

Orientalional distribution functions and order parameters in "De Vries"-type smectics - a simulation study

Frank Jenz,¹ Mikhail A. Osipov,² Stefan Jagiella,¹ and Frank Giesselmann^{1, a)}

¹⁾*Institute of Physical Chemistry, Pfaffenwaldring 55, University of Stuttgart, Stuttgart Germany*

²⁾*Department of Mathematics and Statistics, G1 1XH, University of Strathclyde, Glasgow UK*

(Dated: 13 September 2016)

Simple smectic A liquid crystal phases with different types of prescribed orientational distribution functions have been simulated and compared in order to study the possibility to distinguish between the Maier-Saupe type and cone-like orientational distributions using the popular method of Davidson *et al.* This method has been used to extract the orientational distribution functions from simulated diffraction patterns, and the results have been compared with actual distribution functions which have been prescribed during simulations. It has been shown that it is indeed possible to distinguish between these two qualitatively different types of orientational distribution already from the shape of the 2D diffraction pattern. Moreover, typical experimental diffraction patterns for "de Vries"-type smectic liquid crystals appear to be close to the ones which have been simulated using the prescribed Maier-Saupe orientational distribution function.

Keywords: Liquid Crystals, X-ray Diffraction, Order Parameter, Orientational Distribution Function

I. INTRODUCTION

There exist a number of experimental techniques to determine the orientational order parameters which specify the degree of the orientational order of anisotropic molecules in various liquid crystal phases. In particular, both the second rank orientational order parameter S_2 and the fourth rank order parameter S_4 can be determined from 2D X-ray diffraction patterns as was originally suggested by Leadbetter and Norris¹. A more refined method has later been suggested by Davidson, Petermann and Levelut² and this procedure has been used by different authors to measure the order parameters of the nematic, smectic A and smectic C phases³⁻⁶.

The method of Davidson *et al.* is based on a number of approximations and it is not clear *a priori* what is the accuracy of the results even though the values of S_2 are known to correlate well with the results obtained by other experimental techniques like NMR, via dielectric relaxation, optical birefringence or Raman spectroscopy⁷⁻¹². In a previous paper we have used computer simulations to evaluate the accuracy of this method¹³. We could show that the method of Davidson *et al.* is reliable but, due to translational correlations between orientationally ordered molecules¹⁴, which are not taken into account, it slightly underestimates the order parameter S_2 by approx. 0.05.

One notes that all phases, simulated in¹³, are characterised by a Maier-Saupe like orientational distribution function (Fig. 1a) and rather high values of the orientational order parameter S_2 . On the other hand, it is very interesting to investigate if the method of Davidson *et al.* can be used to distinguish between smectic

liquid crystals with different shapes of the orientational distribution function. In particular, starting from the original works of de Vries^{15,16} some authors assume that in the so-called smectics A of "de Vries" type the long molecular axes are tilted by a more or less constant angle with respect to the smectic layer normal¹⁷. This corresponds to the so-called hollow-cone orientational distribution shown schematically in Fig. 1c. A more general orientational distribution of this kind corresponds to the so-called diffuse cone model presented in Fig. 1b.

A comparison of the initial orientational distribution functions of qualitatively different shapes with the corresponding functions extracted from the simulated diffraction patterns can be undertaken if the actual orientational distribution is fixed during the simulations of the structure factor and the corresponding diffraction pattern. In this paper we undertake such simulations using a very simple model of the smectic A phase with perfect smectic order, prescribed values of the orientational variables, which correspond to a given shape of the distribution function, and 2D positional freedom of molecular centres of mass inside a given smectic layer.

So far, the existing experimental data do not provide conclusive evidence whether or not these hypothetical cone-like distributions really exist in "de Vries"-type smectics¹⁸⁻²¹. This knowledge is however essential to understand the nature of these peculiar phases. The simulation results presented in this paper now clearly indicate how the 2D diffraction patterns which correspond to the cone-like distributions are distinguished from the diffraction patterns which correspond to the conventional Maier-Saupe distributions.

^{a)}f.giesselmann@ipc.uni-stuttgart.de

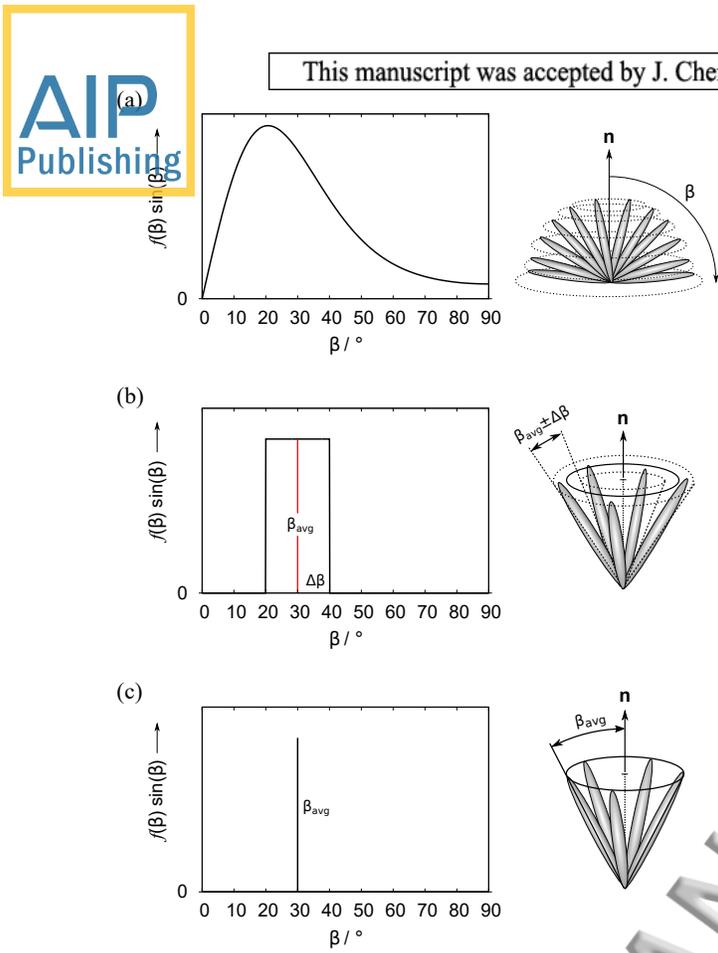


FIG. 1. Probability functions corresponding to the three orientational distribution functions: (a) Maier-Saupe distribution. (b) Diffuse-Cone distribution. (c) Hollow-Cone distribution.

II. SIMULATION PROCEDURE

The smectic A phases composed of uniaxial particles with prescribed orientational distribution function and perfect translational order has been simulated. In this case the translational order parameter $\Sigma = 1.0$ and the instant orientation of a particle is specified by the polar angle θ with respect to the smectic layer normal (or the molecular tilt angle) and the azimuthal angle in the plane of the layers. Then the simulation snapshots have been generated by the following steps:

1. The molecular tilt angles of the particles in the simulation box have been set in accordance to the prescribed ODF.
2. Azimuthal angles of all particle have been set randomly between 0 and 360°.
3. Position of each particle in the simulation box was set randomly. Overlapping of particles has been thereby prevented.
4. The simulation has been equilibrated by Molecular Dynamics (MD) using 200000 integration steps

with fixed rotation angles and fixed positions of the particles along the layer normal (parallel to the z-axis). For simplicity particles have only been allowed to move within the smectic layers to generate the lowest-energy isotropic positional distribution within the layers. The time-step was set to 0.001. The reduced temperature T^* was set to 2.0, the reduced pressure to 1.0 and both were kept constant during equilibration. For all particles a Gay-Berne potential with a length-to-width ratio of $\kappa = 4.0$ and a well depth ratio $\kappa' = 2.0$ was used²².

In Fig. 2a-c three different simulation snapshots are presented which correspond to the Maier-Saupe, diffuse-cone and hollow-cone orientational distribution functions, respectively. All three snapshots in Fig. 2 have the same orientational order parameter $S_2 = 0.4$.

III. RESULTS AND DISCUSSION

At the first stage the 2D diffraction patterns have been calculated for each simulation snapshot using Fast Fourier Transform as introduced in our previous paper¹³. Diffraction patterns for three different types of ODFs are shown in Fig. 3. The intensity profiles $I(\chi)$ in the wide angle range have been obtained by integration between the two red circles as depicted in Fig. 3a on the left. The left column of Fig. 3 shows diffraction patterns for $S_2 = 0.4$ while the right column corresponds to a second simulation series with $S_2 = 0.7$.

One notes that the diffraction pattern obtained from simulations of smectic A phases with different types of prescribed orientational distribution function are qualitatively different. In particular, the diffraction pattern, which corresponds to the Maier-Saupe ODF (Fig. 3a), is characterised by only one maximum in the wide angle range, and the peak is becoming more narrow with increasing S_2 . In contrast, for the smectic A phase with the diffuse-cone distribution (Fig. 3b) one obtains a broad, plateau-like maximum. This maximum becomes sharper for higher S_2 and in this case the pattern is closer to the one obtained for smectics with the Maier-Saupe distribution. Finally the diffraction pattern for the system with the hollow-cone ODF (Fig. 3c) is characterised by two distinct maxima which are visible for both small and large S_2 .

It should be noted also that typical experimentally measured 2D X-ray diffraction patterns^{3,17,23,24} are closer to our simulated patterns obtained for smectics A with the Maier-Saupe ODF.

Another interesting observation in the diffraction patterns of Fig. 3 is that - even though the translational order parameter is fixed to $\Sigma = 1.0$ in all simulations - the intensity ratios of the smectic layer peaks change with both, the shape of the ODF and the orientational order parameter S_2 in a non-obvious way. This observation indicates the relevance of the so called mixed order

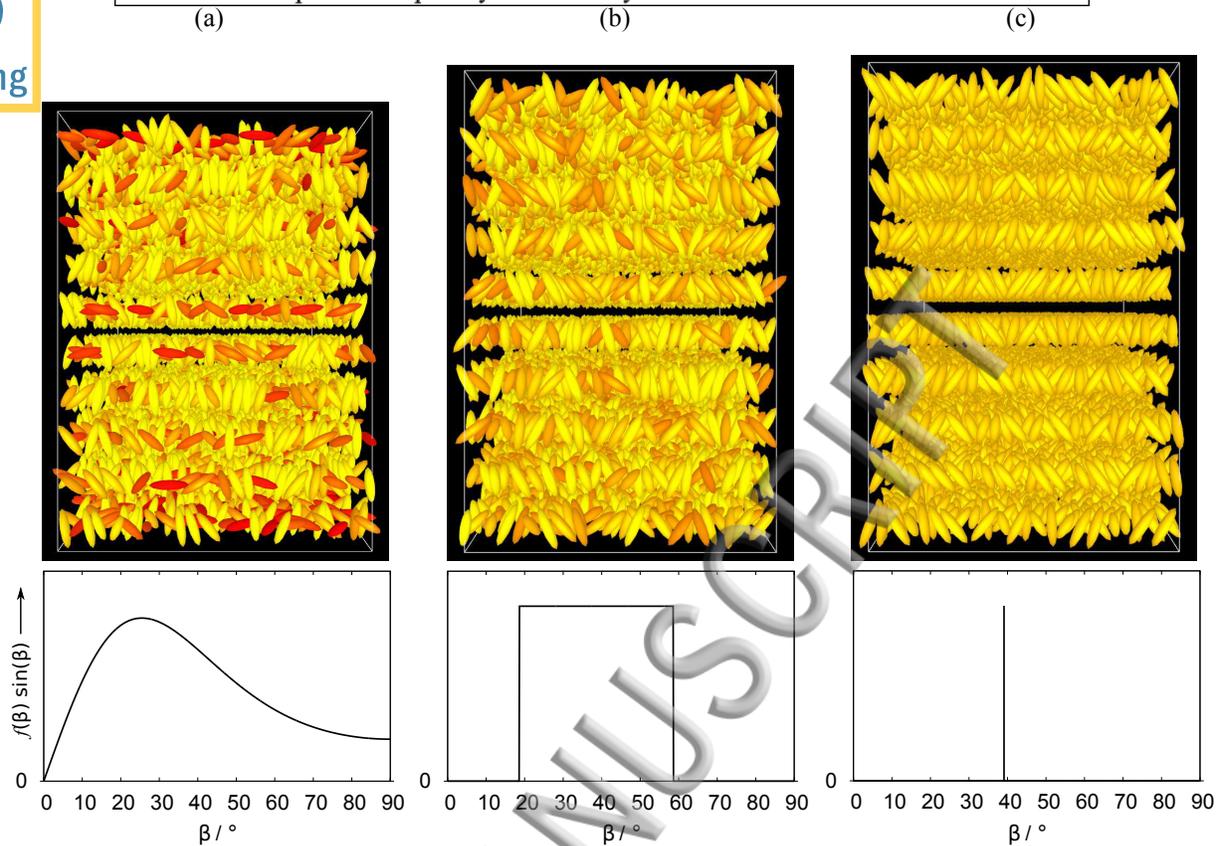


FIG. 2. Top: Simulation snapshots for (a) Maier-Saupe distribution, (b) Diffuse-Cone distribution and (c) Hollow-Cone distribution of polar angles of rod-like particles, respectively. Red particles are perpendicular and yellow particles are parallel to the director. Bottom: Prescribed orientational distribution functions used in the simulation above. All three depicted snapshots are characterised by the same nematic order parameter $S_2 = 0.4$.

parameters such as $\langle P_2(\cos \beta) \cos(2\pi z/d) \rangle$ as it was recently pointed out by Palermo *et al.*²⁵

At the second stage the orientational distribution function was extracted from the calculated diffraction patterns using the method of Davidson *et al.* The results, presented in Fig. 4, have then been compared with the corresponding prescribed ODFs. In the case of smectics A with the Maier-Saupe distribution function the ODF is reproduced very well. In contrast, for systems with cone-like distributions the agreement between the prescribed and the calculated ODFs is rather poor which is related to the cosine series expansion employed in the method of Davidson *et al.* The cone-like distribution functions can adequately be described only using a large number of terms in the series expansion.

Finally we have calculated the values of the orientational order parameter S_4 for all three types of the orientational distribution function. In Figure 5 we depict the error in S_4 obtained by subtracting the values of S_4 , calculated directly from the snapshots, from the values of S_4 , extracted from the simulated diffraction patterns (Fig. 3) using the method of Davidson *et al.* One can readily see that for smectics with Maier-Saupe like distribution the deviation is close to zero, and hence the

calculation of the order parameter S_4 via the method of Davidson *et al.* is reliable. In contrast, for systems with cone-like distributions the calculated values of S_4 are not very reliable which may be due to truncation errors in the expansion of the wide-angle intensity profile in the cosine series.

IV. CONCLUSIONS

In this paper we have calculated the orientational distribution functions and the orientational order parameters S_2 and S_4 , using the method of Davidson *et al.*, from the diffraction patterns which have been simulated for a simple smectic A phase with prescribed orientational distribution of molecules. We have used the orientational distribution, which corresponds to the Maier-Saupe model, typical for conventional smectics A and the cone-like distributions, which are sometimes assumed to characterize smectics A of the "de Vries" type.

Simulation data indicate that it is possible to distinguish qualitatively between the Maier-Saupe type and cone-like orientational distributions of molecules in the smectic A phase just considering the shape of the 2D

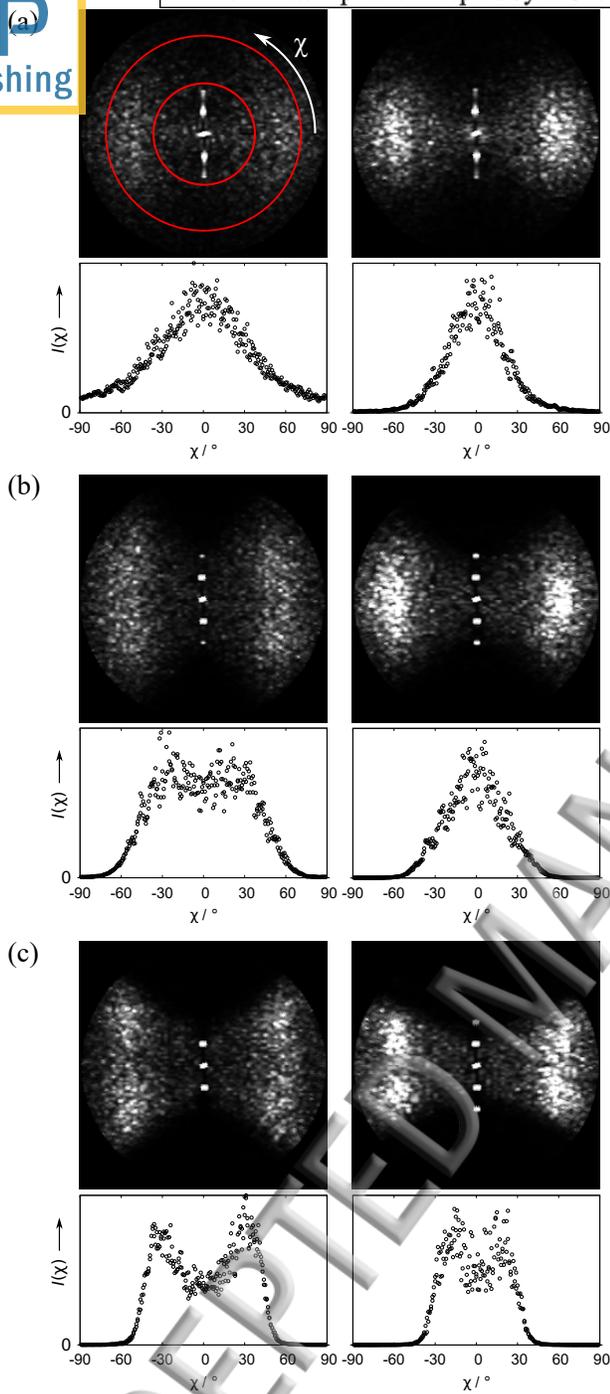


FIG. 3. 2D Diffraction patterns of simulations with prescribed orientational distribution function. The wide-angle intensity profiles $I(\chi)$ are depicted below the related diffraction patterns. Left: Orientational order parameter $S_2 = 0.4$. Right: Orientational order parameter $S_2 = 0.7$. (a) Maier-Saupe distribution (Fig. 2a). The red circles define the region where the $I(\chi)$ -profile has been calculated. (b) Diffuse-Cone distribution (Fig. 2b). (c) Hollow-Cone distribution (Fig. 2c).

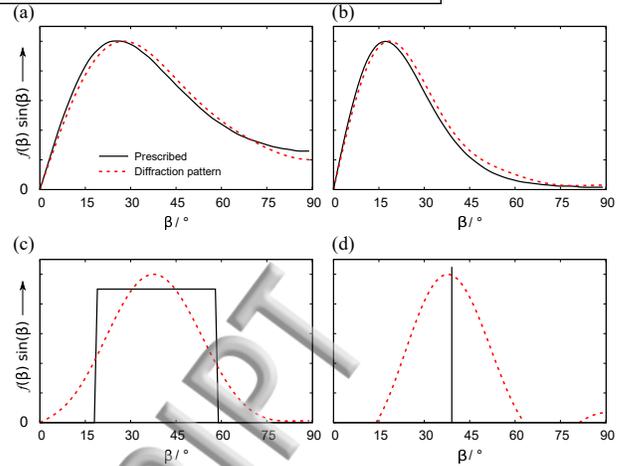


FIG. 4. Comparison of the orientational distribution functions $f(\beta)\sin(\beta)$, prescribed during the simulations (black line), and the corresponding distribution functions extracted from the diffraction patterns using the method of Davidson *et al.* (red dashed line). (a) Maier-Saupe distribution $S_2 = 0.4$. (b) Maier-Saupe distribution $S_2 = 0.7$. (c) Diffuse-Cone distribution $S_2 = 0.4$. (d) Hollow-Cone distribution $S_2 = 0.4$.

diffraction pattern provided the orientational order parameter is not too high, i.e. $S_2 < 0.7$. In particular, in the range of S_2 between 0.4 and 0.6, which is typical for smectics A of "de Vries" type, the azimuthal intensity profile $I(\chi)$ of the diffuse wide-angle scattering possess a rather pronounced and well-defined maximum in the case of a Maier-Saupe type distribution, while in the case of a cone-like distribution the same diffraction profile is characterized by a rather flat plateau or sometimes even a minimum at small azimuthal angles with a significant scattering of data in that region.

As far as we know, the latter type of diffraction profiles have experimentally never been observed so far for various "de Vries"-type smectics with anomalously weak layer contraction. Thus there is no experimental evidence in favour of a cone-like orientational distribution of molecules in smectics of "de Vries" type. The simulation results thus give strong support to earlier claims¹⁸⁻²¹ that cone-like distributions do not exist in "de Vries"-type smectics even though they could nicely explain many of their striking properties, in particular the absence of smectic layer contraction in the tilting transition to smectic C.

A good agreement between the initial values of the order parameter S_2 and the corresponding values, calculated from the diffraction patterns, has been found for all three types of the orientational distribution considered. In all cases the method slightly underestimates the value of S_2 (by approximately 0.04) which is related to the contribution of the translational fluctuations between orientationally ordered molecules¹⁴.

In contrast, the calculated values of the order parameter S_4 are less reliable as the discrepancy between the initial and the calculated values is of the order of 0.1 and

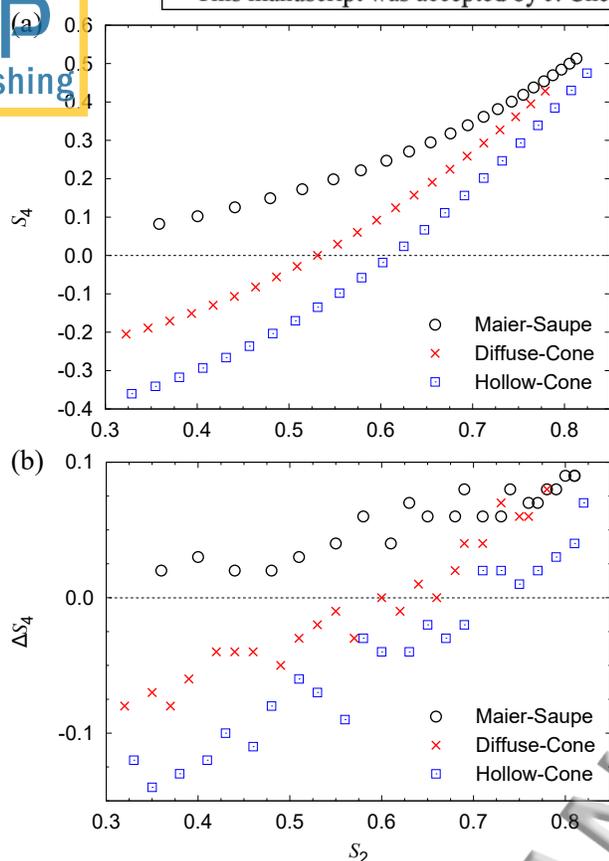


FIG. 5. (a) Absolute values of S_4 vs. S_2 calculated via diagonalisation of the order tensor. In case of Maier-Saupe ODF, S_4 is positive over the total range of S_2 . For Diffuse-Cone distributions, S_4 decreases faster with decreasing S_2 and becomes negative below $S_2 = 0.52$. For Hollow-Cone distributions, S_4 decreases even faster with decreasing S_2 than in the Diffuse-Cone case and becomes negative already below $S_2 = 0.7$. (b) Deviation of higher order parameter S_4 , calculated from the simulated diffraction patterns using the method of Davidson *et al.*, from the value of S_4 calculated directly from simulations for smectics A with Maier-Saupe, Diffuse-Cone and Hollow-Cone orientational distribution functions. Note that the error is small in the case of Maier-Saupe ODF.

thus comparable to the size of S_4 itself. In particular, the relative deviation is particularly large for hypothetical smectics A with a cone-like distribution in the region where S_4 is close to zero. This may be related to the truncation errors. Indeed, both hollow-cone and diffuse cone orientational distributions are discontinuous and thus can be correctly represented by a Fourier series only if a large amount of terms is taken into account. In other words, a large discrepancy in the values of S_4 may represent a sum of discrepancies in the values of other higher order

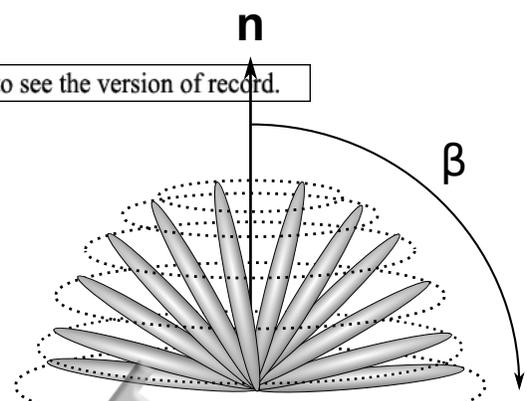
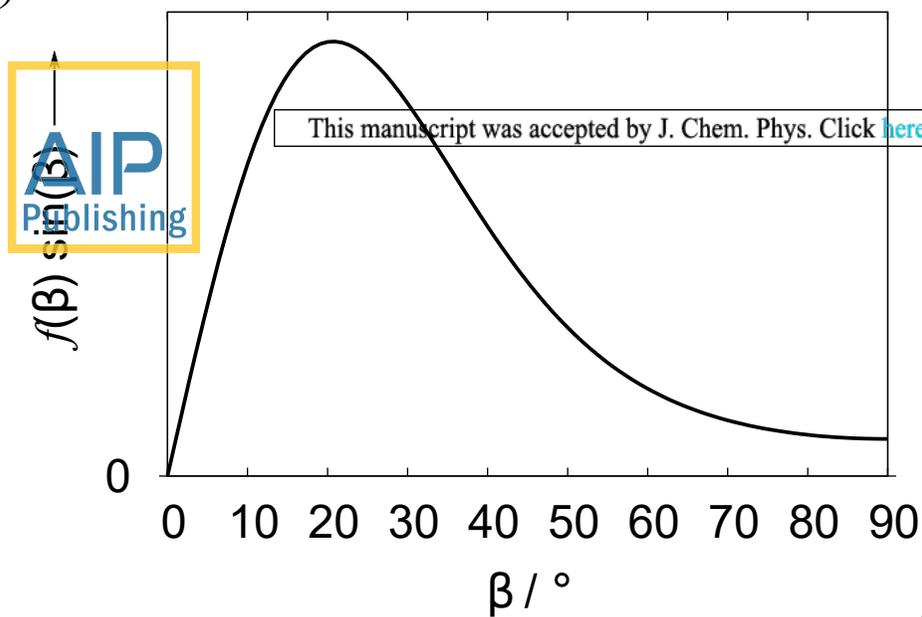
parameters which may be rather large in systems with a cone-like distribution. Better agreement may be achieved if one uses a continuous orientational distribution in the framework of a cone-like model. A corresponding study is currently in progress.

ACKNOWLEDGMENTS

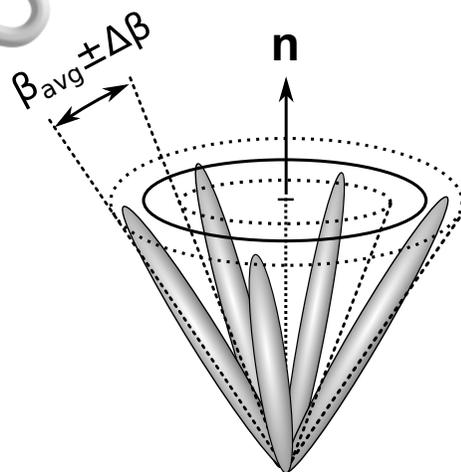
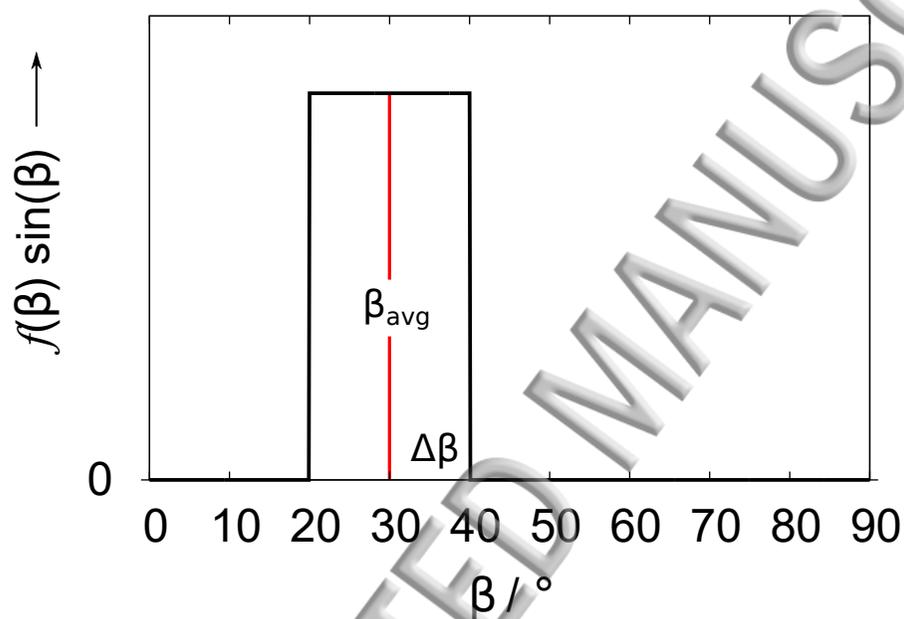
We thank Noel A. Clark for stimulating discussions. Financial support from the *Deutsche Forschungsgemeinschaft* (DFG Gi 243/6-1) is gratefully acknowledged.

- ¹A. J. Leadbetter and E. K. Norris, *Mol. Phys.* **38**, 669 (1979).
- ²P. Davidson, D. Petermann, and A. M. Levelut, *J. Phys. II* **5**, 113 (1995).
- ³D. Nonnenmacher, S. Jagiella, Q. Song, R. P. Lemieux, and F. Giesselmann, *ChemPhysChem* **14**, 2990 (2013).
- ⁴D. Constantin, P. Davidson, and C. Chanac, *Lanmuir* **26**, 4586 (2010).
- ⁵T. T. Mills, G. E. S. Toombes, S. Tristram-Nagle, D.-M. Smilgies, G. W. Feigenson, and J. F. Nagle, *Biophys. J.* **95**, 669 (2008).
- ⁶A. Lorenz, N. Zimmermann, S. Kumar, D. R. Evans, G. Cook, M. Fern, F. Martinez, and H.-S. Kitzerow, *Appl. Opt.* **22**, E1 (2013).
- ⁷W. Guo and B. M. Fung, *J. Chem. Phys.* **95**, 3917 (1991).
- ⁸T. Narasimhaswamy, M. Monette, D. K. Lee, and A. Ramamoorthy, *J. Phys. Chem. B* **109**, 19696 (2005).
- ⁹C. Cramer, T. Cramer, F. Kremer, and R. Stannarius, *J. Chem. Phys.* **106**, 3730 (1997).
- ¹⁰S. Urban, B. Gestblom, W. Kuczynski, S. Pawlus, and A. Wrflinger, *Phys. Chem. Chem. Phys.* **5**, 924 (2003).
- ¹¹W. Kuczynski, B. Zywucki, and J. Malecki, *Mol. Cryst. Liq. Cryst.* **381**, 1 (2002).
- ¹²A. Sanchez-Castillo, M. A. Osipov, and F. Giesselmann, *Phys. Rev. E* **81**, 021707 (2010).
- ¹³F. Jenz, S. Jagiella, M. A. Glaser, and F. Giesselmann, *ChemPhysChem* **17**, 1568 (2016).
- ¹⁴M. A. Osipov and B. I. Ostrovskii, *Cryst. Rev.* **3**, 113 (1992).
- ¹⁵A. de Vries, A. Ekachai, and N. Spielberg, *Mol. Cryst. Liq. Cryst.* **49**, 143 (1979).
- ¹⁶A. de Vries, *J. Chem. Phys.* **71**, 25 (1979).
- ¹⁷H. Yoon, D. M. Agra-Kooijman, K. Ayub, R. P. Lemieux, and S. Kumar, *Phys. Rev. Lett.* **106**, 087801 (2011).
- ¹⁸J. P. F. Lagerwall and F. Giesselmann, *ChemPhysChem* **7**, 20 (2006).
- ¹⁹S. T. Lagerwall, P. Rudquist, and F. Giesselmann, *Mol. Cryst. Liq. Cryst.* **510**, 148 (2009).
- ²⁰A. Sanchez-Castillo, M. A. Osipov, S. Jagiella, Z. H. Nguyen, M. Kaspar, V. Hamplova, J. MacLennan, and F. Giesselmann, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **85**, 061703 (2012).
- ²¹Y. Yamada, A. Fukuda, J. K. Vij, N. Hayashi, and T. Ando, *Liq. Cryst.* **4**, 864 (2015).
- ²²J. G. Gay and B. J. Berne, *J. Chem. Phys.* **74**, 3316 (1981).
- ²³C. P. J. Schubert, A. Bogner, J. H. Porada, K. Ayub, T. Andrea, F. Giesselmann, and R. P. Lemieux, *J. Mater. Chem. C* **2**, 4581 (2014).
- ²⁴K. M. Mulligan, A. Bogner, Q. Song, C. P. J. Schubert, F. Giesselmann, and R. P. Lemieux, *J. Mater. Chem. C* **2**, 82708276 (2014).
- ²⁵M. F. Palermo, A. Pizzirusso, L. Muccioli, and C. Zannoni, *J. Chem. Phys.* **138**, 204901 (2013).

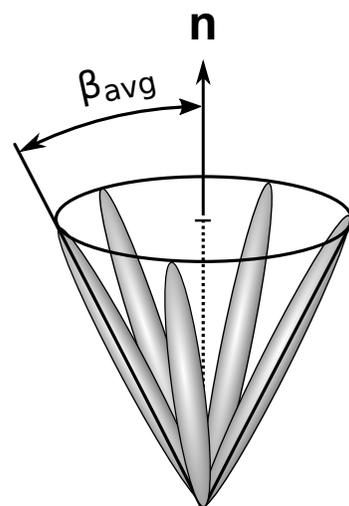
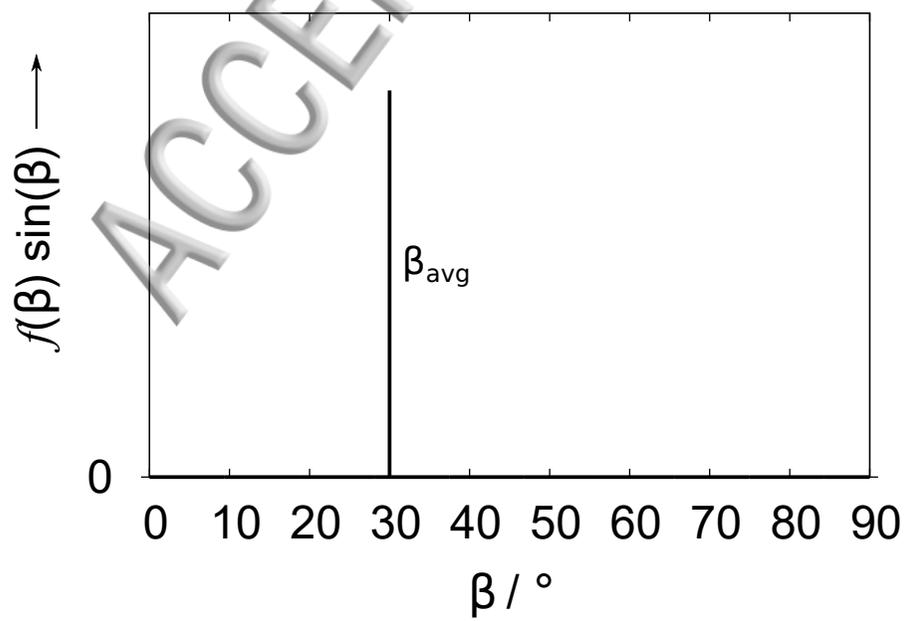
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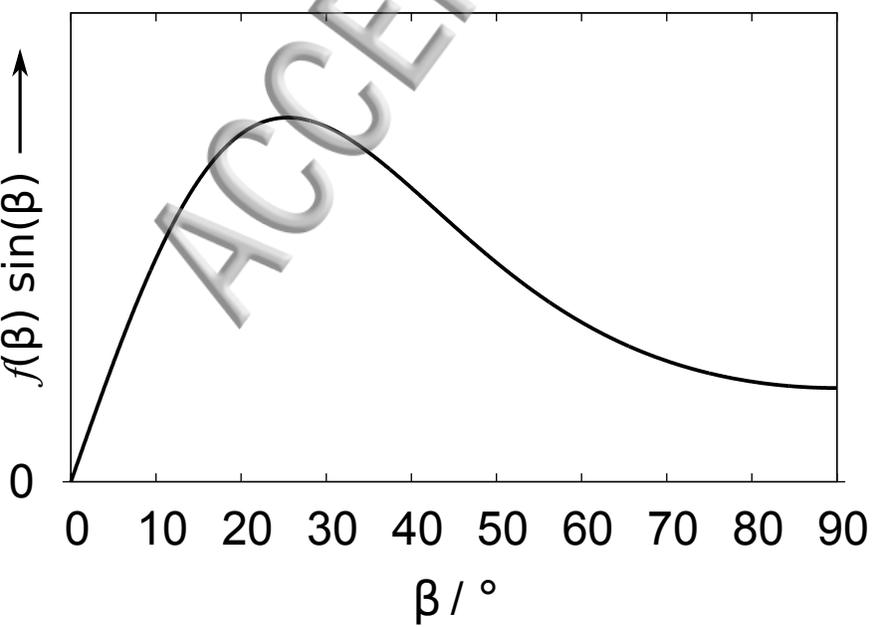
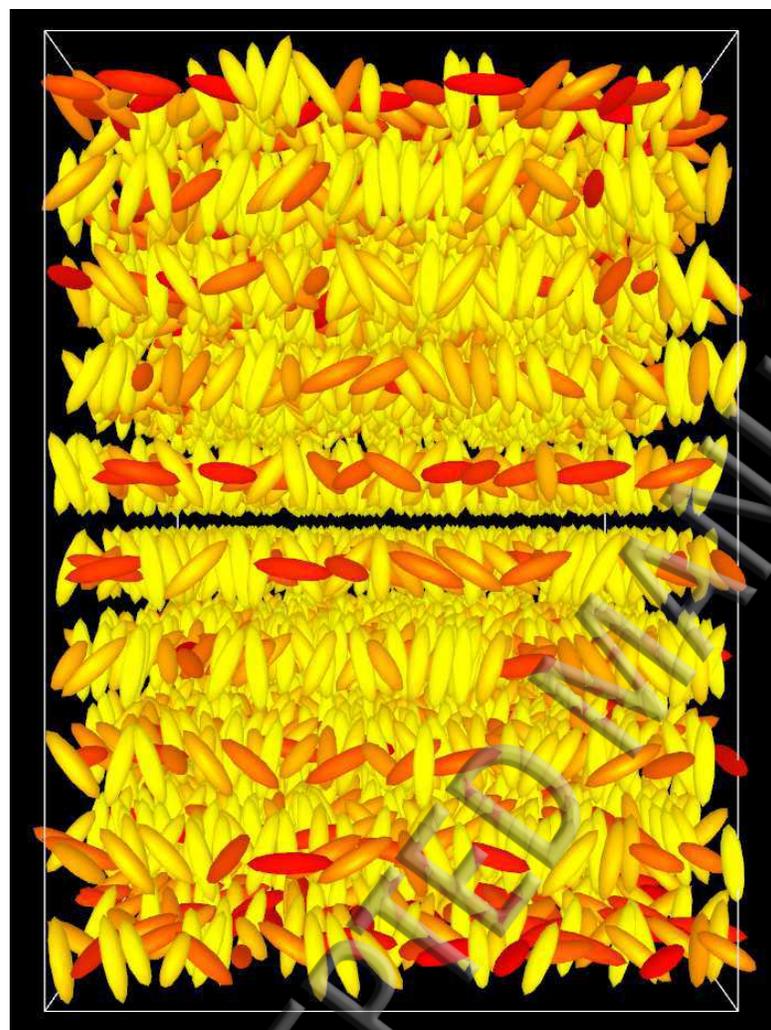
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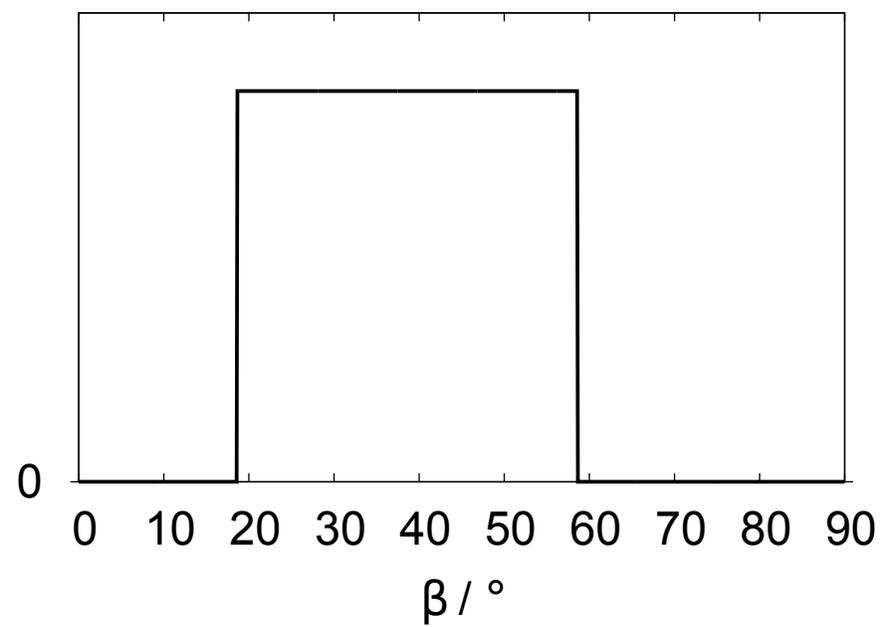
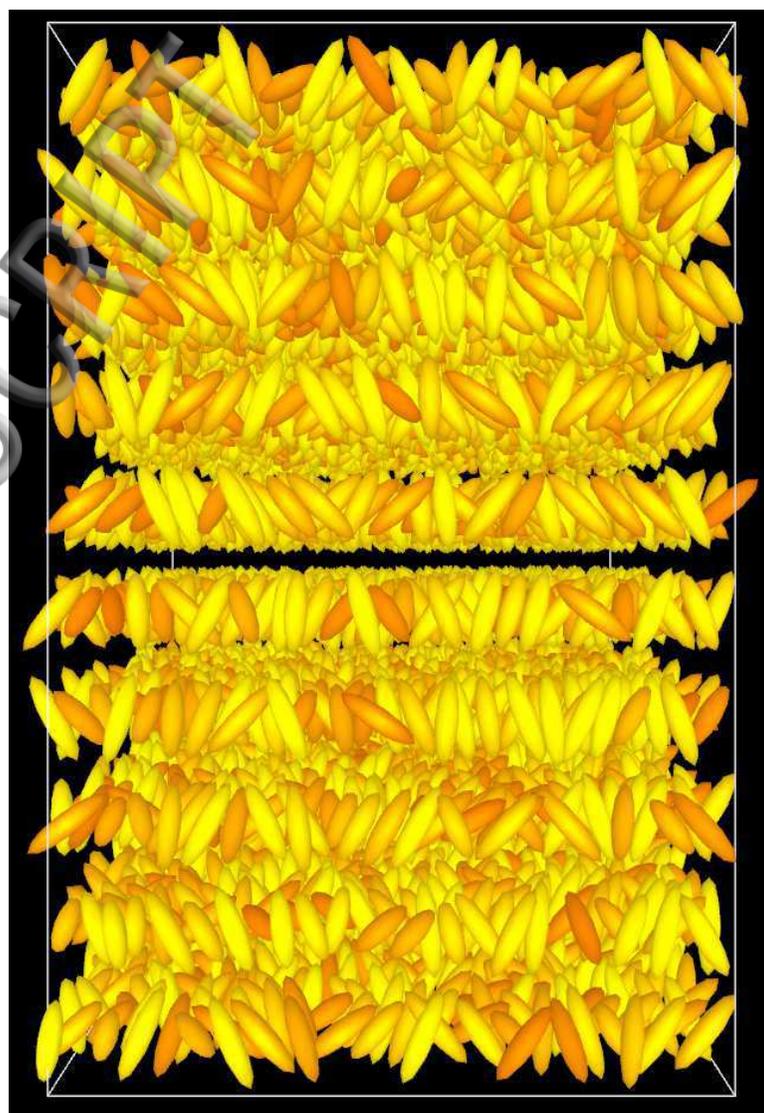
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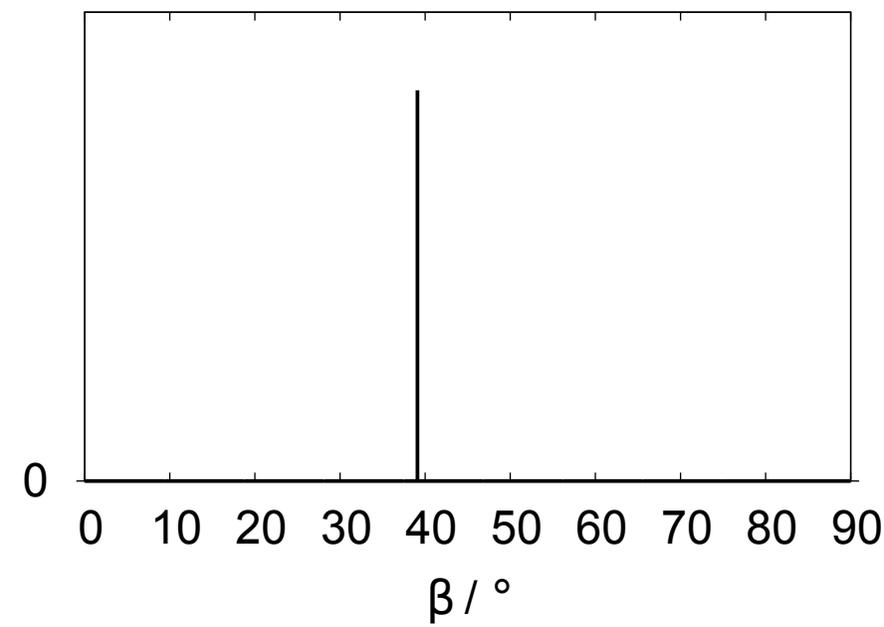
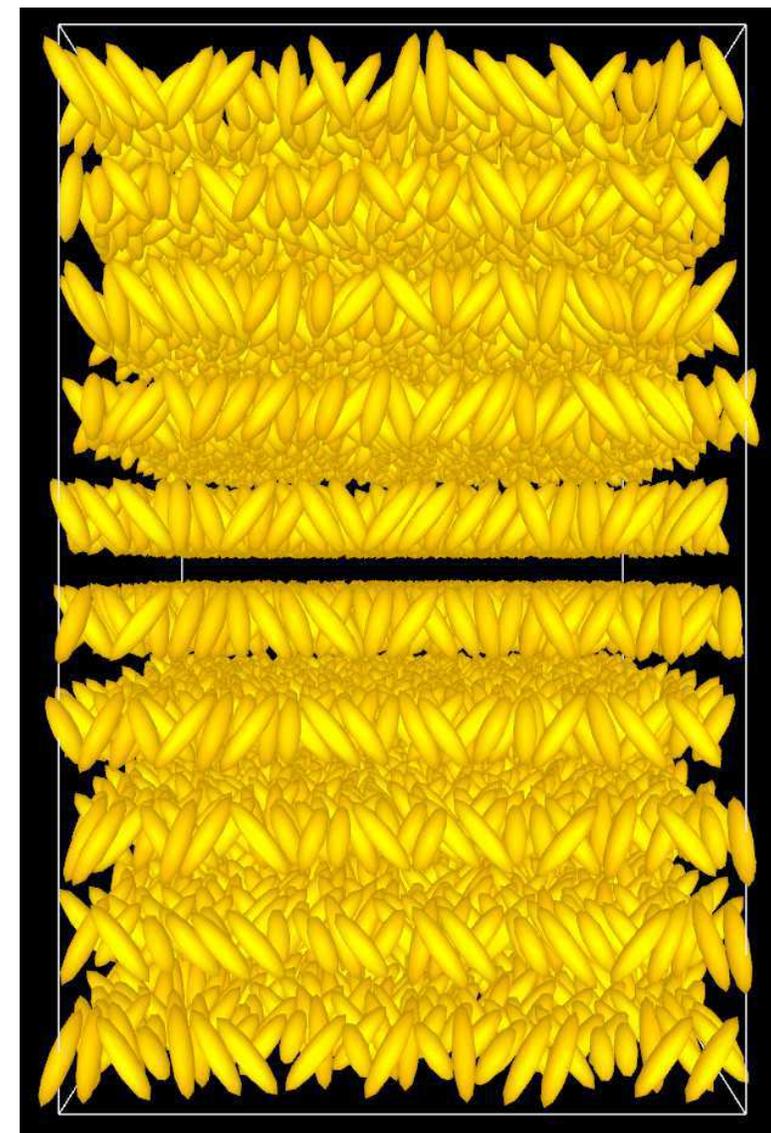
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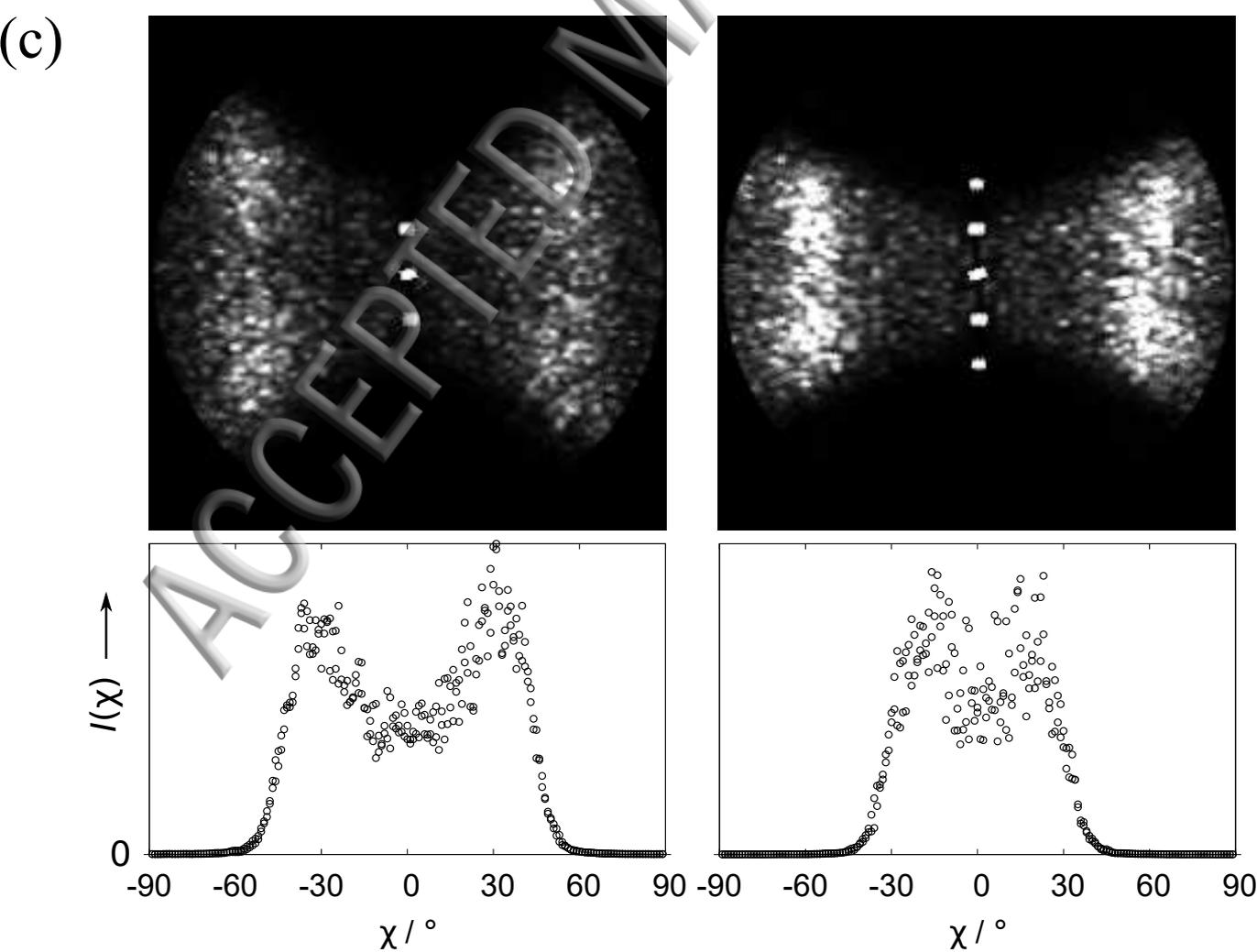
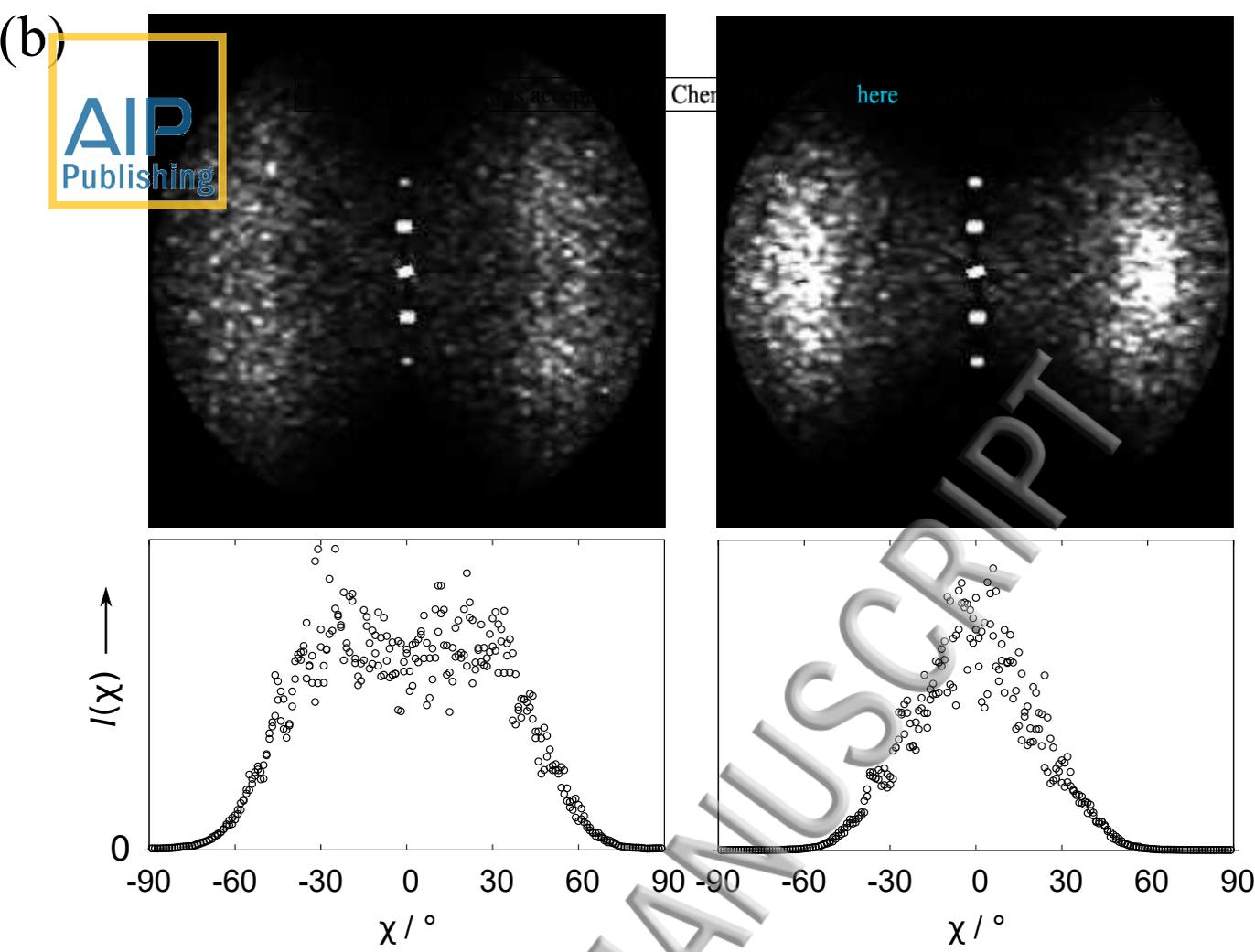
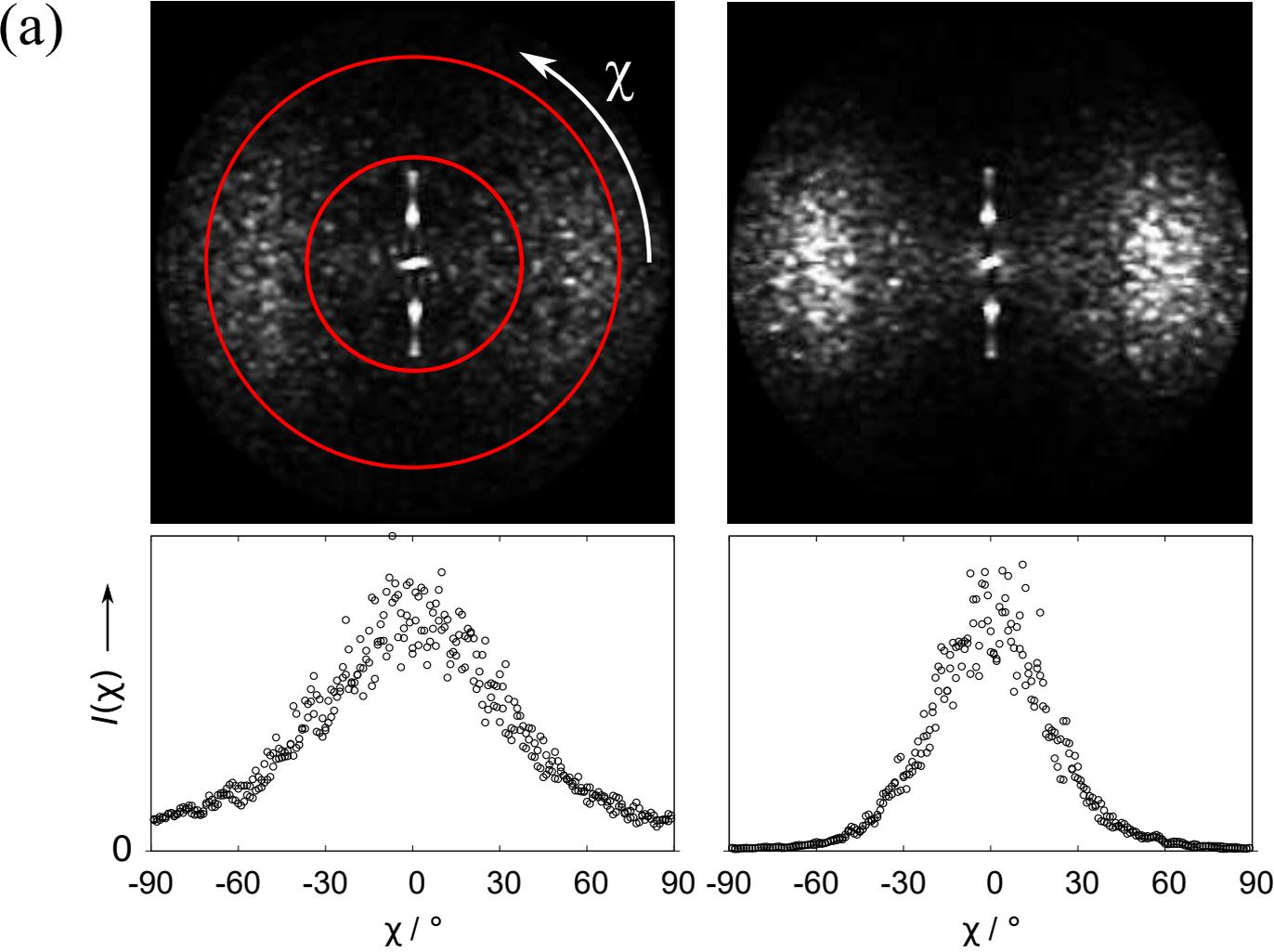


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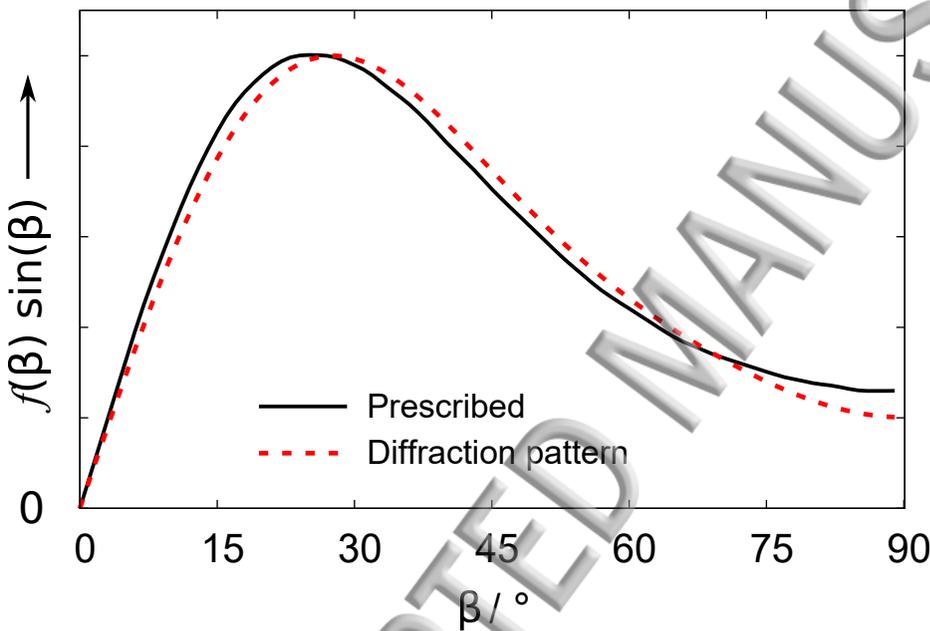


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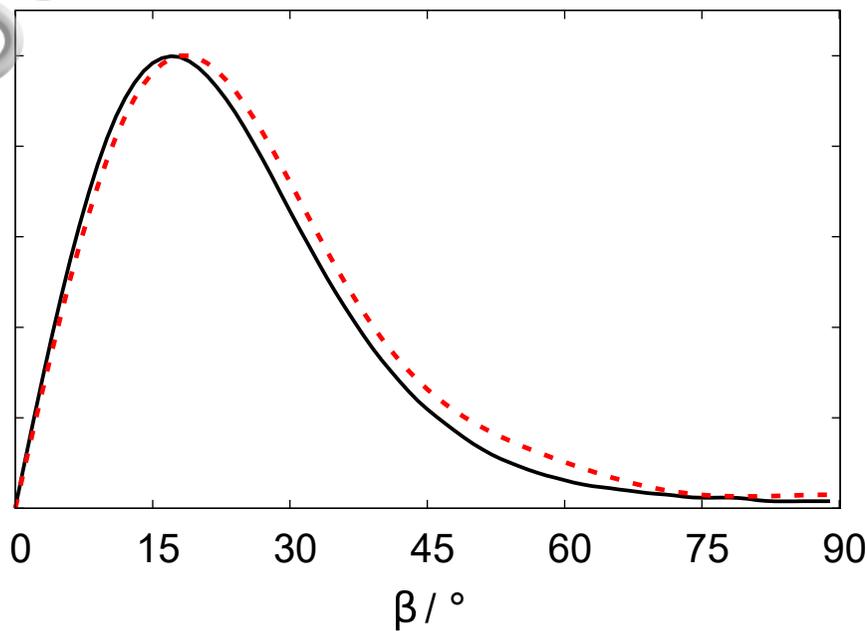




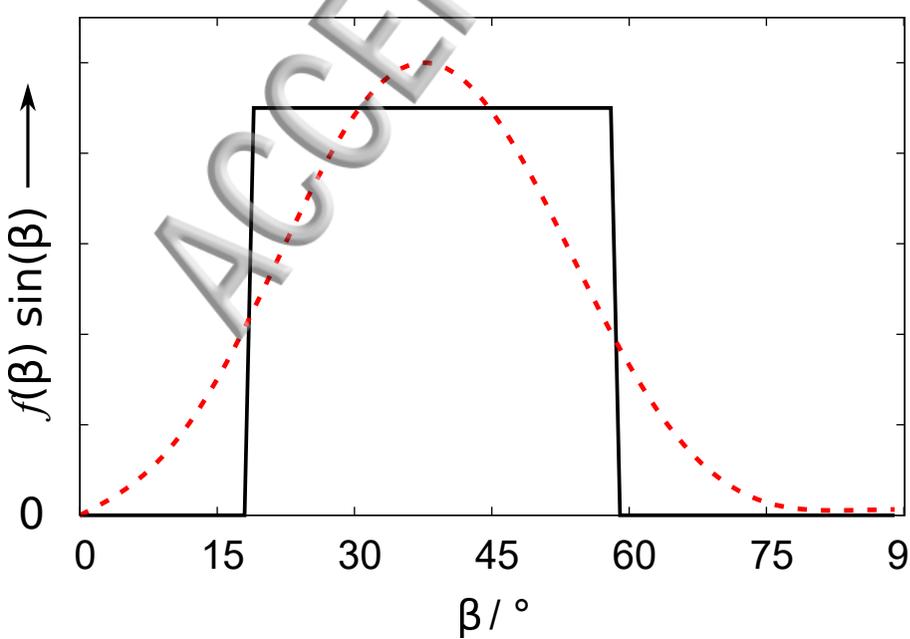
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