Manual of Raman orientation distribution script

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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 very brief explanation of the theory and experiment setup.

The experimental method is that of Yang and Michielsen's complete (tilt) method[5, 6]. For more information on the theoretical background, please consider the referred articles.[1–3, 5, 6]

The complete (tilt) method 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:

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

2.1 Wrapped Lorentzian based analysis of polarized Raman scattering

The complete (tilt) method polarized Raman experiment is modified to employ a wrapped Lorentzian function instead of the sum of weighted Legendre polynomials, through Equation (2). This enables us to perform the experiment with fewer integrals, thus removing the need to perform tedious right angle scattering experiments. The resulting 4 sets of equations has to be solved numerically with a chosen initial condition.

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

The wrapped Lorentzian ODF is given by

$$f_{wL}(\theta) = \frac{1}{\pi} \cdot \frac{\sinh\gamma}{\cosh\gamma + \cos 2\theta} \tag{3}$$

3 Experimental

The complete (tilt) method "RamanODF.m" script requires the 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.

The wrapped Lorentzian based analysis "WL_RamanODF.m" requires fewer measurements $I_{33}^{BS}(0)$, $I_{33}^{BS}(90)$, $I_{31}^{BS}(0)$, $I_{31}^{BS}(90)$, $I_{31}^{BS}(45)$ and the instrumental factor IF.

Notations BS and RAS refer to back scattering and right angle scattering experiments, respectively. The sub scrips 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 β refers to orientation of the fiber in the $\mathbf{x}_3$ and $\mathbf{x}_2$ plane.

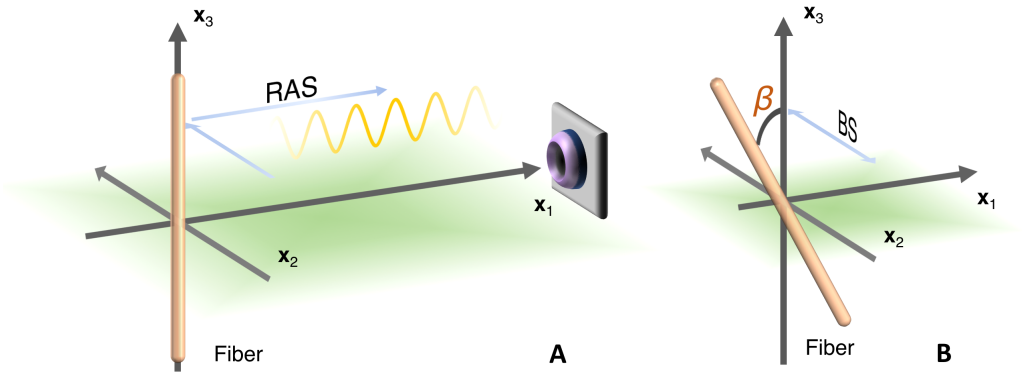

Figure 1: Schematic of the Right Angle Scattering experiment (A) with the incident laser in the $\mathbf{x}_2$ direction and data collection in the direction of $\mathbf{x}_1$. Back Scattering experiment (B) with the incident laser in the $\mathbf{x}_2$ direction and data collection at $\mathbf{x}_2$.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

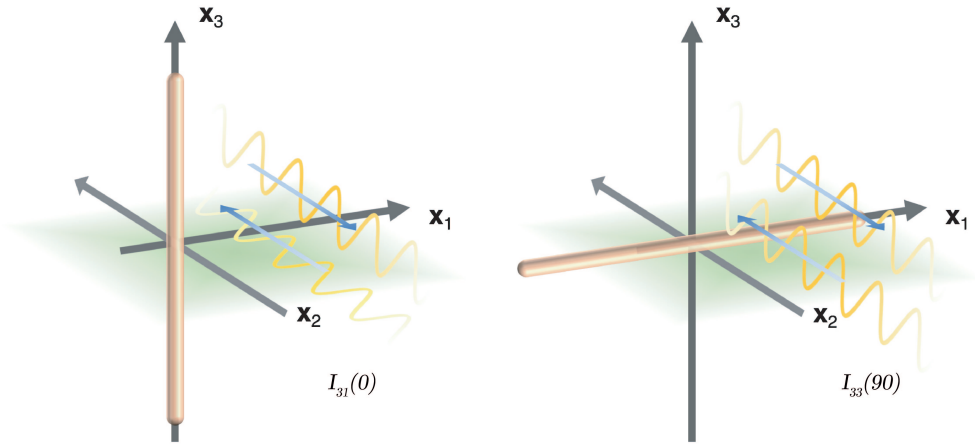

Figure 2: Schematic of the I_{31}^{BS} (0) and I_{33}^{BS} (90) configurations, with polarized laser in the $\mathbf{x}_2$ direction.

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, CCl_4 as reference materials,

Table 1: Depolarization ratios

Chemicals	Raman Shift(cm^{-1})	Depolarization ratio (ρ_{known})
Butyl Benzoate	618	0.73
2-Butanone	1716	0.2
CCl_4	218 314 759 788.9 808.7	0.75
Amorphous PET	631	0.743
	1616	0.517

used by Yang and Michielsen. The depolarization ratios repeated here from Yang's thesis.[4, 6]

$$F(\nu) = \frac{\rho_{known}}{\rho_{exp}} \tag{4}$$

$$\rho_{exp} = \frac{I_{31}}{I_{33}} \tag{5}$$

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

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 along with the ODF reconstruction, if P_2 and P_4 is withing "physical limits"[2].

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. γ should be set close to the expected value, for our example it is set to 0.4. The choice of the three α requires a little more thought. But a good try for stretching modes is to assume α_1 and α_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. Later versions will include a more sophisticated method to choose 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.

6 ODF reconstruction

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 the "wrapped Lorentzian" ODF, "Most Probable" ODF and the "Gaussian" ODF, respectively, for reconstruction in both "WL_RamanODF.m" and "RamanODF.m". The wrapped Lorentzian ODF is given by

$$f_{wL}(\theta) = \frac{1}{\pi} \cdot \frac{\sinh \gamma}{\cosh \gamma + \cos 2\theta} \tag{6}$$

unconstrained with respect to γ. The Most Probable ODF is given by

$$f_{mp}(\theta) = \frac{\mathrm{e}^{\lambda_2 \cdot P_2(\cos\theta) + \lambda_4 \cdot P_4(\cos\theta)}}{\int_0^{\pi} \mathrm{e}^{\lambda_2 \cdot P_2(\cos\theta) + \lambda_4 \cdot P_4(\cos\theta)} \, \mathrm{d}\theta} \tag{7}$$

unconstrained with respect to λ. The Gaussian ODF is given by

$$f_{Gauss}(\theta) = \sqrt{m/\pi} \cdot \mathrm{e}^{-m \cdot (\theta - \phi)^2} \tag{8}$$

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

Reconstruction of the orientation distribution functions are plotted with the wrapped Lorentzian, Most Probable and Gaussian functions, respectively. The wrapped Lorentzian constant γ are saved as "gamma". The Most Probable ODF constants λ_1 and λ_2 are saved as "lambda1and2". The Gaussian constants m and ϕ are saved as "mandphi". Reconstruction is automatically enabled in both "WL_RamanODF.m" and "RamanODF.m".

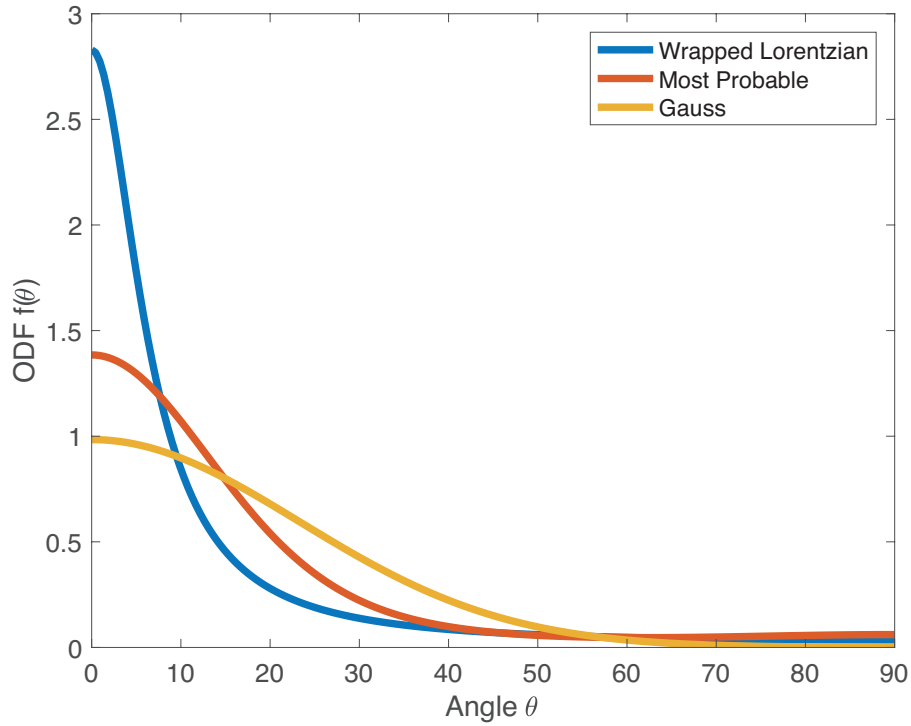

Figure 3: ODF reconstruction with P2=0.50 and P4=0.31 experimentally received from the complete (tilt) method.

7 FAQ

I get a message that there are no physical solutions.
There exist an inequality, provided by Bower[2], 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.
What can i do if ODF reconstruction does not work
If one or more P_ℓ parameter set give strange ODF reconstructions results: Try changing the initial conditions for the ODF reconstruction. Alterna-

tively, disable the malfunctioning reconstruction by "commenting" that section. The Gaussian model has the highest risk of providing strange solutions, since it is not a periodic function.

Change log

V 1.0

Initial commit to github

References

[1] D. I. Bower. Investigation of molecular orientation distributions by polarized raman scattering and polarized flourescence. *Journal of polymer science*, 10:2135–2153, 1972.

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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.

[4] S. Yang. Analysis of poly(ethylene terephthalate) fibers using polarized raman microscopy. *PhD. Thesis, Georgia Institute of Technology*, 2002.

[5] S. Yang and S. Michielsen. Determination of the orientatin parameters and the raman tensor of the 998 cm^{-1} band of poly(ethylene terephthalate). *Macromolecules*, 35:10108–10113, 2002.

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