

# Manual of Raman orientation distribution script

Leo Svenningsson\* Lars Nordstierna

*Department of Chemistry and Chemical Engineering,  
Chalmers University of Technology, Göteborg, Sweden*

Phone: +46 (0)76 1189261

E-mail: leo.svenningsson90@gmail.com

## 1 Requirements

The Raman orientation distribution script was created using Matlab R2016b. Earlier versions are not guaranteed to work.

## 2 Introduction

Orientation distributions of partially oriented solids can be investigated using polarized Raman spectroscopy. The manual will explain how to use the orientation distribution matlab script for this purpose and includes a brief explanation of the theory and experiment setup.

The experimental method is that of Yang and Michielsen<sup>[5, 6]</sup> originally conceived by Bower<sup>[1]</sup> For more information on the theoretical background, please consider the referred articles.<sup>[1-3, 5, 6]</sup>

The model describes the orientation distribution as linear combinations of the Raman tensor in its principal axis system weighted by  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  order parameters for any singular Raman mode. The orientation distribution function, ODF, is described as Legendre polynomial functions weighted by

the order parameter as in:

$$f(\theta) = \frac{1}{2\pi} \sum_{\ell=0}^{\infty} \left( \ell + \frac{1}{2} \right) \cdot \langle P_{\ell} \rangle \cdot P_{\ell}(\cos \theta) \quad (1)$$

The Raman experiment is limited to  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ . By simply plotting the sum of the two contributions in eq.(1) could lead to questionable results such as negative distributions. It is preferable to instead use the order parameters as fitting constraints for an assumed ODF that can better describe the orientation of the fiber. We use and compare the "wrapped Lorentzian" ODF, "Most Probable" ODF and the "Gaussian" ODF, respectively. The wrapped Lorentzian ODF is given by

$$f_{wL}(\theta) = \frac{1}{\pi} \cdot \frac{\sinh \gamma}{\cosh \gamma + \cos 2\theta} \quad (2)$$

unconstrained with respect to  $\gamma$ . The Most Probable ODF is given by

$$f_{mp}(\theta) = \frac{e^{\lambda_1 \cdot P_2(\cos \theta) + \lambda_2 \cdot P_4(\cos \theta)}}{\int_0^{\pi} e^{\lambda_1 \cdot P_2(\cos \theta) + \lambda_2 \cdot P_4(\cos \theta)} \cdot \sin \theta \, d\theta} \quad (3)$$

unconstrained with respect to  $\lambda$ . The Gaussian ODF is given by

$$f_{Gauss}(\theta) = \frac{e^{-m \cdot (\theta - \phi)^2}}{\int_0^{\pi/2} e^{-m \cdot (\theta - \phi)^2} \cdot \sin \theta \, d\theta} \quad (4)$$

with the constraints  $0 < m$  and  $0 \leq \phi \leq \pi/2$ .

## 2.1 wrapped Lorentzian polarized Raman

The Bowers polarized Raman experiment is modified to employ a wrapped Lorentzian instead of the sum of weighted Legendre polynomials. This enables us to perform the experiment with only integrals of  $I_{33}^{BS}(0)$ ,  $I_{33}^{BS}(90)$ ,  $I_{31}^{BS}(0)$ ,  $I_{31}^{BS}(90)$ ,  $I_{31}^{BS}(45)$  but with the drawback that the resulting 4 sets of equations has to be solved numerically with a chosen initial condition.

$$\sum \alpha_{ij} \alpha_{pq} = N_0 \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} f(\theta) \alpha_{ij} \alpha_{pq} d\theta d\psi d\phi \quad (5)$$

### 3 Integrals of Raman modes

The script requires integrals of  $I_{33}^{BS}(0)$ ,  $I_{33}^{BS}(90)$ ,  $I_{31}^{BS}(0)$ ,  $I_{31}^{BS}(90)$ ,  $I_{31}^{BS}(45)$ ,  $I_{21}^{RAS}(0)$ ,  $I_{23}^{RAS}(0)$  as well as the instrumental factor IF. Notations BS and RAS refer to back scattering and right angle scattering experiments, respectively. The sub scripts in  $I_{ij}^{BS}(\beta)$  and  $I_{ij}^{RAS}(\beta)$  refer to the polarization of the analyzer (i) and the incident beam (j) visualized in *figure 1*. The variable  $\beta$  refers to orientation of the fiber in the  $\mathbf{x}_3$  and  $\mathbf{x}_2$  plane.

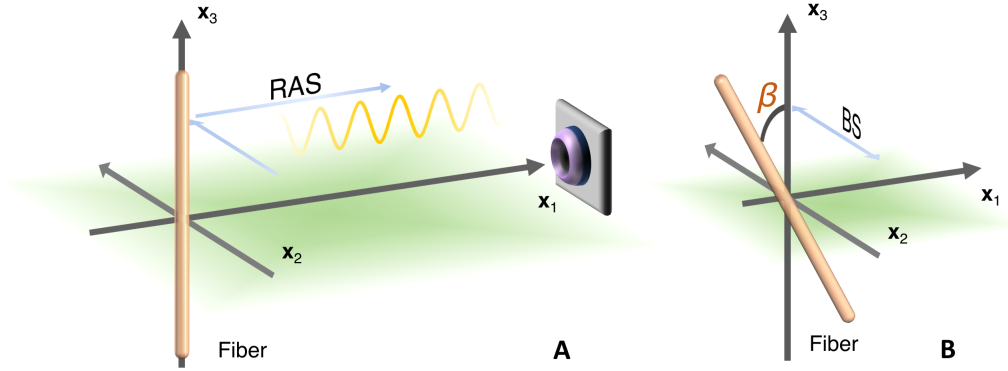


Figure 1: Schematic of the Right Angle Scattering experiment (A) with the laser entering in the  $\mathbf{x}_2$  direction and exiting in the direction of  $\mathbf{x}_1$ . Back Scattering experiment (B) with the laser entering in the  $\mathbf{x}_2$  direction and exiting at  $\mathbf{x}_2$ . The fiber is positioned in the  $\mathbf{x}_1$ - $\mathbf{x}_3$  plane with an angle  $\beta$  that is parallel to  $\mathbf{x}_3$  when  $\beta = 0$ .

The instrumental factor is determined by measuring the depolarization ratio of a substance and divide it by its known depolarization ratio. An example would be butyl benzoate, 2-butanone,  $\text{CCl}_4$  and amorphous PET as reference materials, as in Yang and Michielsen. The depolarization ratios repeated here from Yang's thesis.<sup>[4, 6]</sup>

$$F(\nu) = \frac{\rho_{known}}{\rho_{exp}} \quad (6)$$

Table 1: Depolarization ratios

Chemicals	Raman Shift(cm <sup>-1</sup> )	Depolarization ratio ( $\rho_{known}$ )
Butyl Benzoate	618	0.73
2-Butanone	1716	0.2
CCl <sub>4</sub>	218	0.75
	314	
	759	
	788.9	
	808.7	
Amorphous PET	631	0.743
	1616	0.517

$$\rho_{exp} = \frac{I_{31}}{I_{33}} \quad (7)$$

The integral values and IF are then inserted in the RamanData.txt file by replacing the existing comma delimited example values.

## 4 How to run RamanODF

Fill in your Raman Intensities (integrals) with their corresponding standard deviation in RamanData.txt.

With either the example RamanData.txt or your own results you can now run RamanODF.m. Matlab will after a few seconds display the  $P_2$  and  $P_4$  values with their respective standard deviation.

Reconstruction of the orientation distribution functions are plotted with the wrapped Lorentzian, Most Probable and Gaussian approach, respectively. The wrapped Lorentzian constant  $\gamma$  are saved as "gamma". The Most Probable ODF constants  $\lambda_1$  and  $\lambda_2$  are saved as "lambda1and2". The Gaussian constants  $m$  and  $\phi$  are saved as "mandphi".

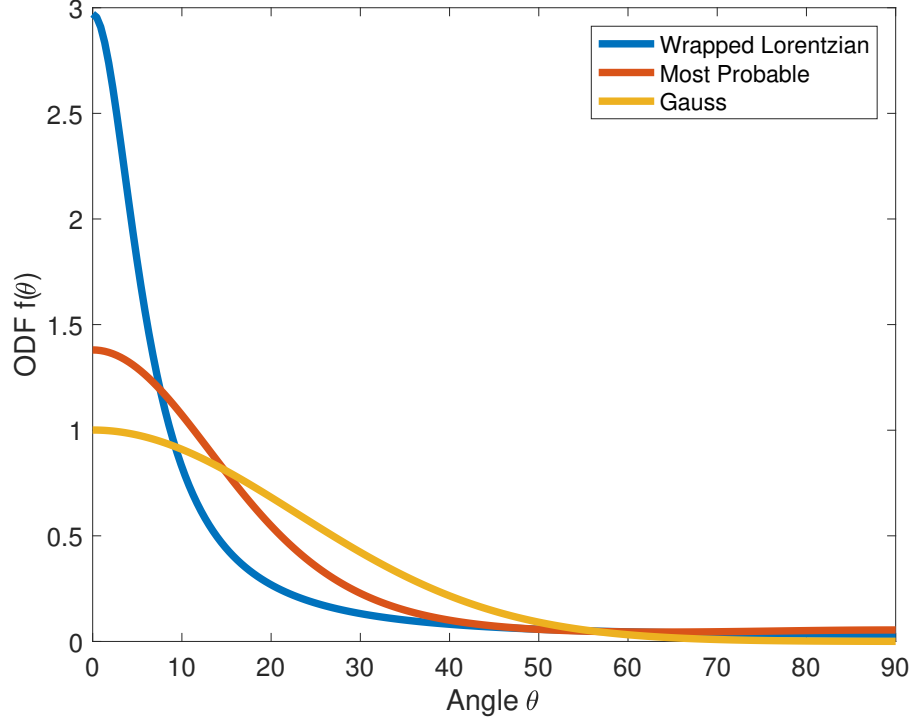


Figure 2: ODF reconstruction with P2=0.51 and P4=0.31 experimentally received from Bowers method.

## 5 How to run WL\_RamanODF

Fill in your Raman Intensities (integrals) with their corresponding standard deviation in WL\_RamanData.txt.  $I_{21}^{RAS}(0)$ ,  $I_{23}^{RAS}(0)$  can be set to zero for the wrapped Lorentzian experiment since they are not used.

The iterative solver requires initial conditions and could be needed to modified for depending on your experiment.  $\gamma$  should be set close to the expected value, for our example it is set to 0.4. The choice of the three  $\alpha$  requires a little more thought. But a good try for stretching modes is to assume  $\alpha_1$  and  $\alpha_2$  are of equal magnitude and opposite sign with  $\alpha_3 > \alpha_{1,2}$ . The example wrapped Lorentzian calculation has  $[\alpha_1, \alpha_2, \alpha_3] = [0.5, -0.5, 1]$ . If no reasonable solution is found, then its likely that you should play around

with the initial conditions.

With either the example RamanData.txt or your own results you can now run RamanODF.m. Matlab will after a few seconds display the  $P_2$  and  $P_4$  values with their respective standard deviation.

Reconstruction of the orientation distribution functions are plotted with the wrapped Lorentzian, Most Probable and Gaussian approach, respectively. The wrapped Lorentzian constant  $\gamma$  are saved as "gamma". The Most Probable ODF constants  $\lambda_1$  and  $\lambda_2$  are saved as "lambda1and2". The Gaussian constants  $m$  and  $\phi$  are saved as "mandphi".

## 6 FAQ

**I get a message that there are no physical solutions.**

There exist an inequality, provided by Bower<sup>[2]</sup>, that describes the limitations of  $P_2$  and  $P_4$  in order for higher orders to exist. If this happens, the result are deemed not physical and you should revisit your experiments.

**Can i force specific values of  $P_2$  and  $P_4$  from other experiments?**

Yes! There is a section in RamanODF.m where you can uncomment forced  $P_2$  and  $P_4$  calculations.

## References

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- [3] M. J. Citra, D. B. Chase, R. M. Ikeda, and K. H. Gardner. Molecular orientation of high-density polyethylene fibers characterized by polarized raman spectroscopy. *Macromolecules*, 28:4007–4012, 1995.

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