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LEADING CONTRIBUTION

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The use of rotation matrices in the mathematical description of molecular orientations in polymers

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Abstract The orientational distribution of chain segments or crystals in polymeric materials is most conveniently described as a series expansion of rotation matrix elements. Rotation matrices are representations of rotation operators, and their elements form a complete set of orthogonal functions. Their use in the mathematical description of molecular orientations therefore yields the advantage that the moments in the series expansion of the orientational distribution, also called order parameters, are the averages of the rotation matrix elements themselves. Furthermore, rotations between molecular and macroscopic frames can easily be carried out to link molecular orientation to a macroscopic observable. In the third place, various symmetries reduce the number of non-vanishing order parameters in a straightforward way. In the case of fiber symmetry and axially symmetric molecular elements, the rotation matrix elements reduce to Legendre polynomials.

The mathematical formalism can be applied to any of the various techniques used to measure the degree of orientation in polymers. IR-dichroism and birefringence yield order parameters of rank 2 only. Fluorescence depolarization and polarized Raman scattering yield order parameters of rank 2 and 4. X-ray scattering and NMR may yield order parameters of higher rank, dependent on the symmetry of the system and the experimental accuracy.

From experimentally derived order parameters, the most probable orientational distribution function can be constructed, using the maximum entropy formalism.

Key words Orientation – orientational distribution function – rotation matrix – Wigner function – order parameter

Introduction

For many years now scientists have been intrigued by the question of how to describe the micro-structure of polymeric materials. Much of the research efforts on polymer morphology has been influenced by the peculiar folded way polymer chains seem to be incorporated into crystals. Simultaneously, much work has been directed towards the understanding of the effect of external deformation on the alignment of chains in the material, and its resultant anisotropic properties.

This latter topic has led to an enormous number of papers that in one way or another try to characterize the amount of chain orientation in the system. In fact, as soon as it was realized that polymers consist of long molecular chains, somehow partly organized in crystals, the relation between molecular orientation and mechanical properties was perceived, especially in the field of natural and synthetic fibers [1].

Although anisotropy in polymeric materials seems to be a subject of prime importance at the present time, not much uniformity exists in its mathematical description. Various orientational parameters have been used and especially all sorts of notations. In general, however, most authors seem to agree that the orientation should be described in terms of a statistical distribution of the orientation of specific subelements with respect to a macroscopic frame of reference. This orientational distribution function (for convenience abbreviated as ODF) is most often written as a series expansion of certain mathematical functions, of which the prefactors are the parameters that are to be experimentally determined. Historically, this approach dates back to Müller [2, 3] who realized that if the spatial distribution of plane normals from an x-ray experiment can graphically be represented on the surface of a sphere, the mathematical description should be in terms of spherical harmonics. It seems, however, that no connection was made between the first even moment in this expansion and the orientation function that Hermans defined in connecting birefringence results with chain orientation [1, 4]. Only much later did Roe and Krigbaum [5–9] expand these early views in a comprehensive description of the orientational distribution of crystals as extracted from x-ray pole figure analysis.

Their papers together with the extensive work by Stein [10, 11] and Ward [12, 13] and their coworkers have laid the basis of what we now know about how the various experimental techniques give quantitative information about molecular orientations. This paper does not aim at expanding this knowledge, but instead reviews the various contributions to the mathematical description of orientations, and secondly, it attempts to bring some order to the diversity of notation. In doing so, it is natural to fall back on the formalism that describes the effect of rotations on physical quantities. Rotation matrices are the matrix representations of the rotation operators from the three-dimensional rotation group. These rotation operators play an important part in quantum mechanics and are closely related to the angular momentum [14]. The principles of the formalism presented in this report are hence to be found in elementary textbooks on the angular momentum in quantum mechanics [15–18]. Rotation matrices represent rotations in 3-D space with respect to a spherical basis. The elements of such a matrix are just like elements of Cartesian rotation matrix goniometric functions of Euler angles. It is, however, possible to write any physical quantity in terms of a spherical tensor, a tensor that transforms under a rotation just like a rotation matrix itself. This means that using the rotation matrix formalism a straightforward mathematical formalism is adopted to express a physical quantity with respect to any frame. Furthermore, since the rotation matrix elements form a complete set of orthogonal functions, the ODF is most conveniently expanded as a series of rotation matrix elements (these elements are also known as Wigner functions or generalized spherical functions). Now any physical measurement will directly lead to ensemble averages of these Wigner functions. Due to the orthogonality of the rotation matrices, these averages turn out to be the moments of the series expansion, and are called "order parameters". This orthogonality, together with the group theoretical properties of rotation matrices, lead to a complete mathematical system that covers most of the problems related to the description of molecular orientations.

The theory has successfully been applied to a variation of techniques to describe molecular orientations, such as x-ray scattering, birefringence, IR dichroism, polarized Raman scattering, fluorescence depolarization, and NMR, and is in principle applicable to any technique in which a molecular quantity is measured that is orientation dependent. The theory has also been used to describe the mechanical anisotropy in polymer systems [19, 20], so that orientational parameters can directly be linked to mechanical properties.

Although the mathematical theory discussed in this report is rather complex, the use of rotation operators yields certain advantages which can be summarized as follows:

1) the results of a large number of experimental techniques are interpreted along similar lines, making it possible to correlate the results obtained in these different ways;
2) the consequences of molecular (or crystal) symmetry and of (statistical) sample symmetry can easily be incorporated into the theory;
3) molecular and macroscopic orientations can be mathematically coupled to one another in a straightforward manner.

The various experimental methods yield one or more order parameters. These are a measure of the degree of order: in the case of an isotropic (unordered) distribution of polymer chains or crystals the order parameters are all zero, in the case of perfect orientation the principal order parameters are one. In order to be able to determine the overall ODF, all of the order parameters of the series expansion have to be known. In principle, they can be determined by means of wide-angle x-ray scattering and NMR, but in practice only a limited number will be determined, from which the ODF can then be estimated.

In the present report no distinction is made between amorphous and crystalline orientations. Which of the two is measured will depend on the experimental method used. In general, it is difficult to draw a sharp distinction with spectroscopic methods such as IR, Raman and NMR, because the recorded spectra will include overlapping bands. X-ray scattering in semi-crystalline polymers yields specific information on the crystalline phase, but correction for an (ordered) amorphous background scattering has to be made. Fluorescence depolarization and ESR provide specific data on the amorphous phase because these methods usually make use of probe or tracer molecules, which lodge in the amorphous phase. Birefringence yields an average orientational order of both the amorphous and crystalline fractions in semi-crystalline materials.

It is important to realize that in general with different experimental techniques different molecular information is obtained. Orientation within the crystalline phase may be different when detected with x-ray or Raman scattering, since (e.g., in PE) all-trans sequences in the amorphous phase may contribute to the crystalline Raman intensity, while being invisible for x-ray scattering [21]. Measurements of the (amorphous) second-rank order parameter from birefringence is known to yield quite large differences with results obtained from fluorescence studies [22, 23]. Thus, the mathematical description does not account for the specific physical origin of the orientational information. It simply assumes that localized rigid subelements exist that independently contribute to the measured macroscopic quantity. Orientational correlations between neighboring subelements are not taken into account. Furthermore, in most of the cases mentioned, intrinsic information is needed, such as crystal unit cell dimensions, transition dipole moment directions or derived polarizability tensor elements. These will be subject to experimental error and together with symmetry assumptions may influence the final results.

No allowance is made for reorientational molecular motion in polymers in this report. This is on the whole justifiable in the case of most techniques, which are only sensitive to motion with very short intrinsic time ranges (below 10^{-14} s for IR and UV dichroism, x-ray and Raman scattering, between 10^{-7} and 10^{-9} s in the case of fluorescence and ESR). NMR, however, is sensitive to movements in a time range larger than 10^{-6} seconds and in interpreting the results of NMR experiments, we will hence have to assume that either all motion has been quenched (e.g., experiments in liquid nitrogen) or that the movements are so fast that it is justifiable to take the average of all allowed orientations. In all other cases a model should be incorporated that takes into account the effects of reorientational motion. Such a theory of molecular motion can in principle be directly incorporated into the theory presented here, in particular because the solutions of the equations describing reorientations are precisely the aforementioned rotation matrix elements [24–26].

The first part of this report discusses a general theoretical background of the description of molecular orientations. For a simple start, it is first assumed that systems with uniaxial statistical symmetry are studied and that molecular elements (i.e., molecules, chain segments or crystals) are axially symmetric. This is followed by a more general approach, in which the rotation matrices will be introduced. At the end of part II a method is presented with which the most probable ODF can be constructed using only a small number of measured order parameters. This method makes use of the maximum entropy formalism.

In the second part the theory is applied to a number of experimental methods. This is extensively illustrated with reference to IR dichroism (for which the theory is the least complicated). The other methods are treated more summarily: it is only indicated how the experimental result in principle determines the order parameters. Experimental difficulties (and any possible impractibility) are ignored for the sake of convenience.

Finally, it should be mentioned that the theory presented here is completely general, and may be applied to any system that contains orientationally (dis) ordered subelements. In fact, the theory has extensively been applied to the texture analysis of metals [27], to the order and dynamics in liquid crystals and lipid membranes [26, 28], to describe disorder in molecular crystals [29], and further to the studies on reorientational motion mentioned before [24–26].

Theoretical background

The orientational distribution function

Before discussing orientational distributions we would first like to define what we mean by an orientation. The orientation of a molecular element M (a molecule, chain segment or crystal) is the spatial position of M relative to a right-handed macroscopic system of axes XYZ, unambiguously defined by three angles: α, β, γ (Euler's angles; see Fig. 1).

If a molecular system of axes xyz is coupled to M then β is the angle between Z and z, α is the angle between X and the projection of z onto the XY plane and γ indicates the degree of (anticlockwise) rotation of M about the z axis, where $\gamma = 0$ when x lies in the plane through z and its projection onto the XY plane (see Fig. 1). The rotation from XYZ to xyz is carried out by first a rotation γ about the Z-axis, then a rotation β about the Y-axis, and, finally, a rotation α about the Z-axis [15].

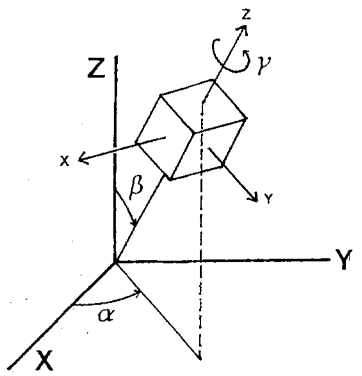


Fig. 1 Definition of Euler's angles α, β, γ which determine the orientation of a molecular element M with a system of axes xyz in a macroscopic system of axes XYZ. The two systems coincide when $\alpha = \beta = \gamma = 0$. Positive γ values are obtained through anticlockwise rotation about the molecular z axis

Different molecular elements in a polymeric material will not usually all have the same orientation: a distribution of orientations will exist. The probability of an element having an orientation between (α, β, γ) and $(\alpha + d\alpha, \beta + d\beta, \gamma + d\gamma)$ is called the orientational probability distribution or the orientational distribution function (ODF) $f(\alpha, \beta, \gamma)$. The orientation with Euler's angles, α, β and γ is also referred to as $\Omega = (\alpha, \beta, \gamma)$.

In principle, it is possible that the form of the ODF is known on the basis of a deformation model, but usually, the form of the function will be unknown. However, we can already stipulate that the ODF must always be positive and normalized:

$$f(\Omega) \geq 0 \quad \text{for all } \Omega \tag{1}$$

$$\int_{\Omega} f(\Omega) d\Omega = \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} f(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma = 1 \ . \tag{2}$$

Uniaxial distribution

To illustrate what an ODF is, we will first, for the sake of simplicity, assume that the ODF is a one-dimensional function and only dependent on the polar angle β (uniaxial symmetry with respect to the Z axis, also known as fibre symmetry, and moreover axially symmetrical molecular elements: $f(\Omega) = f(\beta)$). We could imagine $f(\beta)$ having the form of $\cos^2\beta$. This function reaches its maximum value when $\beta = 0$, i.e., in that case most of the elements lie with their long axis along the Z axis. Perpendicular to it, at $\beta = \pi/2$, $\cos^2\beta$ is zero and there are no elements with this orientation. This seems to be a reasonable guess, but it is not normalized and it incorporates no measure of order. To meet both requirements, we will introduce a parameter P, which determines the width of the ODF, which hence becomes:

$$f(\beta) = 1/2(1 - P + 3P\cos^2\beta) \tag{3}$$

We see that the function is now normalized and when $-1/2 \leq P \leq 1$ it is always positive. Moreover, when $P = 0$, the distribution is independent of β, and hence isotropic, while the maximum degree of order is obtained when $P = 1$ (see Fig. 2). P is called an order parameter.

Of course, the ODF of Eq. (3) presents a large number of drawbacks. The maximum values always lie at 0° and 90° and even for the maximum degree of order ($P = 1$) the distribution is very broad. Both drawbacks can be overcome by adding higher rank terms, such as a $\cos^4\beta$, $\cos^6\beta$, etc. Every extra term adds additional fine structure to the ODF and the sharper the ODF, the more terms are needed. Normalization of this expansion of cosine functions now leads to a series expansion of Legendre polynomials [30]:

$$f(\beta) = \sum_{i=0}^{\infty} a_i P_i(\cos\beta) \tag{4}$$

$P_i(\cos\beta)$ are the Legendre polynomials, defined by:

$$P_i(\cos\beta) = \frac{1}{2_i i!} \frac{d^i}{d(\cos\beta)^i} (\cos^2\beta - 1)^i \tag{5}$$

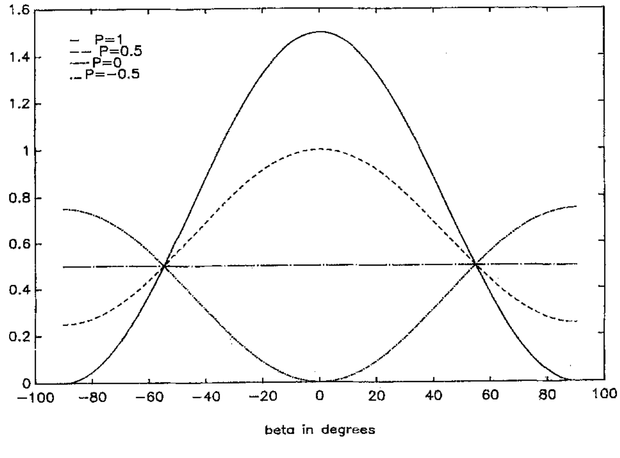
The best known are:

$$P_0(\cos\beta) = 1 \tag{6a}$$

$$P_1(\cos\beta) = \cos\beta \tag{6b}$$

$$P_2(\cos\beta) = 1/2(3\cos^2\beta - 1) \tag{6c}$$

Fig. 2 Orientational distribution function $f(\beta)$ of Eq. (3) for different (indicated) values of the order parameter P. Note that since $f(-\beta) = f(\pi - \beta)$, we may also plot $\beta \in [-90, 90]$ instead of $[0, 180]$



$$P_3(\cos\beta) = 1/2(5\cos^3\beta - 3\cos\beta) \tag{6d}$$

$$P_4(\cos\beta) = 1/8(35\cos^4\beta - 30\cos^2\beta + 3) \tag{6e}$$

$$P_5(\cos\beta) = 1/8(63\cos^5\beta - 70\cos^3\beta + 15\cos\beta) \tag{6f}$$

$$P_6(\cos\beta) = 1/16(231\cos^6\beta - 315\cos^6\beta + 105\cos^2\beta - 5)\,. \tag{6g}$$

We have included uneven powers of $\cos\beta$ in the distribution function in Eq. (4). In practical cases of linear experiments, however, even powers only will appear to play a part. The fact that the ODF is now written as a series expansion of Legendre polynomials offers another advantage. The quantities that we measure when we want to determine the degree of orientation are usually average values: when we are determining a parameter A that is dependent on the molecular orientation, we have to take the average of all possible orientations that may be present in the effective volume that is involved in the experiment. The average value of A is then:

$$\langle A\rangle = \int_0^\pi A(\beta) f(\beta)\sin\beta\, d\beta\,. \tag{7}$$

We would now like to know the average values of the Legendre polynomials $\langle P_j(\cos\beta)\rangle$. These can be easily determined by making use of a particular property of the Legendre polynomials, i.e. their orthogonality:

$$\int_0^\pi P_i(\cos\beta) P_j(\cos\beta)\sin\beta\, d\beta = \frac{2}{(2j+1)}\delta_{ij} \tag{8}$$

and δ_{ij} is the symbol that indicates that $\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$. We find:

$$\begin{aligned}\langle P_j(\cos\beta)\rangle &= \int_0^\pi P_j(\cos\beta)\sum_i a_i P_i(\cos\beta)\sin\beta\, d\beta\\ &= \frac{2}{2j+1} a_j \delta_{ij}\,.\end{aligned} \tag{9}$$

We now see that the weighting factors a_j of the ODF, also known as the moments, are precisely the average values of the Legendre polynomials, with the exception of one constant factor. The ODF now becomes:

$$f(\beta) = \sum_i \frac{2i+1}{2}\langle P_i(\cos\beta)\rangle P_i(\cos\beta)\,. \tag{10}$$

When we now determine a molecular quantity that is dependent on the degree of orientation and we express this dependence in terms of the Legendre polynomials $P_i(\cos\beta)$, the measurement yields one or more moments of the series expansion. We would not have been able to do so if we had expressed the ODF as a series expansion of powers of $\cos^2\beta$. In that case there would not have been a simple relationship between the moments of that series expansion and the average values, $\langle\cos^2\beta\rangle$.

From Eq. (10) it is immediately apparent that an isotropic distribution is obtained when all $\langle P_i(\cos\beta)\rangle = 0$ with the exception of $\langle P_0\rangle = 1$. For a perfect orientation along the Z axis we have $\langle P_i(\cos\beta)\rangle < 1$ for all i. The parameters $\langle P_i(\cos\beta)\rangle$ are called order parameters (or orientation functions or orientation factors). The best known is Hermans' orientation function $f_H = \langle P_2\rangle = 1/2(3\langle\cos^2\beta\rangle - 1)$. Since the order parameters are numbers, $(\cos\beta)$ is usually omitted.

In many practical cases we may assume that the prepared sample that is being studied is symmetrical relative to a plane perpendicular to the axis of uniaxial symmetry (the Z axis, for example the drawing direction). In that case it follows for the ODF that

$$f(\beta) = f(\pi - \beta)\,. \tag{11}$$

Because $P_i\,(\cos(\pi - \beta)) = P_i(-\cos\beta) = (-1)^i P_i(\cos\beta)$ it simply follows from Eqs. (10) and (11) that i is an even number.

Hence, the ODF is now expressed as a series expansion of even Legendre polynomials. On the other hand, for samples that are poled, e.g., in a magnetic or electric field, or for certain minerals, such a symmetry does not exist, and the summation is carried out over uneven powers as well [31].

Order parameters

The order parameters $\langle P_i\rangle$ in Eq. (10) define the ODF completely. However, all of the order parameters have to be known. In practice, wide-angle x-ray scattering yields a direct measure of the ODF, so that in principle all of the order parameters should be extractable. Since the order parameters mostly form a converging series and due to experimental uncertainty, only a limited number is obtained. Other methods yield only a limited number of order parameters: birefringence, IR and UV dichroism yield only $\langle P_2\rangle$, polarized Raman scattering and fluorescence depolarization yield only $\langle P_2\rangle$ and $\langle P_4\rangle$, ESR and NMR usually yield only $\langle P_2\rangle$ and $\langle P_4\rangle$, but in principle higher orders can be obtained. In the second part it will be discussed how the order parameters can be derived from the results of the aforementioned experimental techniques.

Order parameters give an indication of the degree of orientational order in the polymer. As already mentioned, the order parameters are 0 in the case of an isotropic distribution of molecules and 1 in the case of perfect order along the macroscopic Z-axis. When one order parameter, e.g. $\langle P_2\rangle$, has been determined its value may give some indication of the degree of order but this information will not be sufficient. Let us assume, for the purpose of illustration, that $\langle P_2\rangle = 0$ has been determined. This may indicate an isotropic distribution but it is also possible that all of the molecular elements are oriented at an angle of exactly 54.7° with respect to the Z axis (the stretching direction). In that case $\beta = 54.7°$ and because $\cos^2(54.7°) = 1/3$ it follows that $\langle P_2 \rangle = 0$. The determination of $\langle P_2 \rangle$ is here incapable of distinguishing between perfect order and perfect disorder. The higher order parameters are needed to make that distinction. It is therefore not correct to infer an average preferred direction of molecular elements from a determination of $\langle P_2 \rangle$ only. A small number of order parameters does not yield the overall distribution of the molecular elements, but it is possible to make an estimate. This is done by determining the widest possible distribution that is still consistent with the measured order parameters. We will return to this later on.

If one of the order parameters is known, it can be simply calculated that the values of the other order parameters lie within a restricted area [32, 33]. For $\langle P_2 \rangle$ and $\langle P_4 \rangle$ we have $-1/2 \leq \langle P_2 \rangle \leq 1$ and $-3/7 \leq \langle P_4 \rangle \leq 1$ and because $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are both linear combinations of $\langle \cos^2 \beta \rangle$ and $\langle \cos^4 \beta \rangle$, we may argue from:

$$\langle \cos^2 \beta \rangle^2 \leq \langle \cos^4 \beta \rangle \leq \langle \cos^2 \beta \rangle \tag{12}$$

that we have:

$$\langle P_4 \rangle \geq 1/18(35\langle P_2 \rangle^2 - 10\langle P_2 \rangle - 7 \tag{13}$$

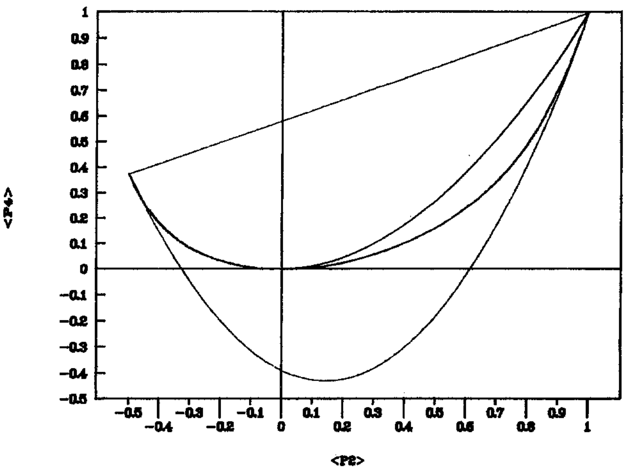
$$\langle P_4 \rangle \leq 1/12(5\langle P_2 \rangle + 7) \tag{14}$$

These two limits are indicated in Fig. 3.

Similar relationships can also be derived for other order parameters [32, 34]. The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ corresponding to Eq. (13) (with the inequality sign replaced by =) indicate perfect order, i.e., all of the molecular elements are oriented towards the Z axis at a fixed angle. For the perfect order where $\langle P_2 \rangle = 0$, we see that $\langle P_4 \rangle = -7/18$, i.e., it is indeed not isotropic. Eq. (14) (with = instead of $\leq$) indicates an ODF with delta function peaks at $\beta = 0$ and $\beta = \pi/2$, at different ratios. The fraction at $\beta = 0$ equals $1/3(2\langle P_2 \rangle + 1)$.

Also indicated in Fig. 3 are the $\langle P_2 \rangle$, $\langle P_4 \rangle$-values that follow from two deformation models that are frequently used, the so called pseudo-affine model [12] following Kratky [35], in which rigid elements are affinely deformed in a matrix, and the Maier–Saupe model [36], which uses an interaction potential based on dispersion forces and which equals the most probable ODF when only $\langle P_2 \rangle$ is known, as discussed later on. We see in the figure that only single lines are followed.

Fig. 3 The $\langle P_2 \rangle - \langle P_4 \rangle$ plane. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can only assume values within the indicated figure. The drawn lines indicate $\langle P_2 \rangle$, $\langle P_4 \rangle$ values for the pseudo-affine deformation model (top) and the Maier-Saupe model (bottom), see text



Non-uniaxial distributions and Wigner functions

So far, we have been discussing uniaxial distributions, but in practice lower symmetries may also occur. The ODF of Eqs. (1) and (2) will now be dependent on α and γ as well as on β. From the above it is clear that expressing the ODF as a series expansion of orthogonal functions has the pleasing effect that the moments of the series expansion are the average values of the corresponding functions. What we are looking for is an orthogonal system of functions which are dependent on α, β and γ and which can be used to construct the ODF. Moreover, the distribution function must reduce to that of Eq. (10) when the dependence on α and γ disappears. It has been found that we can use the elements of the Wigner rotation matrices, also known as Wigner functions, for the above orthogonal functions. They are the matrix representation of the rotation operators of the three-dimensional rotation group. In concrete terms this means that we can directly couple, in a mathematically elegant manner, the orientation dependence of a physical quantity in one system of axes (the macroscopic XYZ system) to its orientation dependence in a different system of axes (the molecular xyz system). This is done via rotation, which transports one system of axes to the other.

The origin of the Wigner functions and their role in quantum mechanics as representations of rotation operators is not discussed at full length here. The reader is referred to the already mentioned textbooks on angular momentum [15–18]. Here, the Wigner functions $D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma)$ are introduced only as complex functions of Euler's angles α, β and γ having a number of favorable properties that make them suitable as means of expressing the ODF. Depending on the value of $L (L \in N)$, the Wigner functions constitute a complete set of $(2L + 1)^2$ orthogonal functions. The indices m and n may assume values between $-L$ and $+L$. An overview of the various properties of rotation matrices can also be found in ref. [37].

The orthogonality of the Wigner functions is expressed by

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} D^{L_1*}_{m_1n_1}(\alpha, \beta, \gamma) D^{L_2}_{m_2n_2}(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma = \frac{8\pi^2}{2L_1 + 1} \delta_{L_1L_2} \delta_{m_1m_2} \delta_{n_1n_2} , \tag{15}$$

where the $*$ stands for the complex conjugate. We can now express a randomly chosen function of Euler's angles as a series expansion of the Wigner functions, in particular the ODF:

$$f(\alpha, \beta, \gamma) = \sum_{L=0}^{\infty} \sum_{m=-L}^{L} \sum_{n=-L}^{L} a^L_{mn} D^L_{mn}(\alpha, \beta, \gamma) . \tag{16}$$

In the same manner as in Eq. (9) it can now be shown that on the basis of the orthogonality, Eq. (15), it follows that:

$$a^L_{mn} = \frac{2L + 1}{8\pi^2} \langle D^{L*}_{mn}(\alpha, \beta, \gamma) \rangle , \tag{17}$$

where the average value is defined as:

$$\langle D^{L*}_{mn}(\alpha, \beta, \gamma) \rangle = \int_{\alpha\beta\gamma} D^{L*}_{mn}(\alpha, \beta, \gamma) f(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma \tag{18}$$

The ODF is hence expressed as:

$$f(\alpha, \beta, \gamma) = \sum_{Lmn} \frac{2L + 1}{8\pi^2} \langle D^{L*}_{mn} \rangle D^L_{mn}(\alpha, \beta, \gamma) . \tag{19}$$

The explicit form of the Wigner functions is given by [15]:

$$D^L_{mn}(\alpha, \beta, \gamma) = \exp(-im\alpha) d^L_{mn}(\beta) \exp(-in\gamma) , \tag{20}$$

where the small Wigner functions $d^L_{mn}(\beta)$ are functions of β only:

$$d^L_{mn}(\beta) = \sum_j v_j(L, m, n)(\cos \beta/2)^{2L+n-m-2j} (-\sin \beta/2)^{m-n+2j} , \tag{21a}$$

with

$$v_j(L, m, n) = \frac{(-1)^j \sqrt{(L + m)!(L + n)!(L - n)!(L - m)!}}{(L - m - j)!(L + n - j)!(j + m - n)!j!} . \tag{21b}$$

From the explicit form of the Wigner functions it follows that they reduce to the Legendre polynomials for $m = n = 0$:

$$D^L_{00}(\alpha, \beta, \gamma) = P_L(\cos\beta) . \tag{22}$$

Likewise, it can be demonstrated that the spherical harmonics Y_{Lm} are simple Wigner functions:

$$D^L_{m0}(\alpha, \beta, \gamma) = \sqrt{\frac{4\pi}{2L + 1}} Y^*_{Lm}(\beta, \alpha) . \tag{23}$$

The Wigner functions of rank 2 are given in the first Appendix. The second appendix gives a number of useful relationships between different Wigner functions.

The rotation operators and their representations, the Wigner rotation matrices, constitute a mathematical group [38]. That means that two successive rotations in turn constitute a rotation, the so-called closure relation. The closure relation can be expressed in matrix terms as follows:

$$D^L_{mn'}(\alpha'', \beta'', \gamma'') = \sum_{n=-L}^{L} D^L_{mn}(\alpha, \beta, \gamma) D^L_{nn'}(\alpha', \beta', \gamma') . \tag{24}$$

This relationship is central to the theory presented here. It dictates that a rotation through an angle $(\alpha'', \beta'', \gamma'')$ can be split up into two successive rotations (α, β, γ) and $(\alpha', \beta', \gamma')$. If, moreover, an orientation dependence in a given system of axes can be expressed as one or more elements of the rotation matrix $D^L_{mn}(\alpha'', \beta'', \gamma'')$, then the orientation dependence in a different system of axes can be expressed as $D^L_{mn'}(\alpha', \beta', \gamma')$, where $D^L_{mn}(\alpha, \beta, \gamma)$ expresses the rotation between the two systems of axes. In other words: the rotation (matrix) required to transfer B into A yields the orientation of a system of axes A in a different system of axes B.

Besides a binary operation, a group also contains a unit element, which is derived from the rotation through an angle $\Omega = (0, 0, 0)$. From the explicit form of the Wigner rotation matrices it follows that $D^L_{mn}(0, 0, 0) = \delta_{mn}$. When this is substituted in Eq. (24) we see that if $(\alpha, \beta, \gamma) = (0, 0, 0)$ it follows that $(\alpha'', \beta'', \gamma'') = (\alpha', \beta', \gamma')$. Besides the unit element there is also the inverse rotation, given by $D^L_{mn}(-\gamma, -\beta, -\alpha) = D^{L*}_{mn}(\alpha, \beta, \gamma)$ (unitary property). Substitution in Eq. (24) yields:

$$\delta_{m'n} = \sum_m D^{L*}_{mm'}(\alpha, \beta, \gamma) D^L_{mn}(\alpha, \beta, \gamma) . \tag{25}$$

Finally, there is the associative property $(R_3R_2)R_1 = R_3(R_2R_1)$, which follows simply from Eq. (24) in the matrix representation. It should be realized that the commutative property $R_2R_1 = R_1R_2$ does not usually apply. With the aid of a matchbox it can easily be checked that the spatial position obtained after two 90° rotations about the (chosen) x and y axes, respectively, is not the same as that obtained when the order is reversed.

We have now found a set of functions that enables us to write an ODF as a series expansion. When the order parameters $\langle D^{L*}_{mn} \rangle$, or moments of the series expansion are known, the ODF is determined. The order parameters can be experimentally determined because a measured quantity can be expressed in terms of the Wigner functions. The number of order parameters to be determined is very large: for a given L there are $(2L+1)^2$ order parameters. In practice, however, this number is in many cases greatly reduced by molecular or sample symmetries present.

Symmetry properties

We will now show that if certain symmetries are present in the system a large number of order parameters becomes zero and may hence be left out of consideration. A distinction has to be made between the symmetry properties of the molecular element (chain segment or crystal) and those of the sample (statistical symmetry). The former affect the γ dependence of the ODF, the latter the α and β dependence, although the different angle dependencies are not entirely unlinked.

The special form of the Wigner functions, Eq. (20), makes it possible to simply translate the symmetry properties into the shape of the ODF. We will demonstrate this for a number of frequently occurring symmetries [39–41].

Note that the terms uniaxial and biaxial are used both for the deformation mechanism of a polymer and for the statistical symmetry of the sample. This is not necessarily the same thing. Uniaxial stretching (i.e., in one direction) of a fiber or a film may very well result in a non-uniaxial distribution (e.g., owing to different macroscopic or molecular causes). A biaxial stretching mechanism (e.g., film blowing) may still (within the experimental errors) result in a uniaxial distribution. The deformation mechanism is usually known but beforehand only very little can be said about the statistical symmetry of the ODF in the sample.

Uniaxial (or fiber) symmetry

This is a sample symmetry for which the ODF does not depend on Euler's angle α. In other words, the ODF does not change with rotation about the Z axis, which is chosen alongside the symmetry axis (e.g., the drawing or extrusion direction). So we have:

$$f(\Omega) = f(\beta, \gamma)\,. \tag{26}$$

The order parameters that are now to be determined are:

$$\begin{aligned}\langle D^{L*}_{mn}\rangle &= \int_{\Omega} D^{L*}_{mn}(\Omega) f(\Omega)\, d\Omega = \int_{\alpha\beta\gamma} \exp(im\alpha)\, d^{L}_{mn}(\beta) \exp(in\gamma) \\ &\quad \times f(\beta,\gamma) \sin\beta\, d\alpha\, d\beta\, d\gamma \\ &= \int_{\alpha} \exp(im\alpha)\, d\alpha \int_{\beta\gamma} d^{L}_{mn}(\beta) \exp(in\gamma) f(\beta,\gamma) \sin\beta\, d\beta\, d\gamma\,.\end{aligned} \tag{27}$$

Since it is given that

$$\int_{\alpha} \exp(im\alpha)\, d\alpha = 2\pi\delta_{m0} \tag{28}$$

it follows that the order parameters $\langle D^{L*}_{mn}\rangle$ only have a value that is not zero when $m = 0$. So the consequence of uniaxial sample symmetry is that only the order parameters $\langle D^{L*}_{0n}\rangle$ have a value which is not zero.

Axially symmetrical molecular elements

In this case the ODF is independent of angle γ. It should be noted that this does not necessarily mean that the molecular elements are cylindrical but it does mean that a rotation about their long axis (of symmetry) does not affect the ODF. In the same way as above it now follows that only the order parameters $\langle D^{L*}_{m0}\rangle$ remain.

Combination of both uniaxial symmetries

If we have both uniaxial sample symmetry and axially symmetrical molecular elements the ODF is only dependent on angle β. The order parameters now reduce to the Legendre polynomials, as described above:

$$\langle D^{L*}_{00}\rangle = \langle P_L\rangle\,. \tag{29}$$

180°-rotational symmetry about Z

A simple symmetry is the one where the ODF is invariant with respect to a 180° rotation about the macroscopic Z axis. This means that

$$f(\alpha,\beta,\gamma) = f(\alpha+\pi,\beta,\gamma)\,. \tag{30}$$

It now follows that

$$\begin{aligned}\langle D^{L*}_{mn}\rangle &= \int_{\alpha\beta\gamma} D^{L*}_{mn}(\alpha,\beta,\gamma) f(\alpha,\beta,\gamma) \sin\beta\, d\alpha\, d\beta\, d\gamma \\ &= \int_{0}^{2\pi} \int_{\beta\gamma} D^{L*}_{mn}(\alpha'+\pi,\beta,\gamma) f(\alpha'+\pi,\beta,\gamma) \sin\beta\, d\alpha'\, d\beta\, d\gamma\,,\end{aligned} \tag{31}$$

where we have substituted $\alpha = \alpha' + \pi$. If we use Eq. (20) to show that

$$D^{L*}_{mn}(\alpha'+\pi,\beta,\gamma) = (-1)^{m} D^{L*}_{mn}(\alpha',\beta,\gamma) \tag{32}$$

then, using Eq. (30), it follows that:

$$\begin{aligned}\langle D^{L*}_{mn}\rangle &= \int_{0}^{2\pi} \int_{\beta\gamma} (-1)^{m} D^{L*}_{mn}(\alpha',\beta,\gamma) f(\alpha',\beta,\gamma) \sin\beta\, d\alpha'\, d\beta\, d\gamma \\ &= (-1)^{m} \langle D^{L*}_{mn}\rangle\,.\end{aligned} \tag{33}$$

The only order parameters that are not zero are those for which m is even.

180°-rotational symmetry about z

Likewise, it can be inferred that if the ODF is invariant with respect to a 180° rotation about the Z axis of the molecular element, i.e., if

$$f(\alpha, \beta, \gamma) = f(\alpha, \beta, \gamma + \pi) \tag{34}$$

the only order parameters that are not zero are those for which n is even.

In many cases in practice mirror symmetries will play a part. These involve the problem that a reflection can never be expressed as a sum of rotations, because a right-handed frame of axes becomes a left-handed one. In most cases this problem can be circumvented with the aid of order parameters $\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle$ for which either $m = 0$ or $n = 0$. We can also consider the effect of two successive mirror reflections (also called "turns" [18]) in systems with several mirror symmetries. In that case a mirrored system of axes remains right-handed.

Central symmetry

An often applied symmetry is point reflection in the origin of the XYZ system of the sample (also known as central symmetry). We will discuss this for an ODF that is independent of γ. The following then applies:

$$f(\alpha, \beta) = f(\pi + \alpha, \pi - \beta) \,. \tag{35}$$

With the aid of the relations in the Appendix, we can demonstrate that

$$D^{\mathrm{L}*}_{\mathrm{m0}}(\pi + \alpha, \pi - \beta, \gamma) = (-1)^{\mathrm{L}} D^{\mathrm{L}*}_{\mathrm{m0}}(\alpha, \beta, \gamma) \tag{36}$$

We can now substitute Eq. (35) in Eq. (18) and use Eq. (36) to calculate the order parameters for this symmetry (just as in the case of the latter symmetry). It follows that L is even, i.e., only the even ranked order parameters are not zero.

Mirror symmetry of the sample

Mirror symmetry in the XY, YZ, and XZ planes of the sample is also known as biaxial or orthorhombic sample symmetry. In order to avoid the problems involved in a left-handed system of axes, we will each time carry out two successive mirror reflections. For the ODF it then follows that (reflection in XY and YZ, XY and XZ and YZ and XZ, respectively):

$$f(\alpha, \beta, \gamma) = f(\pi - \alpha, \pi - \beta, \pi + \gamma) \tag{37a}$$

$$f(\alpha, \beta, \gamma) = f(-\alpha, \pi - \beta, \pi + \gamma) \tag{37b}$$

$$f(\alpha, \beta, \gamma) = f(\pi + \alpha, \beta, \gamma) \,. \tag{37c}$$

Because (see Appendix)

$$D^{\mathrm{L}}_{\mathrm{mn}}(\pi - \alpha, \pi - \beta, \pi + \gamma) = (-1)^{\mathrm{L}+\mathrm{m}} D^{\mathrm{L}}_{-\mathrm{mn}}(\alpha, \beta, \gamma) \tag{38a}$$

$$D^{\mathrm{L}}_{\mathrm{mn}}(-\alpha, \pi - \beta, \pi + \gamma) = (-1)^{\mathrm{L}} D^{\mathrm{L}}_{-\mathrm{mn}}(\alpha, \beta, \gamma) \tag{38b}$$

$$D^{\mathrm{L}}_{\mathrm{mn}}(\pi + \alpha, \beta, \gamma) = (-1)^{\mathrm{m}} D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma) \tag{38c}$$

it now follows for the order parameters

$$\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle = (-1)^{\mathrm{L}} \langle D^{\mathrm{L}*}_{-\mathrm{mn}} \rangle \quad \mathrm{m\ even}\,. \tag{39}$$

Mirror symmetry of the molecular elements

Mirror symmetry in the planes xy, yz and xz of the xyz system of axes fixed to the molecular element is also called orthorhombic molecular or crystal symmetry. Two successive mirror symmetries now yield the following for the ODF (mirroring in xy and yz, xy and yz and xz, respectively):

$$f(\alpha, \beta, \gamma) = f(\pi + \alpha, \pi - \beta, \pi - \gamma) \tag{40a}$$

$$f(\alpha, \beta, \gamma) = f(\pi + \alpha, \pi - \beta, -\gamma) \tag{40b}$$

$$f(\alpha, \beta, \gamma) = f(\alpha, \beta, \pi + \gamma) \,. \tag{40c}$$

Moreover (see Appendix):

$$D^{\mathrm{L}}_{\mathrm{mn}}(\pi + \alpha, \pi + \beta, \pi - \gamma) = (-1)^{\mathrm{L}+\mathrm{n}} D^{\mathrm{L}}_{\mathrm{m}-\mathrm{n}}(\alpha, \beta, \gamma) \tag{41a}$$

$$D^{\mathrm{L}}_{\mathrm{mn}}(\pi + \alpha, \pi - \beta, -\gamma) = (-1)^{\mathrm{L}} D^{\mathrm{L}}_{\mathrm{m}-\mathrm{n}}(\alpha, \beta, \gamma) \tag{41b}$$

$$D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \pi + \gamma) = (-1)^{\mathrm{n}} D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma) \tag{41c}$$

so that it follows that:

$$\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle = (-1)^{\mathrm{L}} \langle D^{\mathrm{L}*}_{\mathrm{m}-\mathrm{n}} \rangle \quad \mathrm{n\ even}\,. \tag{42}$$

Combination of both mirror symmetries

A biaxial or orthorhombic molecular element in a biaxial phase now yields:

$$\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle = \langle D^{\mathrm{L}*}_{-\mathrm{m}-\mathrm{n}} \rangle \tag{43a}$$

$$\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle = (-1)^{\mathrm{L}} \langle D^{\mathrm{L}*}_{\mathrm{m}-\mathrm{n}} \rangle \quad \mathrm{m, n\ even}\,. \tag{43b}$$

Note that in this case we have $\langle D^{\mathrm{L}}_{\mathrm{mn}} \rangle = \langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle$ and all order parameters are real.

Construction of the distribution function

In practice only a limited number of order parameters can be experimentally determined. However, the ODF is not completely known until all of the order parameters that are not zero are known. The simplest solution is to assume that all of the unknown order parameters are zero. Another possibility is to determine the widest possible ODF that is still consistent with the measured order parameters. "Widest possible" is understood to mean the smoothest possible ODF that contains the least possible information. In practical terms this means that the information entropy is maximized [42, 43, 32]. The information entropy is expressed as:

$$S = -K\int_{\Omega} f(\Omega)\ln f(\Omega)d\Omega\,, \qquad (44)$$

where $\Omega = (\alpha, \beta, \gamma)$ and K is a constant. If we now maximize the information entropy S with the following restrictions:

$$\langle D^{L*}_{mn}\rangle = \int_{\Omega} D^{L*}_{mn}(\Omega)f(\Omega)d\Omega \qquad (45)$$

and

$$\int_{\Omega} f(\Omega)d\Omega = 1\,, \qquad (46)$$

then it follows for the ODF that

$$f(\Omega) = f(\alpha, \beta, \gamma) = A\exp\left(-\sum_{lmn}\lambda^{L}_{mn}D^{L}_{mn}(\alpha, \beta, \gamma)\right), \qquad (47a)$$

whereby use has been made of Lagrange's method of multipliers and the number of multipliers λ^{L}_{mn} does not exceed the number of order parameters. A is a constant which can be calculated from Eqs. (45) and (46) along with λ^{L}_{mn} if the order parameters $\langle D^{L*}_{mn}\rangle$ are known. In the simple case that only $\langle P_2\rangle$ is known, Eq. (47) reduces to

$$f(\beta) = A\exp(-\lambda_2 P_2(\cos\beta))\,, \qquad (47b)$$

which also follows from the approach of Maier and Saupe [36].

By way of illustration, a number of ODF's has been constructed for the given order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$ (Fig. 4) and $\langle P_2\rangle$ and $\langle D^{2}_{02}\rangle$ (Figs. 5 and 6).

Applications

The theory discussed in the second part, which describes the ODF in terms of Wigner rotation matrices, has often been used in the literature to interpret the results obtained in a wide variety of experimental methods, such as wide-angle x-ray scattering [5–9, 27], polarized Raman scattering [44], NMR and ESR [45–47], fluorescence depolarization [48–50], and UV and IR dichroism [51, 52]. The results obtained with these methods can be

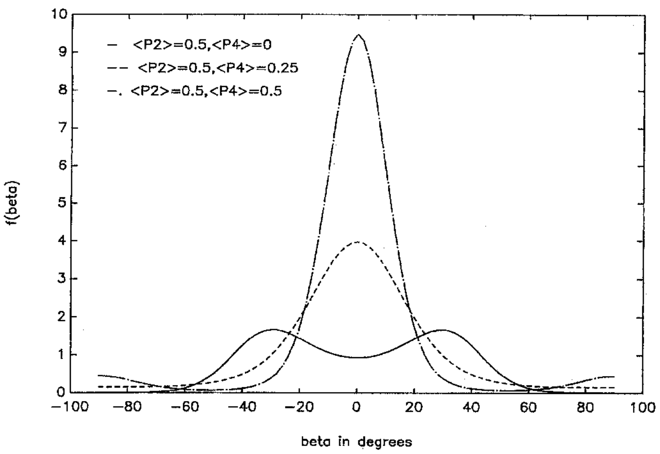
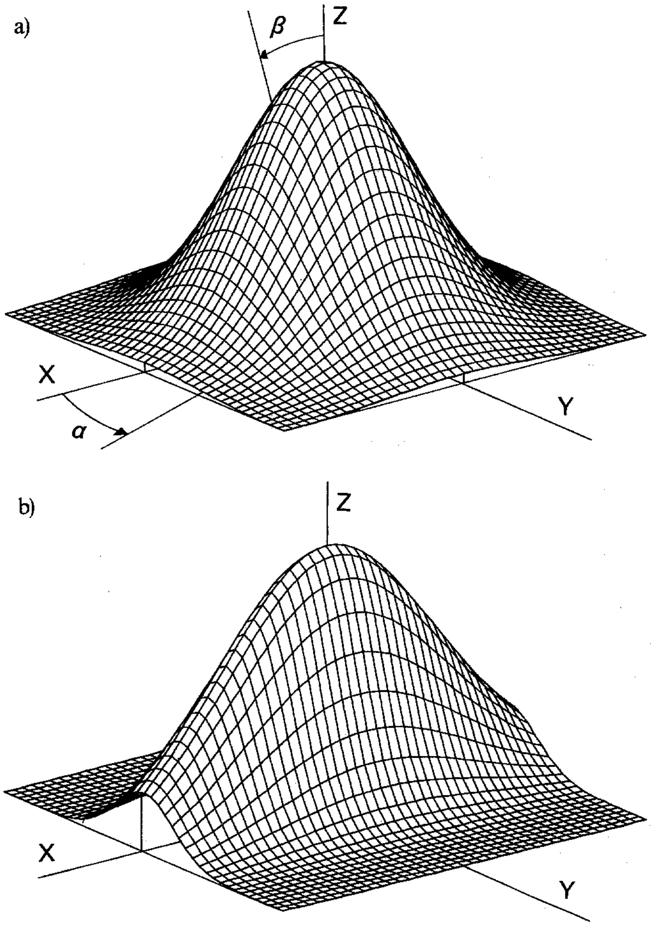


Fig. 4 Distribution functions $f(\beta)$ constructed with help of the maximum entropy formalism, Eq. (47a) from the known values of $\langle P_2\rangle$ and $\langle P_4\rangle$ as indicated

Fig. 5 Distribution functions $f(\alpha, \beta)$ constructed with help of the maximum entropy formalism, Eq. (47a) from the known values of $\langle P_2\rangle$ and $\langle D^{2}_{20}\rangle$ (a) $\langle P_2\rangle = 0.5$, $\langle D^{2}_{20}\rangle = 0$. (b) $\langle P_2\rangle = 0.5$, $\langle D^{2}_{20}\rangle = 0.15$. The macroscopic axes X, Y and Z are indicated. X values equal $\sin\beta\cos\alpha$, Y values equal $\sin\beta\sin\alpha$



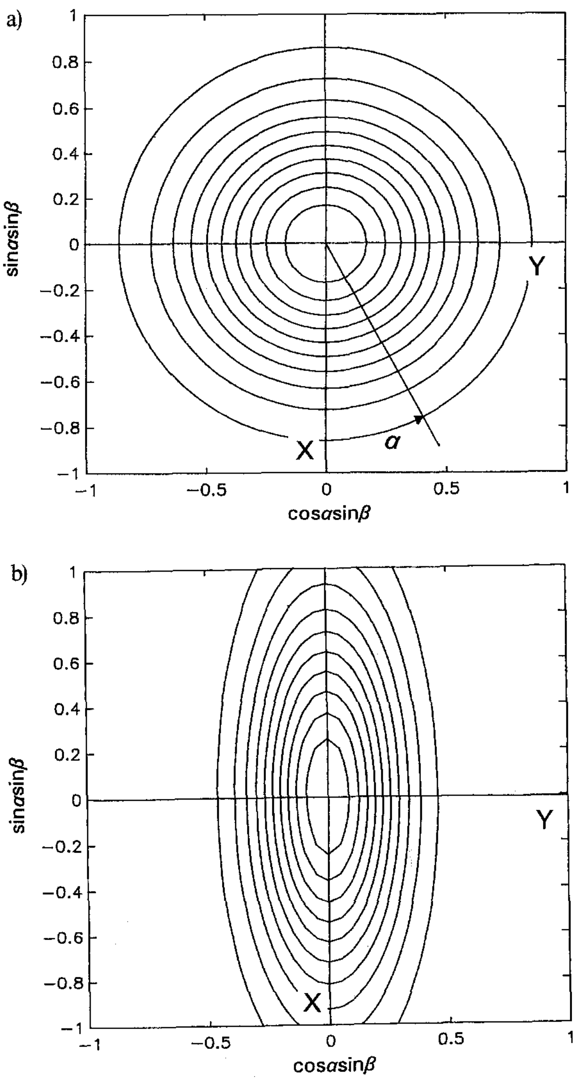


Fig. 6 Pole figures or contour plots of the ODF's from Fig. 5. Given are the projections in the XY plane

directly related to the mechanical anisotropy if the compliance tensor chosen is also spherical [19, 20, 53] and, in general, to the description of any anisotropic physical property [54, 55]. The relationships between molecular orientation and mechanical properties are not discussed here. Details can be found, for example, in the book by Ward [12]. General discussions of the theory used for various methods are given in the works by Nomura and Kawai [33, 56], Roe [57] and McBrierty [58].

We will now apply the theory to a number of frequently used methods, in particular infrared dichroism and birefringence, for which the theory is the least complicated. Other methods, which will be discussed in outline only, are wide-angle x-ray scattering, polarized Raman scattering, fluorescence depolarization and NMR. Specific details (both theoretical and experimental) of the various technique will not be dealt with here and can be found in the numerous papers and textbooks on the subject.

IR dichroism

Infrared dichroism is the difference in absorption of IR radiation with two perpendicular polarization directions. The absorption is caused by the vibrational transition of a specific chemical bond. In order to be able to understand the principle of IR dichroism, it is assumed that the probability of an electric field **E** causing a transition from one vibration level to another is expressed by:

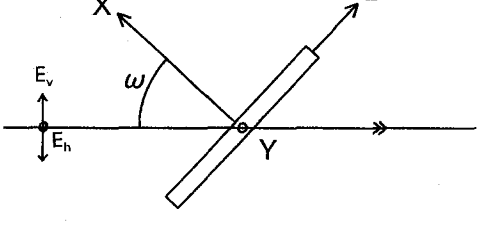
$$p \sim (\mathbf{E}\cdot\boldsymbol{\mu})^2\ , \qquad (48)$$

where $\boldsymbol{\mu}$ is the transition dipole moment corresponding to the vibration transition (Fermi's Golden Rule). $\boldsymbol{\mu}$ can be regarded as a vector with a given direction in the molecular system of axes (e.g., relative to the polymer chain). If the electric field vector is parallel to $\boldsymbol{\mu}$ then infrared rays will be absorbed; if **E** is perpendicular to $\boldsymbol{\mu}$ then no absorption will take place. The absorbance is now expressed by:

$$A = k\langle(\tilde{\mathbf{E}}\cdot\tilde{\boldsymbol{\mu}})^2\rangle = k\langle\cos^2\theta\rangle\ , \qquad (49)$$

where k is a constant (incorporating the length of the light path through the absorbing sample), θ is the angle between **E** and $\boldsymbol{\mu}$ and the values indicated between brackets $\langle\ \rangle$ represent the average of all occurring orientations of $\boldsymbol{\mu}$. The curls here mean that dimensionless unit vectors are taken along **E** and $\boldsymbol{\mu}$. Let us now take a look at the very general experimental situation shown in Fig. 7. The sample is irradiated under an angle ω relative to the surface normal of the sample. For convenience's sake no allowance will be made for any refraction at the surface of the sample: in principle, refraction would only affect the angle ω according to Snell's law. In the case of a birefringent material, it should be taken into account that the index of refraction of one of the polarization directions is angle dependent. One could try to make a correction for such an effect, but in most cases no large error is made in taking an average index of refraction.

Fig. 7 Experimental set-up of an angle-resolved IR dichroism experiment



The laboratory XYZ system is fixed to the sample, the Z axis lying along the principal axis and the Y axis lying in the plane of the film (see Fig. 7). The orientation of the crystal system xyz is expressed by Euler's angles α, β and γ.

We will now make use of the fact that a rotation can be written as a product of rotations (Eq. (24), the closure relation). The absorption given in Eq. (49) will first be expressed in the form of a Legendre polynomial, in fact the representation of a simple rotation over θ from the electric field vector **E** to the dipole moment $\boldsymbol{\mu}$:

$$A = k\langle \cos^2\theta\rangle = \frac{k}{3}(2\langle P_2(\cos\theta)\rangle + 1)\,. \tag{50}$$

Because $P_2(\cos\theta) = D^2_{00}(0\,\theta\,0)$ is a rotation matrix element, we may use the closure relation so as to split the rotation of the light vector **E** to the transition moment μ (with the angle θ in between) into three rotations: from **E** to the XYZ system fixed to the sample, from XYZ to xyz fixed to the crystal lattice and from xyz to $\boldsymbol{\mu}$:

$$\begin{aligned}\langle P_2(\cos\beta)\rangle &= \langle D^2_{00}(0\,\theta\,0)\rangle\\ &= \sum_{ij} D^2_{0i}(\mathbf{E}\rightarrow \mathrm{XYZ})\langle D^2_{ij}(\mathrm{XYZ}\rightarrow \mathrm{xyz})\rangle\\ &\quad\times D^2_{j0}(\mathrm{xyz}\rightarrow \boldsymbol{\mu})\,.\end{aligned} \tag{51}$$

Only the rotation from XYZ to xyz is indicated between average brackets because here there is a statistical distribution of orientations. As it is easier to define **E** in the XYZ system than the other way round, we will reverse the first rotation. This can be easily done by taking the complex conjugate and reversing the indices (see Appendix). If we term Ω_E the orientation of **E** in XYZ and Ω_μ that of $\boldsymbol{\mu}$ in xyz then we may write:

$$\langle P_2(\cos\theta)\rangle = \sum_{ij} D^{2*}_{i0}(\Omega_E)\langle D^2_{ij}\rangle D^2_{j0}(\Omega_\mu)\,. \tag{52}$$

We can write out this summation by substituting the spherical coordinates of the various vectors. It should be borne in mind that the coordinates of $\boldsymbol{\mu}$ are now given in the xyz system. Let us now assume for simplicity that the dipole moment $\boldsymbol{\mu}$ lies along one of the molecular axes x, y or z (e.g., in polyethylene along the crystal a, b and c directions). We then have:

$$x = \left(0, \frac{\pi}{2}, 0\right),\quad y = \left(\frac{\pi}{2}, \frac{\pi}{2}, 0\right),\quad z = (0, 0, 0) \tag{53a}$$

and for the electric field vector **E** as in Fig. 7:

$$E_v = (0, \omega, 0),\qquad E_h = \left(\frac{\pi}{2}, \frac{\pi}{2}, 0\right)\,. \tag{53b}$$

The explicit expressions of the corresponding Wigner functions (Appendix) are now given in Table 1.

Table 1

	x $(0, \pi/2, 0)$	y $(\pi/2, \pi/2, 0)$	z $(0, 0, 0)$	E_v $(0, \omega, 0)$	E_h $(\pi/2, \pi/2, 0)$
D^2_{00}	$-1/2$	$-1/2$	1	$1/2(3\cos^2\omega - 1)$	$-1/2$
$D^2_{\pm 10}$	0	0	0	$\pm\sqrt{3/8}\sin 2\omega$	0
$D^2_{\pm 20}$	$\sqrt{3/8}$	$-\sqrt{3/8}$	0	$\sqrt{3/8}\sin^2\omega$	$-\sqrt{3/8}$

We will now assume both biaxial statistical and molecular symmetry. In that case, we have seen that (Eq. (43)):

$$\langle D^2_{ij}\rangle = \langle D^2_{-ij}\rangle$$

and

$$\langle D^2_{ij}\rangle = \langle D^2_{-i-j}\rangle \quad \text{and } i, j \text{ even}\,. \tag{54}$$

So we see that in the summation in Eq. (52) the terms with uneven i and j vanish. By substitution of Table 1 in Eq. (52), we now find:

1) For $\boldsymbol{\mu}$ along x and y:

$$\begin{aligned}\langle P_2(\cos\theta)\rangle_v &= 1/2(3\cos^2\omega - 1)\{-1/2\langle D^2_{00}\rangle\\ &\quad\pm\sqrt{3/2}\langle D^2_{02}\rangle\} + \sqrt{3/2}\sin^2\omega\{-1/2\\ &\quad\times\langle D^2_{20}\rangle \pm\sqrt{3/2}\langle D^2_{22}\rangle\}\end{aligned} \tag{55a}$$

$$\begin{aligned}\langle P_2(\cos\theta)\rangle_h &= -1/2\{-1/2\langle D^2_{00}\rangle \pm\sqrt{3/2}\langle D^2_{02}\rangle\}\\ &\quad-\sqrt{3/2}\{-1/2\langle D^2_{20}\rangle \pm\sqrt{3/2}\langle D^2_{22}\rangle\}\,,\end{aligned} \tag{55b}$$

where in the $\pm$ sign the $+$ should be taken for x and the $-$ for y and the subscripts v and h denote the chosen polarization directions, Eq. (53a).

2) For $\boldsymbol{\mu}$ along z, we have:

$$\begin{aligned}\langle P_2(\cos\theta)\rangle_v &= 1/2(3\cos^2\omega - 1)\langle D^2_{00}\rangle\\ &\quad+\sqrt{3/2}\sin^2\omega\langle D^2_{20}\rangle\end{aligned} \tag{55c}$$

$$\langle P_2(\cos\theta)\rangle_h = -1/2\langle D^2_{00}\rangle - \sqrt{3/2}\langle D^2_{20}\rangle\,. \tag{55d}$$

If we now substitute Eq. (55) in Eq. (50) it follows for the dichroic ratios that:

1) For x and y:

$$\frac{A_v}{A_h} = \frac{1 - 2a + (3a - b)\sin^2\omega}{1 + a + b}\,, \tag{56a}$$

with

$$a = 1/2\langle D^2_{00}\rangle \pm\sqrt{3/2}\langle D^2_{02}\rangle \tag{56b}$$

$$b = \sqrt{3/2}\langle D^2_{20}\rangle \pm 3\langle D^2_{22}\rangle\,. \tag{56c}$$

2) For z:

$$\frac{A_v}{A_h} = \frac{1 + 2\langle D^2_{00}\rangle - (3\langle D^2_{00}\rangle - \sqrt{6}\langle D^2_{20}\rangle)\sin^2\omega}{1 - \langle D^2_{00}\rangle - \sqrt{6}\langle D^2_{20}\rangle} . \quad (57)$$

We have now interpreted the results of IR dichroism measurements in terms of four different second-rank order parameters. On the basis of these an estimate of the ODF can in principle be made. From the results of the measurements it can be concluded whether the sample is uniaxial ($\langle D^2_{20}\rangle = 0$) or whether the crystals are effectively axially symmetrical ($\langle D^2_{02}\rangle = 0$), or whether it is a matter of both (only $\langle P_2\rangle$ is unequal to zero). In this last case Eqs. (56) and (57) reduce to:

$$\frac{A_v}{A_h} = \frac{1 - \langle P_2\rangle + 3/2\langle P_2\rangle\sin^2\omega}{1 + 1/2\langle P_2\rangle} , \quad (58)$$

for $\boldsymbol{\mu}$ along x and y, and

$$\frac{A_v}{A_h} = \frac{1 + 2\langle P_2\rangle - 3\langle P_2\rangle\sin^2\omega}{1 - \langle P_2\rangle} . \quad (59)$$

The order parameter $\langle P_2\rangle$ can now easily be determined from experiments using normal incidence ($\omega = 0$) which yield

$$\langle P_2\rangle = \frac{2 - 2R}{R + 2} \quad (60)$$

exciting along the x or y transition, or

$$\langle P_2\rangle = \frac{R - 1}{R + 2} \quad (61)$$

exciting the z-vector, where $R = A_v/A_h$ is the dichroic ratio, which is the much used relation in most experimental work.

Birefringence

In an anisotropic system without permanent dipoles, the principal values n_i of the real index of refraction can be written in terms of the sum of all polarizability contributions. This macroscopically averaged polarizability tensor $\langle\alpha\rangle$ is diagonal with respect to the frame through the optical axes. In many cases the Lorentz–Lorenz relation is used to link macroscopically observed refractive indices with the averaged molecular polarizabilities [57]:

$$\langle\alpha_i\rangle = \frac{3\varepsilon_0}{N}\frac{n_i^2 - 1}{n_i^2 + 2} , \quad (62)$$

where N is the number of chain segments per volume, ε_0 the permittivity of vacuum and the indices i stand for X, Y and Z. It has, however, been pointed out that the internal field assumption in the Lorentz–Lorenz equation is not valid in semicrystalline and anisotropic polymers and alternative formulations have been proposed [60–63].

In any case, we are left with a rotation from a molecular polarizability tensor to a macroscopic one and, furthermore, averaging over all possible orientations. The rotation is now carried out by taking the components of the spherical representation of the polarizability tensor, so that the tensor under rotation behaves similarly to a rotation matrix.

If $\alpha^{(2,m)}_{\mathrm{Lab}}$ are the components of the second-rank spherical polarizability tensor in the laboratory system (fixed to the sample) and $\alpha^{(2,n)}_{\mathrm{Mol}}$ are those fixed to the molecular system of axes (the polymer chain or crystal), the transformation is expressed as

$$\alpha^{(2,m)}_{\mathrm{Lab}} = \sum_n D^{2*}_{mn}(\Omega)\alpha^{(2,n)}_{\mathrm{Mol}} \quad (63a)$$

$$\alpha^{(0,0)}_{\mathrm{Lab}} = \alpha^{(0,0)}_{\mathrm{Mol}} , \quad (63b)$$

where Ω is the orientation of the molecular system of axes in the laboratory system. Note that here the reversed rotation is used to transform the molecular system into the laboratory system. The relationships between the most frequent components of the spherical and the Cartesian tensors are [24, 37, 46, 55]:

$$\alpha^{(0,0)} = -(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/\sqrt{3} \quad (64a)$$

$$\alpha^{(2,0)} = -(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})/\sqrt{6} \quad (64b)$$

$$\alpha^{(2,\pm 2)} = (\alpha_{xx} - \alpha_{yy} \pm i(\alpha_{xy} + \alpha_{yx}))/2 \quad (64c)$$

The rotational transformation of the molecular polarizability α_{Mol} into the macroscopic frame is now given by:

$$\langle\alpha^{(2,m)}_{\mathrm{Lab}}\rangle = \langle D^{2*}_{m0}(\Omega)\rangle\alpha^{(2,0)}_{\mathrm{Mol}} + \langle D^{2*}_{m2}(\Omega)\rangle\alpha^{(2,2)}_{\mathrm{Mol}} , \quad (65)$$

where $\Omega = (\alpha, \beta, \gamma)$ is the angle of rotation and again biaxial molecular elements in a biaxial sample are assumed. Working out of the summation leads to:

$$\langle\alpha_{ZZ} - 1/2(\alpha_{YY} + \alpha_{XX})\rangle = \langle P_2\rangle[\alpha_{zz} - 1/2(\alpha_{yy} + \alpha_{xx})] - \sqrt{3/2}\langle D^2_{02}\rangle(\alpha_{yy} - \alpha_{xx}) \quad (66a)$$

$$\langle\alpha_{YY} - \alpha_{XX}\rangle = 2\langle D^2_{22}\rangle(\alpha_{yy} - \alpha_{xx}) - 4\langle D^2_{20}\rangle \times [\alpha_{zz} - 1/2(\alpha_{yy} + \alpha_{xx})] . \quad (66b)$$

Introduction of these relations into Eq. (62) directly gives the principal refractive indices in terms of the second-rank order parameters. We see from Eq. (66) that for uniaxial symmetry $\langle D^2_{22}\rangle = \langle D^2_{20}\rangle = 0$ and therefore $\langle\alpha_{YY}\rangle = \langle\alpha_{XX}\rangle$ and $n_Y = n_X$. On the other hand, for axially symmetric molecular elements, we have $\langle D^2_{02}\rangle = \langle D^2_{22}\rangle = 0$, giving the same result as $\alpha_{xx} = \alpha_{yy}$. This assumption is usually made, so that two second-rank order parameters follow from the birefringence results.

In the simple case of both fiber symmetry and axially symmetric molecular elements (only $\langle P_2 \rangle$ is non-vanishing), we have:

$$\langle \alpha_{ZZ} - \alpha_{YY} \rangle = \Delta\alpha \langle P_2 \rangle , \tag{67}$$

where $\Delta\alpha = \alpha_{zz} - \alpha_{yy}$. Using the Lorentz–Lorenz equation, this leads to:

$$\Delta n = \langle P_2 \rangle \Delta n_{\max} , \tag{68a}$$

with

$$\Delta n_{\max} = \frac{N}{3\varepsilon_0} \Delta\alpha \frac{(n^2 + 2)^2}{6n} , \tag{68b}$$

and n the average refractive index, which equals Hermans' definition of his orientation function [4].

Wide-angle x-ray scattering

Wide-angle x-ray scattering (WAXS) is the coherent scattering of x-rays at the atoms of adjacent crystal planes in a (semi) crystalline polymer. The intensity of the scattered radiation is maximum when the difference in the path lengths of two photons is the wavelength λ multiplied by a whole number. This difference in path length is determined by the distance between the crystal planes d and the angle of incidence and detection θ (Bragg angle): $n\lambda = 2d\sin\theta$. At a certain Bragg angle, corresponding to a given crystal plane, the intensity is now measured for different orientations of the sample. The measured intensity is directly related to the number of crystal planes at the given orientation, and hence to the distribution of plane normal orientations, which means that an orientational distribution function is in fact directly measured. When the plane normal distributions of different crystal planes have been measured these results can be translated to the ODF of the crystals in the sample.

The diffraction intensity of a given reflection is measured as a function of the orientation of the normal r to the corresponding crystal plane in a system of axes XYZ fixed to the sample. The (normalized) intensity as a function of ϕ and θ (the azimuthal and polar angle of r in XYZ) yields the orientational distribution of r and can be expressed as a series expansion of Wigner functions.

$$I(\phi, \theta) = \sum_{\mathrm{Lm}} \frac{2L+1}{4\pi} \langle D^{\mathrm{L}*}_{\mathrm{m0}} \rangle_{\mathrm{r}} D^{\mathrm{L}}_{\mathrm{m0}}(\phi, \theta, 0) \tag{69}$$

When I has been measured, the moments $\langle D^{\mathrm{L}*}_{\mathrm{m0}} \rangle_{\mathrm{r}}$ can be determined using:

$$\langle D^{\mathrm{L}*}_{\mathrm{m0}} \rangle_{\mathrm{r}} = \int_0^{2\pi}\int_0^{\pi} D^{\mathrm{L}*}_{\mathrm{m0}}(\phi, \theta, 0) I(\phi, \theta) \sin\theta\, d\theta\, d\phi , \tag{70}$$

In practice, a finite number of these moments will suffice, some of which can be chosen to be zero for reasons of symmetry. However, we are interested in the ODF $f(\alpha, \beta, \gamma)$ of the crystals in the sample. This distribution is also written as a series expansion:

$$f(\alpha, \beta, \gamma) = \sum_{\mathrm{Lmn}} \frac{2L+1}{8\pi^2} \langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma) . \tag{71}$$

We will now use the closure relation according to Eq. (24) to couple the ODF's $I(\phi, \theta)$ and $f(\alpha, \beta, \gamma)$ to one another because we may regard the rotation of the system of axes XYZ to the crystal plane normal r as two separate rotations: from XYZ to the crystal frame and from the crystal to r:

$$D^{\mathrm{L}}_{\mathrm{m0}}(\phi, \theta, 0) = \sum_{\mathrm{n}} D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma) D^{\mathrm{L}}_{\mathrm{n0}}(\phi_{\mathrm{r}}, \theta_{\mathrm{r}}, 0) , \tag{72}$$

where $(\phi_{\mathrm{r}}, \theta_{\mathrm{r}}, 0)$ is the (known) orientation of r in th crystal frame. For the average values this simply means that:

$$\langle D^{\mathrm{L}*}_{\mathrm{m0}} \rangle_{\mathrm{r}} = \sum_{\mathrm{n}} \langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle D^{\mathrm{L}*}_{\mathrm{n0}}(\phi_{\mathrm{r}}, \theta_{\mathrm{r}}, 0) . \tag{73}$$

In order to determine the order parameters of rank L, we must in principle measure $2L + 1$ reflections so as to be able to solve Eq. (73). In practice, this number can be substantially reduced because of symmetry properties. For example, for a biaxial crystal in a biaxial phase as discussed before, the number is reduced to $L/2 + 1$ reflections (L even). We hence see that the order parameters $\langle D^{\mathrm{L}*}_{\mathrm{mn}} \rangle$, which define the ODF according to Eq. (71), can be determined from a number of reflections with known $(\phi_{\mathrm{r}}, \theta_{\mathrm{r}}, 0)$ [27].

Polarized Raman scattering

Raman scattering is the inelastic collision of a photon and a molecule with an energy loss (or gain) of the scattered light that corresponds to the energy jump associated with a rotational or vibrational transition in the molecule. If the incident light has an electric field vector $\mathbf{E}_{\mathrm{i}}$ and the scattered light is found to have a vector $\mathbf{E}_{\mathrm{s}}$ (with the aid of an analyser), the intensity is:

$$I \sim \langle (\mathbf{E}_{\mathrm{s}} \cdot \boldsymbol{\alpha} \cdot \mathbf{E}_{\mathrm{i}})^2 \rangle , \tag{74}$$

where $\boldsymbol{\alpha}$ is here the derivative of the polarizability tensor with respect to the coordinates of the molecular vibrations involved. The tensor $\boldsymbol{\alpha}$ is defined in the macroscopic system of axes, whereas we would like to see it related to the molecular system of axes. Again, a rotational transformation is carried out that links the laboratory frame to the molecular frame according to Eq. (63). To be able to work out Eq. (74), we will also express the direct product $\mathbf{E}_s\mathbf{E}_i$ as a spherical tensor $\mathbf{E}^{(L,n)}$ so that it follows that:

$$
\begin{aligned}
I &\sim \langle(\mathbf{E}_s\cdot\boldsymbol{\alpha}_{\mathrm{Lab}}\cdot\mathbf{E}_i)^2\rangle = \left\langle\left(\sum_{\mathrm{L},m} E^{(\mathrm{L,m})}\alpha_{\mathrm{Lab}}^{(\mathrm{L,m})*}\right)^2\right\rangle \\
&= \left\langle\left(\sum_{\mathrm{Lmn}} E^{(\mathrm{L,m})}D_{\mathrm{mn}}^{\mathrm{L}}(\Omega)\alpha_{\mathrm{Mol}}^{(\mathrm{L,n})*}\right)^2\right\rangle \\
&= \sum_{\mathrm{Lmn}}\sum_{\mathrm{L'm'n'}} E^{(\mathrm{L,m})}E^{(\mathrm{L',m'})}\langle D_{\mathrm{mn}}^{\mathrm{L}}(\Omega)D_{\mathrm{m'n'}}^{\mathrm{L'}}(\Omega)\rangle\alpha_{\mathrm{Mol}}^{(\mathrm{L,n})*}\alpha_{\mathrm{Mol}}^{(\mathrm{L',n'})*}\,,
\end{aligned}
\tag{75}
$$

where $L, L' = 0, 1, 2$ and m, n, m', n' range from $-L$ to $+L$ and from $-L'$ to L'. Here we have made use of the fact that the scalar product of two spherical tensors introduces the complex conjugate of one of the two [15, 56]. The product, $\langle D_{\mathrm{mn}}^{\mathrm{L}}(\Omega)D_{\mathrm{m'n'}}^{\mathrm{L'}}(\Omega)\rangle$, can be expressed as a single rotation according to the Clebsch–Gordan series [15]:

$$
\langle D_{\mathrm{mn}}^{\mathrm{L}}(\Omega)D_{\mathrm{m'n'}}^{\mathrm{L'}}(\Omega)\rangle = \sum_{\mathrm{J}} C(LL'J;\, mm')C(LL'J;\, nn') \times\langle D_{\mathrm{m+m',n+n'}}^{\mathrm{J}}\rangle\,,
\tag{76}
$$

where the C's are constants, the so-called Clebsch–Gordan coefficients. Values of the Clebsch–Gordon coefficients are tabulated in the last Appendix [64]. The summation goes from $J = L - L'$ to $J = L + L'$. In most cases L and L' will only be 0 and 2 (symmetric tensors), which means that Raman experiments will yield second- and fourth-rank order parameters. $E^{(\mathrm{L,n})}$ follows from the experimental geometry, which means that, if $\alpha_{\mathrm{Mol}}^{(\mathrm{L,m})*}$ is known, Eq. (75) can be solved with the aid of Eq. (76).

Florescence depolarization

Like Raman scattering, fluorescence depolarization is a two-photon process which, in principle, yields only the second- and fourth-rank order parameters. Fluorescence depolarization is based on the fact that after absorption of a photon, a molecule can emit a photon with a slightly lower energy. Just as with IR dichroism, the probability of absorption is proportional to the scalar product of the incident light vector $\mathbf{E}_i$ with a transition moment $\boldsymbol{\mu}$ coupled to the molecule. The emitted photon is polarized along the transition moment for emission, $\boldsymbol{\nu}$. If the emitted light is detected by an analyzer in position $\mathbf{E}_f$, then the measured intensity of the light is:

$$
I \sim \langle(\mathbf{E}_i\cdot\boldsymbol{\mu})^2(\mathbf{E}_f\cdot\boldsymbol{\nu})^2\rangle
\tag{77}
$$

If we now express the direct products $\mathbf{E}_i\mathbf{E}_f$ and $\boldsymbol{\mu}\boldsymbol{\nu}$ as spherical tensors (Eqs. (64)) then the theoretical derivation becomes the same as that of Raman scattering. If the angles between the vector pairs in Eq. (77) are θ_i and θ_f, then we may also write:

$$
I \sim \langle\cos^2\theta_i\cos^2\theta_f\rangle = \langle 1/9(2P_2(\cos\theta_i) + 1) \times(2P_2(\cos\theta_f) + 1)\rangle
\tag{78}
$$

As before, we can work this out with the aid of the closure relation, Eq. (52). It then follows that:

$$
\begin{aligned}
9I \sim 1 &+ 2\sum_{\mathrm{mn}} D_{\mathrm{m0}}^{2*}(\Omega_{\mathrm{E_i}})\langle D_{\mathrm{mn}}^{2}\rangle D_{\mathrm{n0}}^{2}(\Omega_{\mu}) \\
&+ 2\sum_{\mathrm{m'n'}} D_{\mathrm{m'0}}^{2*}(\Omega_{\mathrm{E_f}})\langle D_{\mathrm{m'n'}}^{2}\rangle D_{\mathrm{n'0}}^{2}(\Omega_{\nu}) \\
&+ 4\sum_{\mathrm{mn}}\sum_{\mathrm{m'n'}} D_{\mathrm{m0}}^{2*}(\Omega_{\mathrm{E_i}})D_{\mathrm{m'0}}^{2*}(\Omega_{\mathrm{E_f}})\langle D_{\mathrm{mn}}^{2}D_{\mathrm{m'n'}}^{2}\rangle \\
&\times D_{\mathrm{n0}}^{2}(\Omega_{\mu})D_{\mathrm{n'0}}^{2}(\Omega_{\nu})\,,
\end{aligned}
\tag{79}
$$

where Ω_{E_i} and Ω_{E_f} are the orientations of $\mathbf{E}_i$ and $\mathbf{E}_f$ in the laboratory system and Ω_μ and Ω_ν are the orientations of the transition moments $\boldsymbol{\mu}$ and $\boldsymbol{\nu}$ in the molecular system. We see that we now have the same correlation function $\langle D_{\mathrm{mn}}^{2}D_{\mathrm{m'n'}}^{2}\rangle$ as with Raman scattering (assuming that molecular motion is absent), which can be worked out with the aid of the Clebsch-Gordan series. If the experimental geometry $\Omega_{\mathrm{E_i}}$ and $\Omega_{\mathrm{E_f}}$ and the direction of the transition moments Ω_μ and Ω_ν in the molecular system are known, then Eq. (79) can be solved. In the case of a sufficiently high degree of symmetry it is even possible to determine both the order parameters and Ω_μ and Ω_ν [50].

NMR spectroscopy

Nuclear magnetic resonance (NMR) is a phenomenon which is bound up with transitions that can be induced between magnetic spin energy levels of certain atomic nuclei in a magnetic field, by means of irradiating the sample in the radio frequency range. In the case of common nuclei such as ^{1}H, ^{13}C, and ^{27}Al, the required frequency depends in the first instance on the strength of the magnetic field (Zeeman term). Transition frequencies are furthermore affected by local anisotropic interactions such as spin-spin interactions, chemical shielding (surrounding electrons "screening" the magnetic field applied) or quadrupole interactions (caused by the electric field gradient at the site of a quadrupolar nucleus). Because, in the case of solids, these anisotropic interactions determine the shape and the width of the NMR spectrum, NMR can yield information on the ODF of ordered polymers. In general, the nuclear spin Hamiltonian can be expressed as:

$$
\mathscr{H}_k = \mathbf{I}\cdot\mathbf{R}_k\cdot\mathbf{J}_k\,,
\tag{80}
$$

where **I** is the nuclear spin vector operator, **R** is the second-rank interaction tensor, and **J** represents a vector which may be the same spin vector, another spin vector, or the induction of an external magnetic field. The suffix k denotes the specific interaction that is present. Because the interaction tensor **R** is defined in the macroscopic laboratory system (fixed to the magnetic field), we will express **R** as a spherical tensor to enable rotations to the molecular system of axes. We will also express the direct product of the vectors **I** and **J** as a spherical tensor so that if follows:

$$\mathscr{H} = \sum_{\mathrm{k}} \mathscr{H}_{\mathrm{k}} = \sum_{\mathrm{k}} \sum_{\mathrm{Lm}} C_{\mathrm{k}} T_{\mathrm{k}}^{(\mathrm{L,m})} R_{\mathrm{Lab,k}}^{(\mathrm{L,m})*} , \tag{81}$$

where $T_{\mathrm{k}}^{(\mathrm{L,m})}$ is the spherical notation of the direct product **IJ** and the summation over k takes the various interactions into account.

As above, we can now easily express the tensor **R** in the system of principal axes with the aid of the known rotation transformation:

$$R_{\mathrm{Lab}}^{(\mathrm{L,m})*} = \sum_{\mathrm{n}} D_{\mathrm{mn}}^{\mathrm{L}}(\Omega_{\mathrm{pL}}) R_{\mathrm{Prin}}^{(\mathrm{L,n})*} , \tag{82}$$

where Ω_{pL} is the orientation of the principal axes system in the laboratory system. We can split this up even further by coupling a system of axes XYZ to the sample, since the sample will be set in different positions relative to the magnetic field **B**. Furthermore, a frame xyz is coupled to the molecular chain. We then find that

$$D_{\mathrm{mn}}^{\mathrm{L}}(\Omega_{\mathrm{pL}}) = \sum_{\mathrm{pq}} D_{\mathrm{pm}}^{\mathrm{L}*}(\Omega_{\mathrm{B}}) D_{\mathrm{pq}}^{\mathrm{L}}(\Omega) D_{\mathrm{qn}}^{\mathrm{L}}(\Omega_{\mathrm{prin}}) , \tag{83}$$

where Ω_{B} is the known orientation of **B** in XYZ, Ω is the orientation of the molecular system in XYZ, and Ω_{prin} is the orientation of the principal axes in the molecular frame. For the Hamiltonian, we now write:

$$\mathscr{H} = \sum_{\mathrm{k}} \sum_{\mathrm{Lmnpq}} \sum C_{\mathrm{k}} T_{\mathrm{k}}^{(\mathrm{L,m})} D_{\mathrm{pm}}^{\mathrm{L}*}(\Omega_{\mathrm{B}}) D_{\mathrm{pq}}^{\mathrm{L}}(\Omega) D_{\mathrm{qn}}^{\mathrm{L}}(\Omega_{\mathrm{prin}}) R_{\mathrm{prin}}^{(\mathrm{L,n})*} \tag{84}$$

If this Hamiltonian is diagonalized with respect to M and N, which are the eigenvectors of $\mathscr{H}$, the probabilities of transitions $W_{\mathrm{MN}}^{\mathrm{k}}$ at resonance frequencies $\nu_{\mathrm{MN}}^{\mathrm{k}}$ are obtained. The shape of the NMR line $I(\nu)$ is now given by:

$$I(\nu) = \sum_{\mathrm{k}} \sum_{\mathrm{MN}} \langle W_{\mathrm{MN}}^{\mathrm{k}} \cdot \delta[\nu - \nu_{\mathrm{MN}}^{\mathrm{k}}] \rangle , \tag{85}$$

where the summation MN is carried out over all allowed transitions and the ensemble average is taken over all occurring orientations. For details the reader is further referred to Hentschel et al. [47]. Here, we follow along their lines.

If we assume that first-order perturbation theory can be applied, it follows for the resonance frequencies that:

$$\nu_{\mathrm{MN}}^{\mathrm{k}} = \sum_{\substack{\mathrm{j}=-2 \\ \mathrm{j\ even}}}^{2} N_{\mathrm{k}}^{\mathrm{j}} D_{\mathrm{j0}}^{2}(\Omega_{\mathrm{pL}}) , \tag{86}$$

where the values of the moments $N_{\mathrm{k}}^{\mathrm{j}}$ are dependent on the type of interaction. In principle, Eq. (85) can now be worked out to yield the line shape in terms of order parameters $\langle D_{\mathrm{mn}}^{\mathrm{L}}(\Omega) \rangle$, but in practice some simplifications are necessary. In the case of a uniaxial ODF with an axially symmetric interaction tensor, and assuming $W_{\mathrm{MN}}^{\mathrm{k}} = 1$, we can write Eq. (85) as:

$$I(\nu) = 8\pi^2 \sum_{\mathrm{L}} \langle P_{\mathrm{L}} \rangle P_{\mathrm{L}}(\cos\theta_{\mathrm{prin}}) P_{\mathrm{L}}(\cos\theta_{\mathrm{B}}) \frac{P_{\mathrm{L}}(\cos\theta_{\mathrm{pL}})}{6N_{\mathrm{k}}^{0}\cos\theta_{\mathrm{pL}}} , \tag{87}$$

where

$$P_2(\cos\theta_{\mathrm{pL}}) = \frac{\nu}{2N_{\mathrm{k}}^{0}} \tag{88}$$

and θ is the polar angle with subscripts as above. We now see that from the NMR spectra the order parameters $\langle P_{\mathrm{L}} \rangle$ can be calculated when θ_{prin}, θ_{B} and N_{k}^{0} are known.

Discussion

We have shown here how the mathematical formalism that describes the properties of rotation matrices can be used to quantify the orientational distribution function of polymeric chain segments or crystals in an orientationally ordered material. This ODF is characterized by a number of order parameters that can experimentally be determined by a variety of techniques. Very often, we may (or have to) assume that the molecular elements are cylindrically symmetric and that the statistical distribution around the main symmetry axis is also axially or fiber symmetric. In that case the only order parameters that remain are the well-known Legendre polynomials $\langle P_2 \rangle$, $\langle P_4 \rangle$, etc. In the case of lower symmetries we have to use spherical harmonics or Wigner functions for the order parameters. In the case of biaxial sample symmetry with orthorhombic molecular elements we find order parameters $\langle D_{\mathrm{mn}}^{\mathrm{L}} \rangle$ with m and n even and positive. For still lower symmetries complex order parameters are found and experimental techniques will yield only combinations of order parameters, such that the outcome is real again (e.g., $\langle D^{2}_{-10} \rangle + \langle D^{2}_{10} \rangle$, see the first Appendix).

The symmetry of the system determines the number of non-vanishing order parameters. Whether or not the total number of order parameters of a certain rank is experimentally attainable will depend on the specific conditions of the experimental technique. In general, birefringence offers no more than two second-rank order parameters and IR-dichroism maximally four second-rank order parameters. Raman and fluorescence offer in practice not more than two second- and three fourth-rank order parameters. NMR in most cases gives only $\langle P_2 \rangle$ and $\langle P_4 \rangle$, but sometimes also $\langle P_6 \rangle$ and $\langle P_8 \rangle$. X-ray measurements can give much higher numbers of order parameters of lower symmetries. It should be kept in mind, however, that the success of the technique which is applied depends strongly on the amount of information about intrinsic chain or crystal cell parameters that is available. It is therefore obvious that especially the orientational properties of polyethylene are widely studied.

Summarizing, we may state that the approach presented here offers the following advantages:

1) Various experimental techniques yield results in terms of order parameters, which can directly be compared;
2) Symmetry properties of both the sample and the molecular elements directly result in vanishing order parameters;
3) The order parameters follow explicitly in expressions of the macroscopic observable. This is the result of the formal spherical notation of a rotation, when the physical quantity involved is rotated from a macroscopic to a microscopic frame of axes;
4) The mathematical notation dates back to the original description of rotation matrices and is generally accepted and widely documented.

Certainly, the proposed mathematical description has some disadvantages. The mathematics are not easy and in many cases the summations over various indices may not look very inviting. It is therefore advisable to apply the Cartesian description in those simple cases where uniaxial sample symmetry and axially symmetric molecular elements apply (that is, only the polar angle β enters the ODF) and only $\langle P_2 \rangle$, or possibly $\langle P_4 \rangle$ are to be determined. In the analysis of IR-dichroism, e.g., the spherical notation is practically never applied. There may be some discussion on whether or not to use the rotation matrix formalism on polarized fluorescence or Raman analysis. Working the analysis of these techniques out in Cartesian notation leads to tedious formulas, especially when α or γ enters the ODF [34, 65]. As soon as molecular motion is considered, or when more than one rotational transformation is performed, or in cases of lower symmetry, the approach presented above is to be preferred.

Another disadvantage of the use of rotation matrices may be that the lowest-rank Wigner functions are very broad, and are therefore not adequate in describing very sharp ODF's. For the ODF of the crystalline phase of polyethylene fibers it has been reported that up to 16 order parameters were necessary to quantify the almost perfect orientation [66]. In most other cases, however, where broad and smooth ODF's exist, the above approach is more than sufficient.

In the elaboration of the mathematics of the various experimental techniques, we have used two different mathematical approaches. In the first, the macroscopic observable is written in terms of an orientation-dependent term with certain Euler angles incorporated, but with any orientation dependent physical quantity left out; see Eqs. (49), (69) and (78). The angle-dependent function is then written as a Wigner function and the necessary rotational transformations are applied to this function. In the second approach, the physical quantity that enters the macroscopic observable is written as a spherical tensor, which is then transformed to another frame of axes; see Eqs. (62), (75) and (84). In principle, both approaches could be used in any case, but the latter seems to be preferred in most instances. As said, fluorescence depolarization could be worked out with the direct product of absorption and emission moment as a spherical tensor. Similarly, instead of the absorption moment in IR measurements, one could define an extinction tensor that is multiplied on both sides by the same electric field vector [67]. Finally, x-ray scattering studies could be evaluated by defining a spherical polarizability tensor, so that the measured intensity distribution of a pole figure can be written directly in terms of order parameters when the rotational transformation of the polarizability tensor is carried out.

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Appendices

Second-rank Wigner functions

The rotation matrix elements $D^2_{\mathrm{mn}}(\alpha, \beta, \gamma)$ are given in the table for various values of m and n.

	$n = -2$	$n = -1$	$n = 0$	$n = 1$	$n = 2$
$m = -2$	$1/4\mathrm{e}^{2\mathrm{i}\alpha}(1 + \cos\beta)^2\mathrm{e}^{2\mathrm{i}\gamma}$	$1/2\mathrm{e}^{2\mathrm{i}\alpha}\sin\beta(1 + \cos\beta)\mathrm{e}^{\mathrm{i}\gamma}$	$\sqrt{3/8}\mathrm{e}^{2\mathrm{i}\alpha}\sin^2\beta$	$1/2\mathrm{e}^{2\mathrm{i}\alpha}\sin\beta.$ $(1 - \cos\beta)\mathrm{e}^{-\mathrm{i}\gamma}$	$1/4\mathrm{e}^{2\mathrm{i}\alpha}(1 - \cos\beta)^2\mathrm{e}^{-2\mathrm{i}\gamma}$
$m = -1$	$-1/2\mathrm{e}^{\mathrm{i}\alpha}\sin\beta.$ $(1 + \cos\beta)\mathrm{e}^{2\mathrm{i}\gamma}$	$1/2\mathrm{e}^{\mathrm{i}\alpha}(2\cos\beta - 1).$ $(1 + \cos\beta)\mathrm{e}^{\mathrm{i}\gamma}$	$\sqrt{3/2}\mathrm{e}^{\mathrm{i}\alpha}\sin\beta\cos\beta$	$1/2\mathrm{e}^{\mathrm{i}\alpha}(2\cos\beta + 1).$ $(1 - \cos\beta)\mathrm{e}^{-\mathrm{i}\gamma}$	$1/2\mathrm{e}^{\mathrm{i}\alpha}\sin\beta.$ $(1 - \cos\beta)\mathrm{e}^{-2\mathrm{i}\gamma}$
$m = 0$	$\sqrt{3/8}\sin^2\beta\mathrm{e}^{2\mathrm{i}\gamma}$	$-\sqrt{3/2}\sin\beta\cos\beta\mathrm{e}^{\mathrm{i}\gamma}$	$1/2(3\cos^2\beta - 1)$	$\sqrt{3/8}\sin\beta\cos\beta\mathrm{e}^{-\mathrm{i}\gamma}$	$\sqrt{3/8}\sin^2\beta\mathrm{e}^{-2\mathrm{i}\gamma}$
$m = 1$	$-1/2\mathrm{e}^{-\mathrm{i}\alpha}\sin\beta.$ $(1 - \cos\beta)\mathrm{e}^{2\mathrm{i}\gamma}$	$1/2\mathrm{e}^{-\mathrm{i}\alpha}(2\cos\beta + 1).$ $(1 - \cos\beta)\mathrm{e}^{\mathrm{i}\gamma}$	$-\sqrt{3/2}\mathrm{e}^{-\mathrm{i}\alpha}\sin\beta\cos\beta$	$1/2\mathrm{e}^{-\mathrm{i}\alpha}(2\cos\beta - 1).$ $(1 + \cos\beta)\mathrm{e}^{-\mathrm{i}\gamma}$	$1/2\mathrm{e}^{-\mathrm{i}\alpha}\sin\beta.$ $(1 + \cos\beta)\mathrm{e}^{-2\mathrm{i}\gamma}$
$m = 2$	$1/4\mathrm{e}^{-2\mathrm{i}\alpha}(1 - \cos\beta)^2\mathrm{e}^{2\mathrm{i}\gamma}$	$-1/2\mathrm{e}^{-2\mathrm{i}\alpha}(1 - \cos\beta)\mathrm{e}^{\mathrm{i}\gamma}$	$\sqrt{3/8}\mathrm{e}^{-2\mathrm{i}\alpha}\sin^2\beta$	$-1/2\mathrm{e}^{-2\mathrm{i}\alpha}\sin\beta.$ $(1 + \cos\beta)\mathrm{e}^{-\mathrm{i}\gamma}$	$1/4\mathrm{e}^{-2\mathrm{i}\alpha}(1 + \cos\beta)^2\mathrm{e}^{-2\mathrm{i}\gamma}$

Some relationships between Wigner functions

$$D^{\mathrm{L}}_{\mathrm{mn}}(0, 0, 0) = d^{\mathrm{L}}_{\mathrm{mn}}(0) = \delta_{\mathrm{mn}}$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\pm\pi) = (-1)^{\mathrm{L}\pm\mathrm{n}}\delta_{\mathrm{m-n}}$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(2\pi) = (-1)^{2\mathrm{L}}\delta_{\mathrm{mn}}$$

$$D^{\mathrm{L}*}_{\mathrm{mn}}(\alpha, \beta, \gamma) = D^{\mathrm{L}}_{\mathrm{mn}}(-\alpha, \beta, -\gamma)$$

$$D^{\mathrm{L}*}_{\mathrm{mn}}(\alpha, \beta, \gamma) = D^{\mathrm{L}}_{\mathrm{nm}}(-\gamma, -\beta, -\alpha)$$

$$D^{\mathrm{L}*}_{\mathrm{mn}}(\alpha, \beta, \gamma) = (-1)^{\mathrm{m-n}}D^{\mathrm{L}}_{-\mathrm{m}-\mathrm{n}}(\alpha, \beta, \gamma)$$

$$D^{\mathrm{L}}_{\mathrm{mn}}(\alpha, \beta, \gamma) = (-1)^{\mathrm{L+m}}D^{\mathrm{L}}_{-\mathrm{mn}}(-\alpha, \pi + \beta, \gamma)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\pi + \beta) = (-1)^{\mathrm{L-m}}d^{\mathrm{L}}_{-\mathrm{mn}}(\beta)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\pi - \beta) = (-1)^{\mathrm{L-m}}d^{\mathrm{L}}_{\mathrm{m}-\mathrm{n}}(\beta)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\beta) = d^{\mathrm{L}}_{\mathrm{nm}}(-\beta)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\beta) = (-1)^{\mathrm{m-n}}d^{\mathrm{L}}_{-\mathrm{m}-\mathrm{n}}(\beta)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\beta) = d^{\mathrm{L}}_{-\mathrm{n}-\mathrm{m}}(\beta)$$

$$d^{\mathrm{L}}_{\mathrm{mn}}(\beta) = (-1)^{\mathrm{m-n}}d^{\mathrm{L}}_{\mathrm{mn}}(-\beta)$$

Clebsch–Gordon coefficients

The table gives the Clebsch–Gordon coefficients $C(j_1 j_2 J; m_1 m_2)$ for $j_1 = j_2 = 2$, $M = m_1 + m_2$. Note that the square root of all values given should be taken: for $-3/7$ read $-\sqrt{3/7}$

M	m_1	m_2	$J = 0$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
−4	−2	−2	–	–	–	–	1
−3	−1	−2	–	–	–	1/2	1/2
−3	−2	−1	–	–	–	−1/2	1/2
−2	0	−2	–	–	2/7	1/2	3/14
−2	−1	−1	–	–	−3/7	0	4/7
−2	−2	0	–	–	2/7	−1/2	3/14
−1	1	−2	–	1/5	3/7	3/10	1/14
−1	0	−1	–	−3/10	−1/14	1/5	3/7
−1	−1	0	–	3/10	−1/14	−1/5	3/7
−1	−2	0	–	−1/5	3/7	−3/10	1/14
0	2	−2	1/5	2/5	2/7	1/10	1/70
0	1	−1	−1/5	−1/10	1/14	2/5	8/35
0	0	0	1/5	0	−2/7	0	18/35
0	−1	1	−1/5	1/10	1/14	−2/5	8/35
0	−2	2	1/5	−2/5	2/7	−1/10	1/70
1	2	−1	–	1/5	3/7	3/10	1/14
1	1	0	–	−3/10	−1/14	1/5	3/7
1	0	1	–	3/10	−1/14	−1/5	3/7
1	−1	2	–	−1/5	3/7	−3/10	1/14
2	2	0	–	–	2/7	1/2	3/14
2	1	1	–	–	−3/7	0	4/7
2	0	2	–	–	2/7	−1/2	3/14
3	2	1	–	–	–	1/2	1/2
3	1	2	–	–	–	−1/2	1/2
4	2	2	–	–	–	–	1