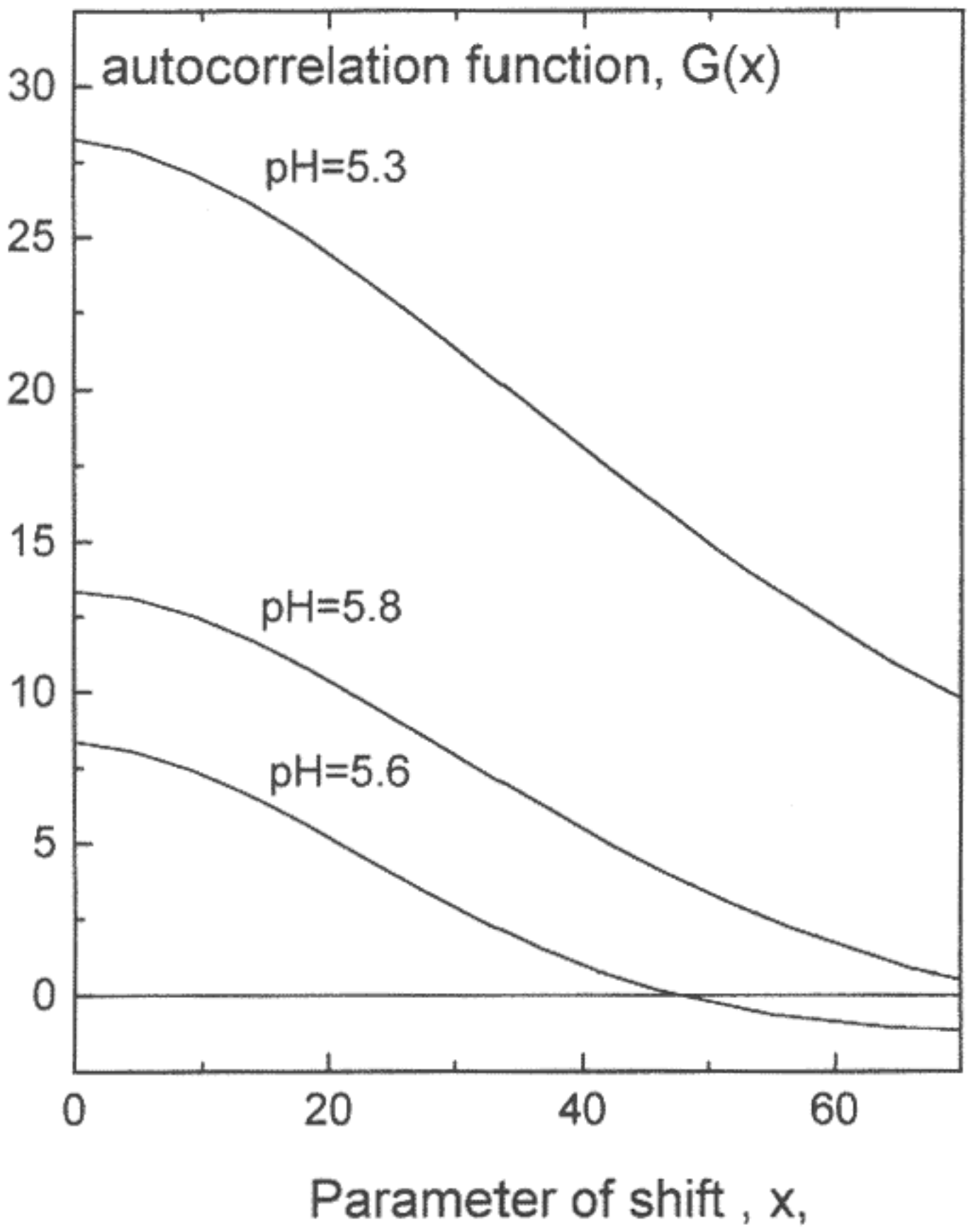

FIGURE 5 One-dimensional autocorrelation functions $G(x)$ calculated for AFM relief images of LB-films built up at three different pH values of water subphase. Statistical parameters of the surface (rms roughness σ and correlation length Λ) have the following values: $\sigma = 2.9\,\text{nm}$, $\Lambda = 26\,\text{nm}$ for pH 5.6; $\sigma = 3.7\,\text{nm}$, $\Lambda = 42\,\text{nm}$ for pH 5.8 and $\sigma = 5.3\,\text{nm}$, $\Lambda = 67\,\text{nm}$ for pH 5.3.

TABLE I Dependence of statistical parameters of the studied surfaces (rms deviation of height from the average level σ and correlation length Λ) on the composition of LB films

pH	σ, *nm*	Λ, *nm*	α, cm^{-1} [17]
5.3	5.3	67	7
5.6	2.9	26	2.5
5.8	3.7	42	3.2

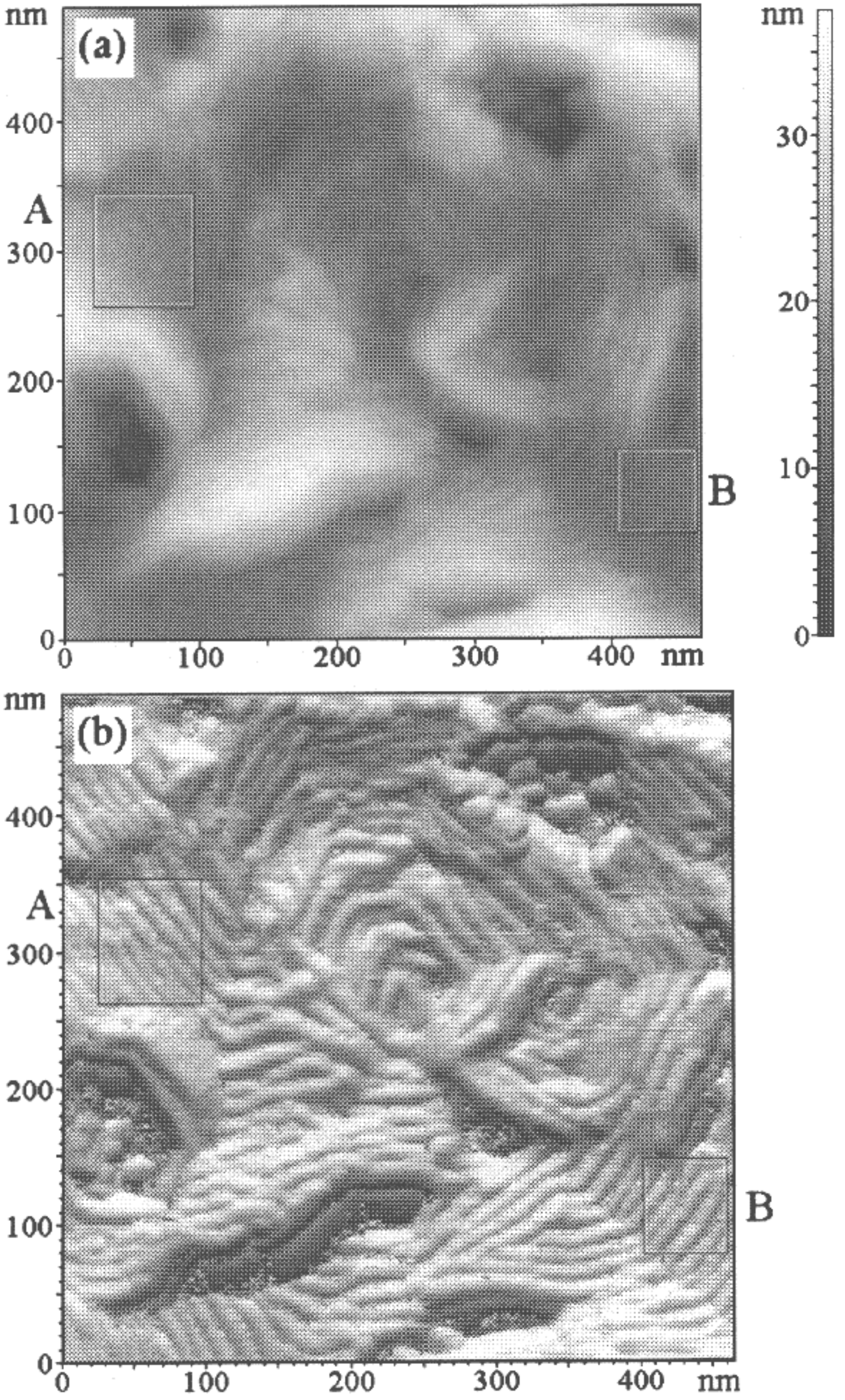

FIGURE 6 (a) AFM image of topography of CdA-A LB-film, built up at pH = 5.3. The thickness of the film 120 monolayers. (b) the same AFM image contrasted by simulated illumination with an oblique light beam.

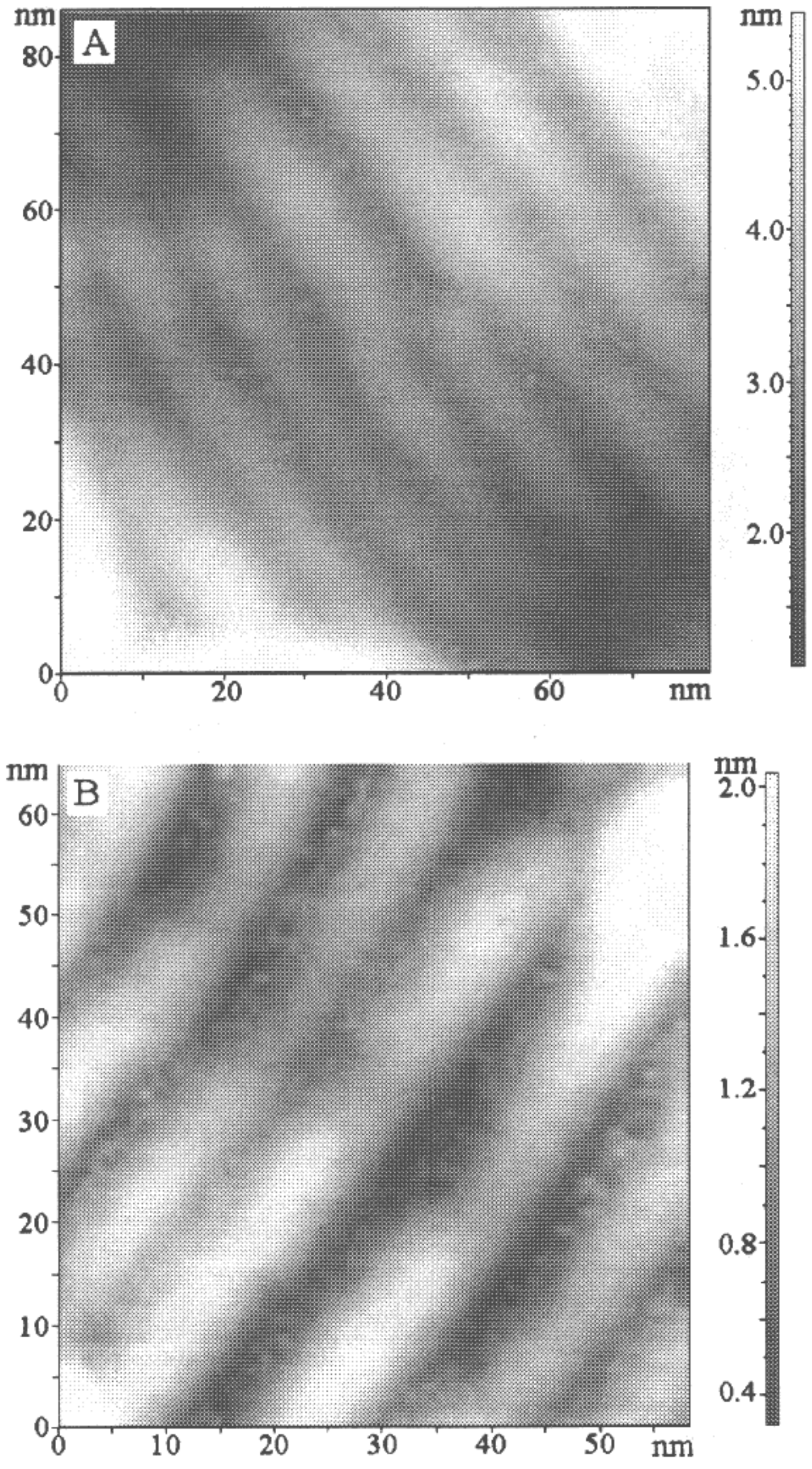

FIGURE 7 The magnified AFM images of two regions marked A and B in Figure 6.

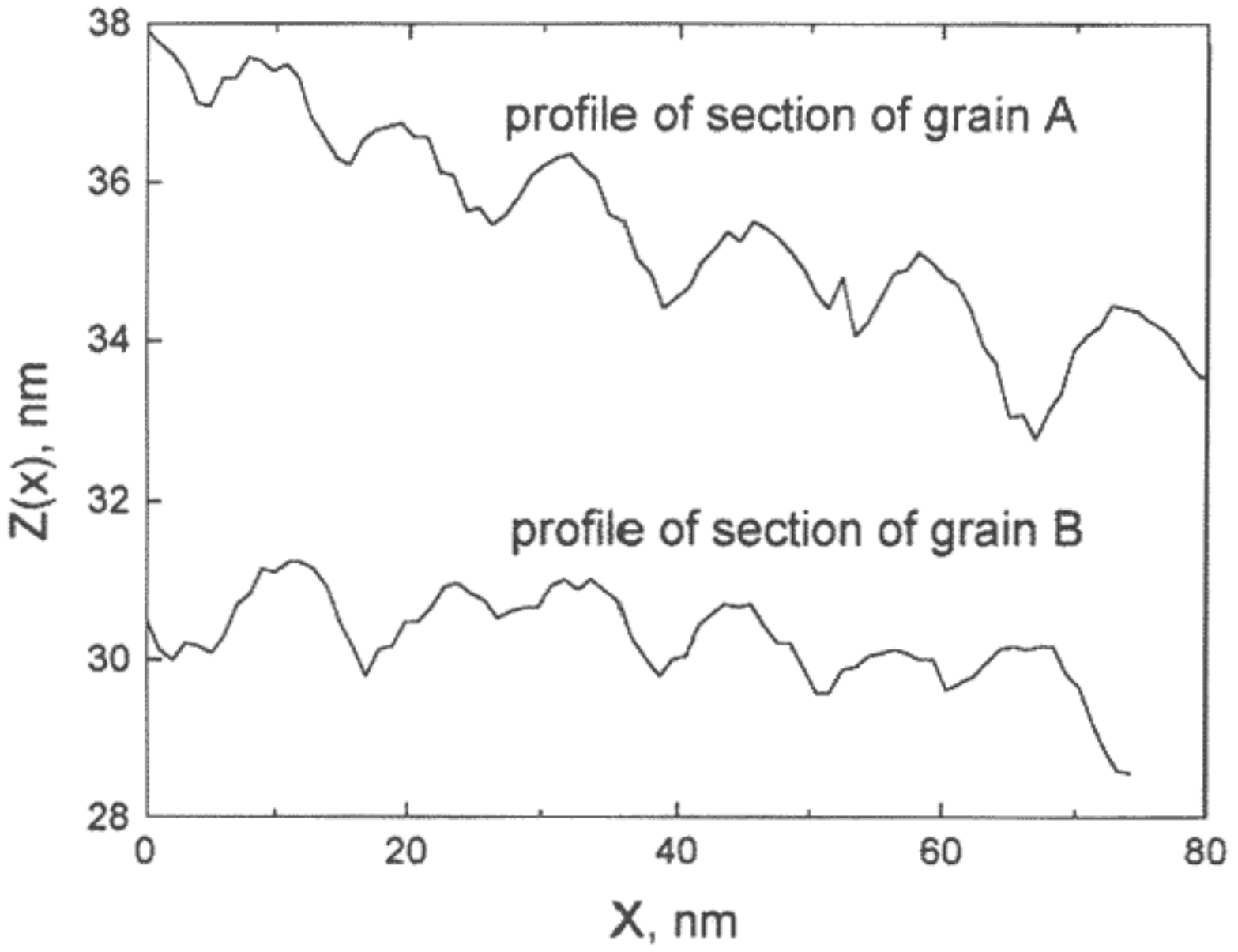

FIGURE 8 Cross-section profile in direction perpendicular to streaky domains of the grains A and B.

the normal [28–30]. In the case of cadmium arachidate multilayers (salt), the hydrocarbon chains are packed in the orthorhombic unit cell and oriented perpendicular to the substrate surface [31, 32]. In the case of the mixed multilayers of cadmium arachidate/arachidic acid (pH = 5.5), the slope of the aliphatic tails is about 15 degrees [33]. Thus, it may be suggested that molecular crystallites, consisting of the molecules with the tilted orientation have a shape of streaky domains. At the same time the molecules in the adjacent domains have different orientation in the plane of film and, therefore, there are disclinations at their boundaries. As another possible explanation, it can be assumed that multilayers (at pH 5.3) are heterophase and the streaky structure forms by alternating crystallites of acid and salt. The molecules in the acid and salt crystallites have different tilt and therefore the thickness of acid and salt crystallites is different.

For complete understanding of the nature of the observed streaky structure in multilayers of cadmium arachidate/arachidic acid, additional structural studies of such films by IR, X-ray and electron diffraction methods are necessary.

4. CONCLUSIONS

The topography and surface structure of mixed LB films of cadmium arachidate/arachidic acid (built up at pH = 5.3, 5.6 and 5.8) were studied by methods of scanning atomic-force microscopy. On the base of the obtained AFM images the autocorrelation functions were calculated and the statistical parameters of the studied surfaces (rms deviation of height from the average level and correlation length) were determined. There was found a correspondence of the statistical parameters of the surfaces with the data on the losses of light wave in light-guiding LB films from work [17]. It was observed a streaky structure of the surface of multilayers of cadmium arachdate/arachidic acid built up at pH = 5.3, similar to that earlier observed [27] on platinum/carbon replicas of multilayers of cadmium arachidate.

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