

The distortion and tilt parameters for a 2D Bravais lattice of rod-like molecules

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This paper defines the distortion and tilt parameters for a 2-dimensional Bravais lattice of the sort found in monolayer of long-chain amphiphiles at liquid-gas interfaces. It derives the fundamental formulae for computing them from experimental data and gives their relationships.

1. Introduction

Over the past decade, the technique of grazing-incidence X-ray diffraction (GID) has vastly increased our knowledge of the structure of Langmuir monolayers [2,4]. These are single layers of molecules existing stably at the interface between a gas and a liquid, usually water, and the molecules which form them are usually amphiphiles, i.e., containing both polar and nonpolar moieties. The technique can provide information about monolayer structure because many of them show local translational order giving rise to diffraction reflections.

Organic crystallography is long established, and crystal structures can be reported classically in terms of the parameters of the unit cell, and by the position and thermal ellipsoid of each atom within it. This is convenient for most bulk molecular materials which comply with the dense-packing principle first enunciated by Kitaigorodskii [3]. They show only one packing which maximises the density, subject to the restriction that the van der Waals surfaces of molecules do not interpenetrate. Consistent with this idea, the variation of the unit cell with pressure and temperature is small. Polymorphism is found occasionally, but in most of these cases there are only a very small number of discrete polymorphs with densities equal to within a fraction of a percent, confirming the principle. Kitaigorodskii showed that the densest packing often has many symmetry elements involving rotation as well as translation.

For monolayer work, standard crystallographic parameters have a number of shortcomings, related to the fact that many recently observed systems are exceptions to the dense-packing principle. Their densities can be many percent lower than that of the crystalline phase attained at sufficiently low temperature. The packings vary

continuously and markedly with surface pressure and temperature, and there are many discontinuous changes of packing symmetry. The packings often show inherent conformational disorder, most clearly in the case of rotator phases, in which molecules can take up a range of distinct arrangements within each unit cell. In these packings, which cannot be described by the standard Debye–Waller theory, it is impossible to specify the positions of individual atoms, but at most vager averages like the orientation of the molecular axis. Chiral packings with no symmetry apart from translational are common, and for these there are three equivalent ways of specifying the unit cell whose equivalence is not obvious. Phase changes between primitive and centered packings are also common, and standard crystallographic notation for the latter actually involves the dual cell, rather than the unit cell. Hence it is of interest to have a notation which is both more transparent and more appropriate.

Such a notation was first proposed by Sirota in his studies of the rotator phases and surface phases of the alkanes [6], and it has been used by other authors [1,5]. The present paper refines his original definition of the distortion parameters and shows how it is possible to combine them with parameters for molecular tilt which can readily be calculated from the observed diffraction measurements.

2. Analysis

The parameters are based on an ellipse drawn through the six nearest neighbors of a given lattice point. If the major and minor semiaxes of the ellipse are denoted a and b , respectively, then Sirota defined the distortion magnitude ξ by

$$\xi = \frac{a}{b} - 1. \quad (1)$$

Sirota's definition is asymmetric in the two semiaxes. The following definition is uniquely determined by Sirota's value, is essentially equal to it for small values, and has nicer mathematical properties:

$$\xi = \frac{a^2 - b^2}{a^2 + b^2}. \quad (2)$$

This definition of the distortion magnitude will be used exclusively in the present analysis. As defined by Sirota, the distortion direction ω is the azimuth of the major axis with respect to a given lattice direction.

First note that a 2D Bravais lattice has a very simple relationship to its dual lattice in reciprocal space. The two are similar and rotated 90° relative to one another. Hence their distortion magnitudes ξ and directions ω are the same.

The distortion–tilt relationships are derived most elegantly using complex numbers. If w is the space of an undistorted unit h.c.p. lattice and z the space of an

arbitrary 2D Bravais lattice, then in general, the mapping can be expressed in terms of Cartesian coordinates as

$$\begin{bmatrix} \operatorname{Re} z \\ \operatorname{Im} z \end{bmatrix} = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} \operatorname{Re} w \\ \operatorname{Im} w \end{bmatrix}. \quad (3)$$

Re-expressing the right-hand side in terms of w and w^* and combining the real and imaginary parts of z leads, after some rationalization, to

$$z = \frac{A}{\sqrt{1 - \chi\chi^*}} (w + \chi w^*), \quad (4)$$

where the modulus of A , $|A|$, defines the area scale of the actual lattice, and its angle $\angle A$ an average nearest-neighbor (NN) direction which can be used as the reference for ω . The parameter χ vanishes when there is no distortion, i.e., when the transformation consists purely of rotation and magnification.

The six nearest neighbors of the origin in w -space lie on the unit circle at intervals of $\pi/3$ radians:

$$w = e^{i\varphi}, \quad \varphi = \frac{\pi n}{3}. \quad (5)$$

Since the transformation of equation (3) is linear, not only do the lattice points map to one another (by definition), but the unit circle in w -space maps to the required ellipse in z -space. The square of the radius in z -space is given by

$$zz^* = \frac{AA^*}{1 - \chi\chi^*} \{ (1 + \chi\chi^*) + 2 \operatorname{Re}(\chi e^{-2i\varphi}) \}. \quad (6)$$

After combining magnitude and direction and inverting, the definition of equation (1) yields

$$\chi = \frac{\xi e^{2i\omega}}{1 + \sqrt{1 - \xi^2}}. \quad (7)$$

Equation (6) can now be rewritten in terms of ξ and ω instead of χ :

$$r^2 = \frac{AA^*}{\sqrt{1 - \xi^2}} \{ 1 + \operatorname{Re}(\xi e^{2i\omega} e^{-2i\varphi}) \}. \quad (8)$$

Considering just the values of r^2 at the lattice points, equation (8) is the discrete Fourier transform of three distinct values. Inverse transformation gives

$$\xi e^{2i\omega} = 2 \cdot \frac{\sum r_n^2 e^{-2\pi i n/3}}{\sum r_n^2}. \quad (9)$$

The values of ξ and ω so defined are not unique, because it is possible to map a 2D Bravais lattice to itself in a countably infinite number of nontrivial ways. However, of the resulting values of $\xi e^{2i\omega}$, only one lies within the heavily-shaded 30° – 60° – 90° triangle shown in figure 1. The other 30° – 60° – 90° lightly-shaded subprincipal

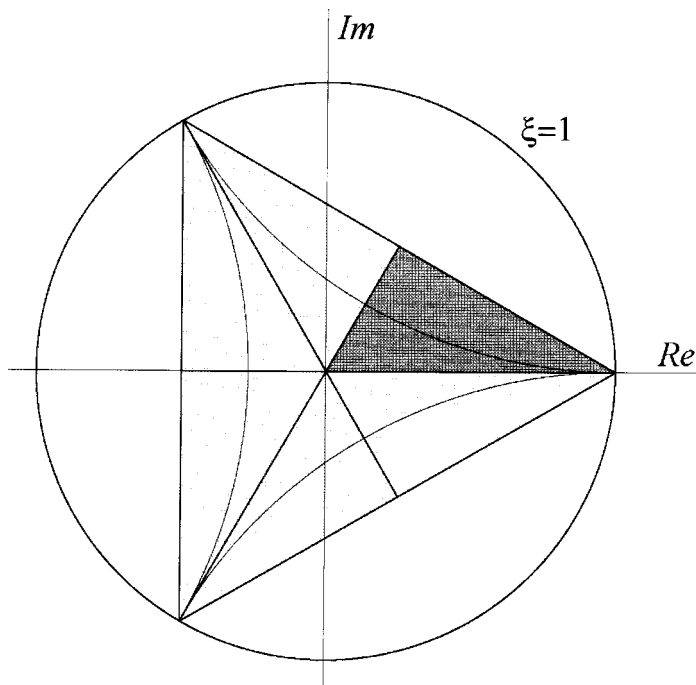


Figure 1. Region of the complex plane covered by principal values of the complex distortion parameter $\xi e^{2i\omega}$.

triangles are related to the first by reflection and by rotation through multiples of 120° and correspond to taking the six nearest neighbors in a different order. The union of all six triangles, principal and subprincipal, is a larger equilateral triangle centered on the origin, outside of which equation (4) generates six points of the Bravais lattice which are not the nearest neighbors of the origin. The three-sided concave shape gives the regions of principal values for the complex distortion parameter χ . These contain the three vertices of the $\xi e^{2i\omega}$ triangle, and the sides are circles of radius $\sqrt{5}$.

Many packings of planar monolayers consist of rod-like molecules. These define two 2D packings, the first in the plane of the monolayer, and the second in a plane normal to the molecular axes. Equation (9) gives the lattice distortion parameters in both planes directly from grazing-incidence diffraction measurements. For the monolayer plane the distances r are taken to be the monolayer-plane coordinates Q_{xy} of the diffraction peaks. For the axis-normal plane, they are taken to be the moduli $\sqrt{Q_{xy}^2 + Q_z^2}$.

The direction of the rod-like molecules defines a projective mapping between points in the monolayer plane and points in a plane normal to the rods. This mapping is of the same form as equation (3) and hence can be assigned a distortion parameter τ ,

which is given in terms of the tilt magnitude θ and direction β by

$$\tau = \tan^2\left(\frac{\theta}{2}\right)e^{2i\beta}. \quad (10)$$

The direction of the real axis in the monolayer plane can be chosen parallel to the average NN direction closest to the reflection labelled '0', making the scale factor A of equation (4) real and positive. The inverse mapping of the monolayer-plane lattice to an undistorted lattice can now be combined with the further mapping to the chain-normal plane, allowing the tilt parameter τ to be expressed in terms of the complex distortion parameters χ and χ' in the monolayer and axis-normal planes, respectively:

$$\tau = \frac{\chi' - \chi}{1 - \chi'\chi^*}. \quad (11)$$

3. Discussion

Given the experimentally-determined positions of the diffraction reflections from a monolayer of a long-chain amphiphile, the equations derived here allow rapid computation of the distortion and tilt parameters of the local Bravais lattice. Equation (9) is better conditioned than other expressions which have been published previously.

The distortion parameters vary continuously at a second-order transition, even if the symmetry changes. Nevertheless the symmetry of the Bravais lattice is readily determined from them. Hexagonal packing is characterized by a distortion magnitude ξ equal to zero, centered packings by a distortion direction (principal value) equal to 0° or 30° , and oblique (chiral) packings by any other value of distortion direction.

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