The Orientational Distribution Function of de Vries Smectics†
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The smectic materials that show very small layer shrinkage in the SmC phase remain relevant in liquid crystal research in order to eradicate the zigzag defects associated with the formation of chevron layer structure. These materials are known as de Vries smectics attributed to Adriaan de Vries [1] who discovered them. He proposed the diffuse cone model in which the molecules already possess a large polar tilt in the SmA but are azimuthally degenerate, forming a “hollow cone distribution”. In the SmC phase, the azimuthal tilt distribution becomes biased in a preferred direction rendering the phase biaxial with a minimal change in layer spacing. Over the years, the hollow cone distribution remains widely accepted for the many de Vries smectics materials, but its direct confirmation has not been reported.

Lagerwall, et al.[2] suggested that de Vries behavior is not related to any exotic molecular distribution on a hollow cone, but instead is a consequence of an unusual combination of low nematic order and high smectic order in the de Vries SmA phase. Further, they have illustrated that the shape of the orientational distribution function (ODF) is either volcano-like belonging to hollow cone distribution or sugarloaf-like (Gaussian-shaped). Both shapes could account for de Vries behavior.

Using high resolution x-ray diffraction, we obtained the structure parameters such as layer spacing, tilt of the SmC phase, orientational order parameters, \( \langle P_2 \rangle \), \( \langle P_4 \rangle \) and \( \langle P_6 \rangle \), and determined the ODF of six de Vries mesogens, two of which are chiral (ferroelectric) and four non-chiral. Results show that the \( \langle P_2 \rangle \) values range from 0.58 to 0.75 for the non-chiral smectics but remain smaller (~0.45) for the chiral compounds. The \( \langle P_4 \rangle \) values are positive and the shape of ODF is sugarloaf for all materials. We will show that the hollow cone type behavior can have sugarloaf ODF when the molecular orientational fluctuations are equal to or larger than the director tilt.

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References:

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