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Geometric boundary condition for the chain alignment in lipid monolayers

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Abstract

Langmuir monolayers consisting of phospholipids have been studied intensively in the past using gracing incidence X-ray diffraction (GIXD). Recent investigations focus on monolayers prepared on the surface of complex fluids like hydrogels or -sols (Phys. Rev. Lett. 88 (2002) 25502). These systems allow to modify the properties of the surfactant layer via the tuneable characteristics of the subphase. Using GIXD, the parameters of the lattice formed by the lipid chains are accessible. In addition, the alignment of the scatterer in the unit cell can be extracted from modelling the measured Bragg rods (Transitions in Soft-Condensed Matter, Plenum Press, New York, 1989, pp. 113–138). In this work, we present a boundary condition for the perpendicular wave vector transfer that has to be considered in the calculation of the chain alignment from Bragg rod scans. The theoretical part is illustrated with GIXD measurements of the in-plane structure of lipid monolayers in repulsive electrostatic interaction with charged nano-particles.

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1. Theoretical part

Bragg rod analysis is a powerful method to obtain information about the form of the scatterer and its alignment in monolayers.

For known positions of the Bragg peak maxima in q_z and q_{xy} the alignment of the lipid chains in the unit cell, namely the tilt direction Ψ^* in reciprocal space and the tilt angle t between the lipid chains and the surface normal can be calculated using the relation $q_z = q_{xy} \cos \Psi^* \tan t$ [2,3]. The tilt direction Ψ^* is thereby defined as the angle between the reciprocal lattice vector and the projection of the chain length axis onto the q_{xy}-plane. For the most general case of an oblique lattice this equation is expanded to a system of equations [4] :

$$q_z^a = q_{xy}^a \cos \Psi_a^* \tan t, \tag{1a}$$

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$$q_z^b = q_{xy}^b \cos \Psi_b^* \tan t, \tag{1b}$$

$$q_z^{ab} = q_{xy}^{ab} \cos \Psi_{ab}^* \tan t. \tag{1c}$$

A boundary condition for solving this set of equations is the demand that the largest wave vector transfer perpendicular to the monolayer surface can be calculated as the sum of the two smaller ones:

$$q_z^a = q_z^b + q_z^{ab}. \tag{2}$$

From Fig. 1a one can derive

$$\frac{q_z^a}{a^* \cos \upsilon} = \frac{q_z^b}{b^* \cos(\upsilon + \gamma^*)} + \frac{q_z^{ab}}{ab^* \cos(\beta^* - \upsilon)},$$

from which immediately follows:

$$q_z^b + q_z^{ab} = q_z^a \left[\frac{b^* \cos(\upsilon + \gamma^*)}{a^* \cos \upsilon} + \frac{ab^* \cos(\beta^* - \upsilon)}{a^* \cos \upsilon} \right]. \tag{3}$$

Here, the reciprocal lattice vectors are denoted as a^*, b^* and ab^* to clearly imply that the unit cell is two-dimensional with the consequence that the three lattice vectors are linearly dependent. The term in square brackets in Eq. (3) sums to unity by applying the 'cosine law'

$$\cos \gamma^* = \frac{a^{*2} + b^{*2} - ab^{*2}}{2a^* \cdot b^*}$$

and

$$\cos \beta^* = \frac{a^{*2} + ab^{*2} - b^{*2}}{2a^* \cdot ab^*}$$

in conjunction with the 'sine law'

$$\sin \gamma^* = \frac{ab^*}{b^*} \sin \beta^*.$$

According to Fig. 1b the relation

$$\Psi_a^* = \Psi_b^* + \gamma^* \tag{4}$$

follows immediately, where the angle γ^* coincides with the angle γ_D of the two-dimensional unit cell in real space. With the relation (4) the combination of the Eqs. (1a) and (1b) results in

$$\Psi_b^* = \arctan \left\{ \frac{1}{\sin \gamma_D} \left[\cos \gamma_D - \frac{q_z^a q_{xy}^b}{q_z^b q_{xy}^a} \right] \right\}. \tag{5}$$

With Ψ_b^* known from Eq. (5), combination of Eqs. (1a) and (1c) leads to

$$\Psi_{ab}^* = \arccos \left\{ \frac{q_z^{ab} q_{xy}^b \cdot \cos \Psi_b^*}{q_z^b q_{xy}^{ab}} \right\}. \tag{6}$$

Once the angles between the reciprocal lattice vectors and the tilt direction are known, the tilt angle t can be calculated from each of the Eqs. (1a)–(1c)

$$t = \arctan \left\{ \frac{q_z^i}{q_{xy}^i \cdot \cos \Psi_i^*} \right\}, \quad i = a, b, ab. \tag{7}$$

The Eqs. (2), (4), (6) form a set of boundary conditions that has to be fulfilled if the rods of the different reflections are modelled individually.

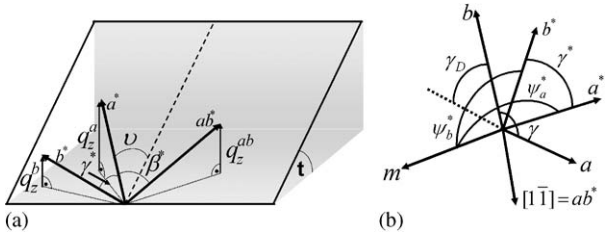

Fig. 1. (a) Wave vector transfers perpendicular to the surface for the case that the chains include a tilt angle $t>0$ with the surface normal; (b) definitions of the angles of the tilt direction in reciprocal space: m is the projection of the chain length axis onto the q_{xy}-plane; reciprocal lattice vectors a^* and b^* define the directions [1 0], respectively [0 1]; from the definition of the reciprocal space $b \perp a^*$ and $a \perp b^*$ follows.