Structural reorganization in collapsed Langmuir monolayers
Структурная реорганизация ленгмюровских монослоев в области коллапса

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Методом рентгеновской дифракции в геометрии скользящего падения исследованы монослои арахиновой кислоты на поверхности раствора нитрата церия. Обнаружено, что при поджатии в области коллапса монослой неожиданно сохраняет трансляционный порядок, формируя при этом гофрированную структуру. Предложен новый подход к численному моделированию двумерных дифракционных картин от монослоев с нарушенным ориентационным порядком. С использованием этого подхода описан механизм формирования необычных дифракционных карт, полученных от гофрированных монослоев в ходе синхротронных экспериментов.

Arachidic acid monolayers formed on an aqueous solution of cerium nitrate have been studied by grazing incidence X-ray diffraction. Despite compression beyond the collapse point, the monolayer unexpectedly retains its translational order and develops corrugation. This paper presents a method for simulating the two-dimensional diffraction patterns characteristic of monolayers with perturbed orientational order. The unusual diffraction data obtained from corrugated monolayers during synchrotron experiments are described using this approach.

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Introduction

Modern surface sensitive X-ray techniques have been recognized to offer the immense opportunities for investigations of structural reorganization in 2D nanosystems at liquid interfaces. Deeper understanding of molecular mechanisms governing these complicated processes has significant implications both for life sciences and for nanotechnologies (ranging from industrial applications to biomedicine). Nowadays, X-ray reflectometry, grazing incidence diffraction, grazing incidence small-angle scattering, the X-ray waves standing method, etc. are extensively used for characterization of organic and bioorganic monolayers formed on liquid subphase. But the intricacy of structural processes in such exceptionally challenging objects as molecular layers on liquid surface requires the development of new adequate approaches to analysis and interpretation of experimental data.

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Grazing incidence diffraction (GID) [1, 2] is one of the most informative methods for structural studies of organic monolayers. In this work we present the new theoretical formalism for quantitative analysis of experimental 2D diffraction maps from molecular monolayers with perturbed orientational order. The possibilities of the developed approach were demonstrated by interpretation of the GID data obtained for collapsed fatty acid monolayer formed on the water subphase in the presence of Ce(III) ions [3]. Cerium induced effects on the structural reorganization in collapsed phases have been elucidated. Unexpected trends in collapse behavior of fatty acid monolayer are discussed.

Results: experimental data and numeric simulations

The arachidic acid monolayers formed on a solution of cerium nitrate salt $Ce(NO_3)_3$ were studied. The monolayer has been compressed beyond the collapse point at surface pressure $\pi = 52$ mN/m, after which the compression was stopped. The GID measurements were carried out at the «Langmuir» station of the Kurchatov synchrotron radiation source. The photon energy of the incident beam was 13 keV. The GID measurements were performed at $\theta = 0.8\theta_c$ (θ_c is the critical angle of total external reflection for water) at a temperature of $T = 21°$C. The experimental results are given in Fig. 1(a).

The unusual features of the 2D diffraction maps were observed, in particular the rounding of the Bragg rods, which lie precisely on the circle in reciprocal space. This is unexpected for a two-dimensional polycrystalline structure. In a two-dimensional monolayer, the diffraction map typically exhibits a triplet of vertical Bragg rods: (02), (11) and $(1\overline{1})$ (rectangular centered cell assumed). This features of diffraction maps are clearly seen in Fig. 1(a). The rounding of the Bragg rods was observed to lie exactly on a circle in reciprocal space with a center at the horizon $Q_z = 0\,\text{Å}^{-1}$. This suggests the presence of an specific type of structural ordering in such monolayers.

To describe the obtained 2D maps, a theoretical diffraction model for distorted Langmuir monolayers was proposed. A stationary wave equation was used to describe the scattering processes. In the case of a plane continuous medium the solution $E_{i,f}(\boldsymbol{r}) = \left[R_{i,f}(z)e^{ik_z z} + T_{i,f}(z)e^{-ik_z z}\right] e^{-i\boldsymbol{k}_\parallel \cdot \boldsymbol{r}}$ describes the electric field of the incident and scattered waves in the scalar approximation, where the indices i and f denote the incident and scattered waves, respectively; amplitudes $R_{i,f}(z)$ and $T_{i,f}(z)$ are reflection and transmission coefficients. The solution was derived from the Helmholtz equation [4]. However, this was not enough to describe the scattering pattern, since the approximation of plane continuous medium does not describe the lateral structure of the monolayer.

The Distorted wave Born approximation (DWBA) uses the solution $E_{i,f}(\boldsymbol{r})$ for a planar structure, and the monolayer itself is perceived as a disturbance V_δ. As a disturbance V_δ we consider the addition $V_\delta(\boldsymbol{r})$ to the potential $V(z)$,

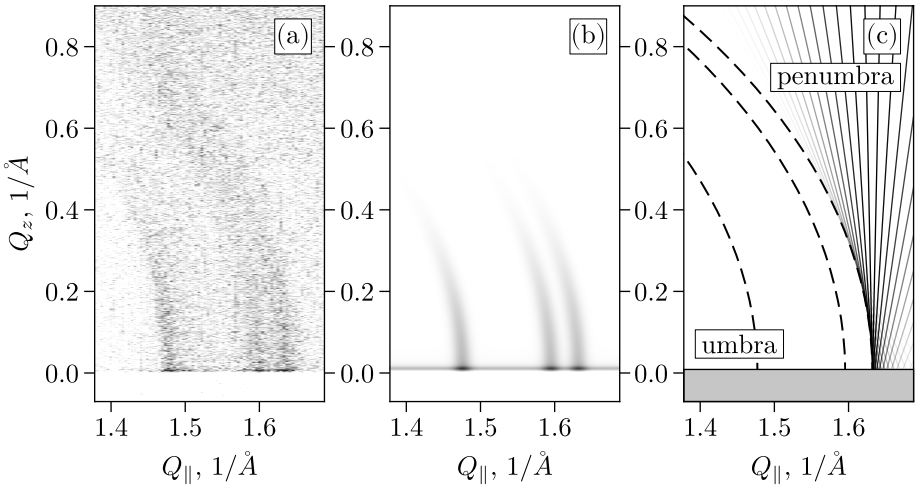

Fig. 1. (a) The diffraction map obtained from arachidic acid monolayer formed on cerium nitrate solution. In this context, $Q_\parallel$ and Q_z represent the horizontal and vertical components of the scattering vector, respectively. (b) Corresponding numerical simulation of diffraction map. (c) A simulated schematic diffraction map, that demonstrate the mechanism of the formation of Bragg rods roundings. The picture consists of "umbra" and "penumbra", which are separated by rounded diffraction rods.

so that the resulting potential $V(\boldsymbol{r}) = V_\delta(\boldsymbol{r}) + V(z)$. The reciprocity principle is used to calculate the scattering amplitude f [5]:

$$f \propto \int_{\mathbb{R}^3} E_f V_\delta E_i \, d^3r. \tag{1}$$

The diffraction intensity distribution is calculated by means of the well-known formula for the differential scattering cross section $d\sigma/d\Omega \propto ff^*$. The diffraction pattern from a 2D cristallite consists of rods in reciprocal space. These rods are perpendicular to the plane of the structure, which are observed as 2D diffraction pattern on the detector. Substitutions yield an expression for the differential scattering cross section, which consists of sixteen terms (scattering channels). In calculations, fifteen terms, containing the amplitudes $R_{i,f}$ from the solution $E_{i,f}(\boldsymbol{r})$, are frequently neglected. This results in the expression taking a simplified form only with coefficient $|T_i T_f|^2$:

$$\frac{d\sigma}{d\Omega} \propto |T_i T_f|^2 \langle \hat{V}_\delta(\boldsymbol{Q}) \hat{V}^*_\delta(\boldsymbol{Q}) \rangle, \tag{2}$$

where T_i and T_f are the transmission coefficients for the incident and scattered waves, respectively. The dynamic scattering effects of an evanescent wave were taken into account through the amplitude coefficients, and the multiplier $|\hat{V}_\delta|^2$ is responsible for diffraction. In this study, we considered the Langmuir monolayer within the two-dimensional polycrystal approximation. Subsequently, this multiplier is the modulus-square of the scattering potential, which can be calculated in accordance with the tenets of the kinematic

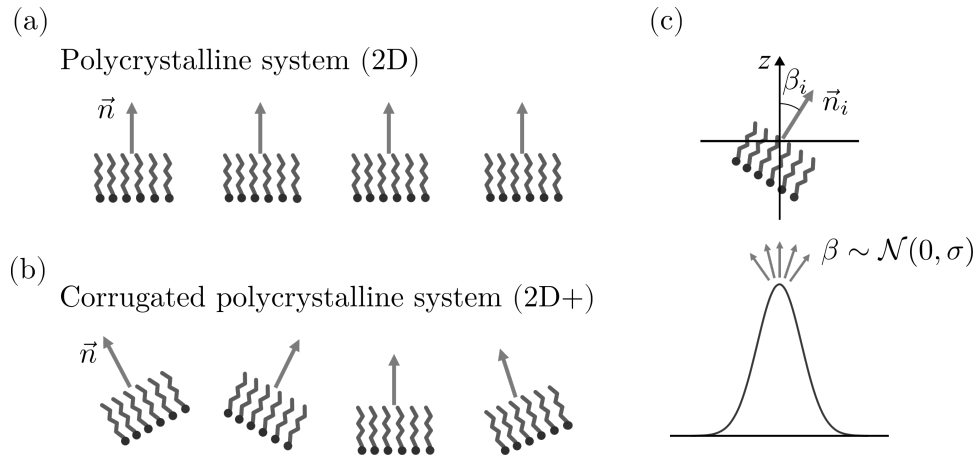

Fig. 2. Schematic representation of a two-dimensional monolayer (a) evolving into a corrugated film with crystallite deviation relative to the horizon (b) distributed as a normal stochastic variable (c).

theory of diffraction:

$$\frac{d\sigma}{d\Omega} \propto |T_i T_f|^2 \langle |S(\boldsymbol{Q})|^2 |F(\boldsymbol{Q})|^2 J(\boldsymbol{Q}) \rangle, \tag{3}$$

where $S(\boldsymbol{Q})$ is a structural factor of the plane ordering and $F(\boldsymbol{Q})$ is a form factor of a molecule. $J(\boldsymbol{Q})$ represents the correlation function that accounts for the angular deviations of the crystallites, while also encompassing the effects of interference from coherently scattering molecules within each ordered crystallite. It is important to note that each ordered crystallite has a finite correlation length, meaning that the summation in $J(\boldsymbol{Q})$ occurs for all molecules within one coherently scattering domain. In such a case, the reduction in peak width can be explained by the increase in the size of coherently scattering domains.

It should be noted that if the system were three-dimensional, classical Debye-Scherrer rings would be observed. However, the observed sections of the rings are incomplete, indicating that the system is not of the three dimensional nature, but represent some type of distorted 2D lattice. A natural explanation is that the pieces of the plane lattice (2D crystallites) are inclined in the direction of the monolayer normal. This leads to a tilt of the crystallites relative to the horizon, as illustrated in Fig. 2(a, b). Furthermore, we assumed that the tilt of the plane crystallites follows a normal distribution [Fig. 2(c)]. In such a way, the tilt of the crystallites was incorporated into the model through the application of the probability density function of the normal distribution, resulting in the formation of rounded rods through numerical integration. Using the aforementioned corrugated monolayer model, we conducted numerical modeling [Fig. 1(b)] and reconstruct the parameters associated with the distortion of the plane order in a polycrystalline monolayer. The numerical modeling can be implemented using a Python software.

Fig. 1(c) demonstrates the mechanism of the formation of Bragg rods curvature. A simulated schematic diffraction map is shown in the Fig. 1(c).

For clarity, the simulation was performed only for the rightmost curved Bragg rod. The three circles on which the rounded Bragg rods lie are marked with dotted lines. The scattering picture consists of a "umbra" (shadow) and "penumbra" (partial shade), which are separated by a set of diffraction rods. The boundary between umbra and penumbra runs exactly along the diffraction ring (dotted line), and the sum from the set of diffraction rods gives the maximum intensity along the ring. Bragg rods are represented by solid lines (the colors of which are represented in shades of gray in accordance with the normal distribution). The increased intersection of diffraction lines near the ring, as opposed to the region further away, results in the formation of a caustic, which manifests as a rounded diffraction rod.

In conclusion, the theoretical model for the analyzing of diffraction from two-dimensional molecular ensembles, taking into account their corrugated structure, has been proposed. This approach allows the calculation of 2D diffraction maps obtained by the grazing incidence X-ray diffraction method. This analysis provides the possibility to obtain quantitative information about the structure and organizational processes in Langmuir monolayers with unusual types of ordering, in particular in corrugated monoloyers.

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