1 Thin Rod Model of the ripple phase

The thin rod model will be applied to the ripple phase WAXS. In this model, electron density of lipid chains are described as delta functions and lipid head groups are assumed not to contribute to scattering. Since the molecular packing of the major side of ripple phase is hypothesized to be gel-like, the model may be adequate. First, we will study diffraction from chains packed in gel phase manner whose system size is infinite but whose packing plane make an angle ξ with the xy plane. This infinite case is adequate for indexing the ripple Bragg peaks while it ignores the peak broadening effect. The system will later be truncated along the ripple direction to see the effect of the finite size on peak broadening. Finally, in-plane powder will be taken into account to derive a peak intensity pattern.

First, let us calculate the positions of the diffraction peaks from a two dimensional orthorhombic lattice whose plane makes an angle ξ with respect to the xy plane and extends to infinity. As a unit cell, we will take a parallelpipedon containing two rods, one located at the origin and the other located at the center (Fig. 1). The lattice vectors are $\mathbf{a_1} = a_1 \cos\xi \hat{\mathbf{x}} + a_1 \sin\xi \hat{\mathbf{z}}$ and $\mathbf{a_2} = a_2 \hat{\mathbf{y}}$. There are other choices for how the lattice is oriented with respect to the ripple direction, which should be considered as well. Then, the Laue conditions are given by

$$2\pi h = \mathbf{q} \cdot \mathbf{a_1} = (a_1 \cos\xi) q_x + (a_1 \sin\xi) q_z \tag{1}$$

$$2\pi k = \mathbf{q} \cdot \mathbf{a_2} = a_2 q_y, \tag{2}$$

with h and k being zero or integer. Let us define the chain tilt angle θ to be the angle between the stacking z direction and the chain direction. We also define ϕ to represent the direction into which chains are tilted. In other words, θ and ϕ are usual spherical coordinates with respect to the ripple x, y, and z axes, not the local bilayer Cartesian axes. With this choice of coordinates, chains are tilted with respect to the local bilayer normal if $\theta = 0$. $\theta = \xi$ and $\phi = \pi$ gives chains parallel to the local bilayer normal, or $\theta_t = 0$. It would be good to work out the relation between θ and θ_t, θ_t being the chain tilt with respect to the local bilayer normal.

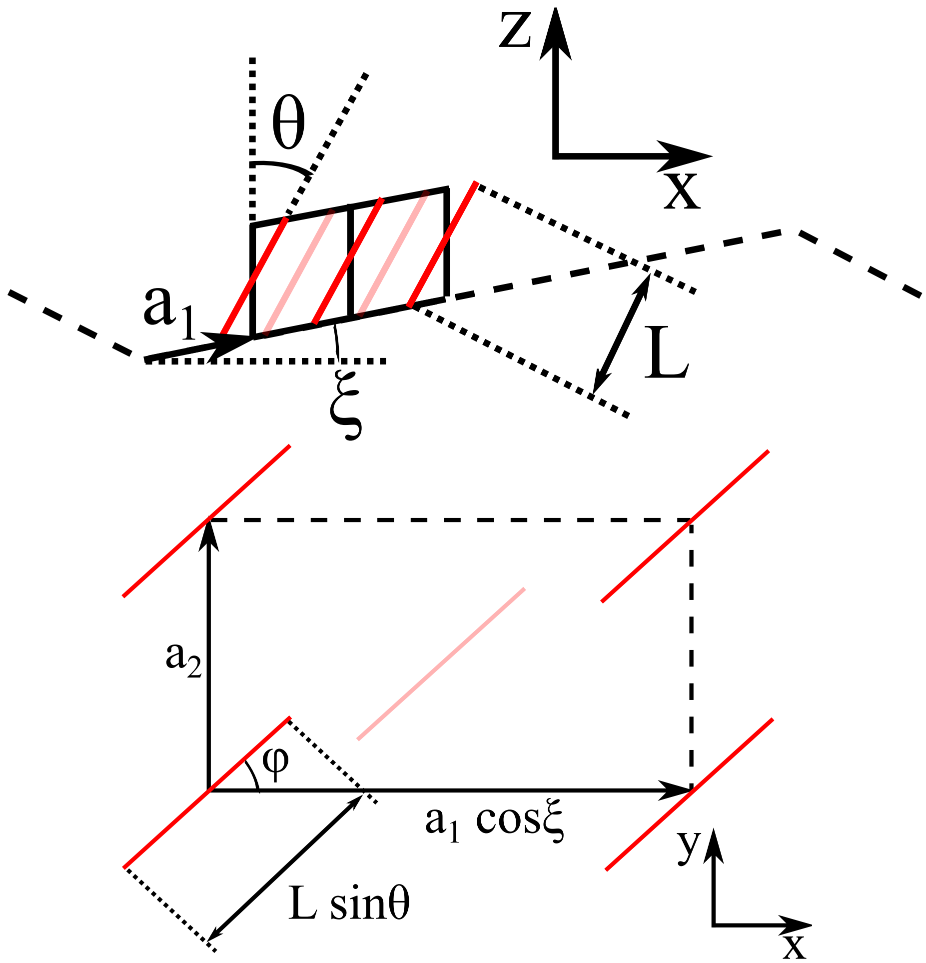

Figure 1: Unit cell for chain packing in the major arm. (top) Projection of the unit cell in the xz-plane. The unit cell is taken as a parallelpipedon shown by black solid lines, each unit cell containing two chains. Chains located at the center of the unit cell are drawn as opaque red lines while chains at the lattice points are drawn as solid red lines. The dash line indicates the mid-plane of a rippling bilayer. Chains are tilted with respect to the stacking z direction by θ and the major arm is tilted with respect to the ripple x direction by ξ. The chain length is denoted by L. $\mathbf{a_1}$ and $\mathbf{a_2}$ are orthorhombic unit cell vectors. (bottom) Projection of the unit cell in the xy-plane. $\phi = 0$ means chains are tilted in the xz plane and $\phi = \pi/2$ means chains are titled into the direction perpendicular to the ripple direction.

The electron density, assuming a delta function for each chain, is given by

$$\rho(\mathbf{r}) = \delta(x - \alpha z, y - \beta z) + \tag{3}$$

$$\delta\left[x - \frac{a_1 \cos\xi}{2} - \alpha\left(z - \frac{a_1 \sin\xi}{2}\right), y - \frac{a_2}{2} - \beta\left(z - \frac{a_1 \sin\xi}{2}\right)\right], \tag{4}$$

where $\alpha = \tan\theta\cos\phi$ and $\beta = \tan\theta\sin\phi$. The first rod extends for

$$-L/2\sin\theta\cos\phi \leq x \leq L/2\sin\theta\cos\phi \tag{5}$$

$$-L/2\sin\theta\sin\phi \leq y \leq L/2\sin\theta\sin\phi \tag{6}$$

$$-L/2\cos\theta \leq z \leq L/2\cos\theta, \tag{7}$$

and the second rod for

$$-L/2\sin\theta\cos\phi + a_1/2\cos\xi \leq x \leq L/2\sin\theta\cos\phi + a_1/2\cos\xi \tag{8}$$

$$-L/2\sin\theta\sin\phi + a_2/2 \leq y \leq L/2\sin\theta\sin\phi + a_2/2 \tag{9}$$

$$-L/2\cos\theta + a_1/2\sin\xi \leq z \leq L/2\cos\theta + a_1/2\sin\xi. \tag{10}$$

Then, the form factor is given by

$$F(\mathbf{q}) = \int dx \int dy \int dz\, \rho(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}} \tag{11}$$

$$\begin{aligned}
&= \int_{-\frac{L}{2}\cos\theta}^{\frac{L}{2}\sin\theta} dz e^{i(\alpha q_x + \beta q_y + q_z)z} + \\
&\int_{-\frac{L}{2}\cos\theta + \frac{a_1}{2}\sin\xi}^{\frac{L}{2}\cos\theta + \frac{a_1}{2}\sin\xi} dz\, e^{\frac{i}{2}[q_x(a_1\cos\xi - \alpha a_1 \sin\xi) + q_y(a_2 - \beta a_1 \sin\xi)]}\, e^{i(\alpha q_x + \beta q_y + q_z)z} \\
&= \left[1 + e^{\frac{i}{2}(a_1\cos\xi q_x + a_1 \sin\xi q_z + a_2 q_y)}\right] \frac{2}{\gamma} \sin\left(\frac{\gamma L \cos\theta}{2}\right)
\end{aligned}$$

$$= \left[1 + e^{i\pi(h+k)}\right] \frac{2}{\gamma} \sin\left(\frac{\gamma L \cos\theta}{2}\right), \tag{12}$$

where $\gamma = \alpha q_x + \beta q_y + q_z$. Eq. 12 shows that peaks with $h + k$ being odd is extinct. For $h + k$ even, we have

$$F(\mathrm{q}) = \frac{4}{\gamma} \sin\left(\frac{\gamma L \cos\theta}{2}\right). \tag{13}$$

For (20) peak, $q_y = 0$ and $4\pi = a_1 \cos\xi q_x + a_1 \sin\xi q_z$. The second equation can be rewritten to give

$$q_z = -\frac{1}{\tan\xi} q_x + \frac{4\pi}{a_1 \sin\xi} \tag{14}$$

which defines a straight line in $q_x q_z$-plane along which (20) Bragg rod appears. Eq. 13 has a peak at $\gamma = 0$. Hence, the maximum intensity of (20) peak is at q_x and q_z that satisfy Laue conditions and $\gamma = 0$. This gives three equations and three unknowns. Explicitly written, we have

$$q_y = 0 \tag{15}$$

$$4\pi = a_1 \cos\xi q_x + a_1 \sin\xi q_z \tag{16}$$

$$0 = \tan\theta \cos\phi q_x + q_z \tag{17}$$

Solving these, we get

$$q_x = \frac{4\pi}{a_1 \cos\xi (1 - \tan\theta_t \cos\phi \tan\xi)} \tag{18}$$

$$q_z = \frac{-4\pi \tan\theta_t \cos\phi}{a_1 \cos\xi (1 - \tan\theta_t \cos\phi \tan\xi)} \tag{19}$$

For $\phi = \pi/2$, we have $q_x = 4\pi/(a_1 \cos\xi)$ and $q_z = 0$, so one would expect to see a peak on the equator, the case of which is similar to $L_{\beta I}$ phase in gel phase. To get back to ordinary gel phase, ξ should be set equal to zero.

For any (hk) line, we again have three equations and three unknowns as

$$2\pi h = q_x a_1 \cos\xi + q_z a_1 \sin\xi \tag{20}$$

$$2\pi k = q_y a_2 \tag{21}$$

$$0 = q_x \tan\theta_t \cos\phi + \frac{2\pi k}{a_2} \tan\theta_t \sin\phi + q_z \tag{22}$$

Solving for q_x, q_y, and q_z, we obtain

$$q_x = \frac{2\pi(h + ka\beta\sin\xi)}{a_1\cos\xi(1 - \alpha\tan\xi)} \tag{23}$$

$$q_y = \frac{2\pi k}{a_2} \tag{24}$$

$$q_z = \frac{-2\pi(h\alpha + ka\beta\cos\xi)}{a_1\cos\xi(1 - \alpha\tan\xi)}, \tag{25}$$

where $a = a_1/a_2$.