Chapter II. Molecular segments orientation study using $^{29}$Si NMR methods.

2.1. NMR Spectroscopy, Anisotropic Nuclear Spin Interaction.

The term Nuclear Magnetic Resonance (NMR) unifies a big variety of the quantum phenomena based on the interaction of the nuclear spins with magnetic fields and radiofrequency irradiation. Generally, NMR denotes the resonance response of the spin system polarized in the magnetic field on the rf-irradiation. The spectrum of the response signal reflects the picture of the energy levels of the atomic nuclei spins and therefore can be effectively used in many ways for the probing the molecular, structural, dynamical and other properties both on micro and macro level. The basics of the NMR spectroscopy both in theoretical and applied aspects can be found in many textbooks [II.1-3]. Appendix II collects some important information about the NMR theory, which is relevant for current work.

The appearance of a NMR spectrum is determined by the various interactions of the nuclear spins with each other as well as with quantities like local and external magnetic fields, electric field gradient and coupling to the surroundings or lattice. In this section, the most attention will be given to the anisotropic spin interactions, which have a great importance for the NMR investigation of the structure and orientational ordering of the systems of our interest.

The most important interaction in the NMR is the coupling of the nucleat spins to the applied external magnetic field. It is Zeeman interaction (see AII.2), which defines the basic (non-perturbed) resonance frequency of the spins system. In reality, this frequency is often changed due to the chemical shift and the indirect couplings. Both of them depend on the features of the electron shielding in the surroundings of nuclei. They are often used as «portraits» of the molecules chemical properties. Generally, the spin interactions have a vector properties i.e they are quantified with the magnitude and orientation. The interaction of two vectors is described by a tensor, which is normally represented by a matrix in Cartesian coordinates. Such kinds of properties have (i) the direct dipole-dipole coupling, (ii) the indirect coupling between two spins, and (iii) the coupling of the spins with a local magnetic field (chemical shift). The similar description has the quadrupolar coupling, which is denotes the interaction of the spins with the tensor of electric field gradient. In liquids the tensorial properties of the interactions, normally are eliminated by the averaging due to the fast molecular motion, so that only the orientation-independent parts corresponding to the traces of the coupling tensors are effective. From all the interactions mentioned above, only chemical shift and indirect coupling have non-zero traces of tensor matrices. Nevertheless, in solids, the motional averaging is not so effective, and tensorial properties of the interactions lead to the resonance frequency changes, which are orientationally dependent. In this case the description of the interaction Hamiltonian operator in
terms of irreducible spherical tensors instead of Cartesian matrices is helpful [II.4] (see also AII.2).

If the orientation dependence of the resonance line frequency of spin \( I=1/2 \) is determined only by just one type of the interaction it is possible to use it for measuring the angles of chemical bonds, and other structural characteristic of the molecules. In polycrystalline solid powder, molecular and liquid crystals, polymers and other partially oriented or disoriented samples the angles of the interaction tensor main axes with respect to the external magnetic field and, therefore, the corresponding resonance frequencies are distributed over large range of values. This leads to the broadening of the NMR spectrum to some pattern of the specific shape, so-called **wideline NMR spectrum**.[II.1.2] Generally, the shape of this pattern is, in addition, influenced by the molecular reorientation on the time scale of inverse width of the resonance line. Therefore, the lineshape provides the information on structural, orientational and dynamical properties of the solid sample. [II.5-7]

### 2.1.1 Anisotropic chemical shift interaction tensor.

The external magnetic field \( B_0 \) applied to nuclear spins is always shielded by the surrounding electron clouds. The resulting local field \( B_{\text{loc}} \) influencing on nuclei in this case is given by

\[
\tilde{B}_{\text{loc}} = (1 - \hat{\sigma}_{zz}) \tilde{B}_0
\]

where \( \sigma_{\text{CS}} \) is the chemical shift tensor. As it was mentioned above, the orientation dependence of the resonance frequencies in the most convenient manner can be treated in terms of irreducible spherical tensors of the second rank. In Appendix II it is shown that the offset of the resonance line due to the anisotropic chemical shift can be separated in isotropic, symmetric and antisymmetric parts. Only isotropic and symmetric parts influence on NMR spectrum [A2.2, II.4,8]. In principal axes system the tensor is characterized only by the combination of three diagonal elements \( \sigma_{xx}, \sigma_{yy} \) and \( \sigma_{zz} \). The resonance frequency offset \( \sigma_{zz} \) caused by the anisotropic chemical shielding can be given as

\[
\sigma_{zz} = \sigma_{\text{iso}} + \frac{\Delta \sigma}{2} (3 \cos^2(\theta) - 1) - \frac{\Delta \sigma}{2} \eta \sin^2(\theta) \cos^2(\varphi)
\]

where \( \sigma_{\text{iso}} \) is the isotropic part of the frequency shift defined by the tensor trace:

\[
\sigma_{\text{iso}} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})
\]

\( \Delta \sigma \) is the tensors anisotropy parameter:
\[ \Delta \sigma = \sigma_{zz} - \sigma_{xx} + \sigma_{yy} \]  \hspace{1cm} (2.2b)

and \( \eta \) is the parameter of asymmetry:

\[ \eta = \frac{\sigma_{xy} - \sigma_{xz}}{\sigma_{zz} - \sigma_{iso}} \]  \hspace{1cm} (2.2c)

which has non-zero value if the tensor has no axial symmetry. In this case only two main values of tensor \( \sigma_{xx} = \sigma_{yy} = \sigma_{L} \) and \( \sigma_{zz} = \sigma_{||} \) are relevant. Here, \( \theta \) and \( \phi \) denote the polar and azimuthal angles between \( \sigma_{||} \) and \( B_0 \), respectively. The tensor properties of chemical shift means that the local field influenced on nuclei differs from the external field \( B_0 \) in both magnitude and direction due to the shielding effect of the surrounding electrons. Generally, a connection between external field \( B_0 \) and local filed \( B_{loc} \) can be represented graphically as a second order surface (ovaloid). (see Fig 2.1). The perfect detailed explanation of the pictorial representation of CS tensor can be found in [II.9]

![Fig 2.1](image)

More details about the expansion into the irreducible tensors and transformation between laboratory and the principal axes frames using Wigner matrices can be found in (AII.2). Expressions 2.2 allow one finding the lineshape of the NMR spectra determined mainly by chemical shift interaction. For the powder sample, when all the orientations of individual tensors main axis have equal probability the shape of the wideline NMR spectrum can be obtained by the integration over the whole sphere the contributions of corresponding individual resonance lines shifted according to 2.1.

\[ S(\sigma) = \iiint_{\Omega} f(\sigma - \sigma_{e}(\theta, \phi)) \sin \theta d\theta d\phi \]  \hspace{1cm} (2.3)

Here \( f(\sigma) \) denotes the shape of the individual lines.

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\[ \Delta \sigma = \sigma_{zz} - \sigma_{xx} + \sigma_{yy} \]  \hspace{1cm} (2.2b)

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In ideal case for $\delta$-like intrinsic lineshape, i.e. $f(\sigma) = \delta(\sigma - \sigma_{\text{iso}}(\theta, \phi))$, for the axially symmetric CS tensor ($\eta=0$) after integration the characteristic spectral density pattern can be obtained:

$$S(\sigma) = \begin{cases} 2\sqrt{2\Delta\sigma} & \text{if } \sigma_{\parallel} \leq \sigma \leq \sigma_{\perp} \text{ or } \sigma_{\perp} \leq \sigma \leq \sigma_{\parallel} \\ 0 & \text{for other } \sigma \end{cases}$$

(2.4)

**Fig 2.2** demonstrates the lineshape pattern, which is built according to Eqn 2.4. The spectral line has a singularity at the frequency $\sigma=\sigma_{\perp}$ corresponding to the angle $\theta=\pi/2$ between the magnetic field $B_0$ and Z-axis of coupling tensor. For this angle, $B_0$ lies in XY plane of the principal axes system. The cut-off at $\sigma_0$ corresponds to an orientation of $B_0$ parallel to Z-axis. Thus, when the orientation of the CS tensor with respect to molecule-fixed coordinate frame is known a wideline CS spectrum can be used to determine the molecular orientation. On the other hand, the assumption of $\delta$-like intrinsic lineshape $f(\sigma)$ is, of course, nonrealistic. The inhomogeneity of the CS tensor values distribution and variety of the structural conformation leads to the finite width of the resonance line corresponding to some specific orientation. In this case the CS spectrum is represented by the convolution of the «ideal» pattern corresponding to the $\delta$-like individual lineshape with Gaussian or Lorenz patterns according to Eqn 2.3 (see **Fig 2.3**)[II.10]. It can be noticed that the formula 2.3 can be reversed and the broadening lineshape function $f(\sigma)$ can be recovered from the experimental powder spectrum. The example of such a deconvolution will be shown in following section.

Distribution of the NMR frequencies due to the anisotropic chemical shift

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**Fig 2.2.** Distribution of the resonance frequencies due to the anisotropic chemical shift. Different orientations of the tensor axis with respect to the external field $B_0$ contribute to the different resonance positions (Eqn 2.2). The example of the powder averaged wideline NMR spectrum for axial symmetric CS tensor is built according to Eqn 2.4.
Fig 2.3 Convolution of the «ideal» powder CS pattern with Gaussian broadening function $f(\sigma - \sigma_0)$ for realistic spectrum representation in simulations. The value of broadening factor $b$ reflects the distribution of CS parameters corresponding to the specific tensor axis orientations. This distribution can be caused by a variety of conformations, thermal molecular motion or other reasons.

### 2.2. Orientation Distribution Function (ODF)

#### 2.2.1 Theoretical background.

The state of orientation of any ordered system can be described in general manner by the orientation distribution function (ODF) $W(\theta, \phi, \psi)$. This function, practically, represents a probability density to find an element of the system in certain orientation with respect to the given coordinate frame. Considering orientation of a partially ordered system (polymers, liquid crystals and others), the most convenient way, usually, is to use the set of Eulerian angles [II.2, 4, 6, 11] to describe the probability that the certain element (whole molecule, molecular segment, chemical bond) lays within an infinitesimal interval around angles $\theta, \phi, \psi$, with respect to the local director $N$. (see Fig 2.4)

Fig 2.4 Set of Eulerian angles needed for fixing the object's orientation in space. The orientation distribution can be represented like a function of all or some of the angles depending on internal symmetry of the system.

To make further simplification it is comfortable to represent the dependence of ODF $W$ from azimuthal angle $\theta$ via its cosine. The advantage of this approach is demonstrated by Fig 2.5. Obviously, the amount of elements in direction $\theta$ distributed according to some ODF $U(\theta)$ is proportional to the area of the corresponding spherical element $\Delta \theta$. Rings around the sphere with equal $\Delta \theta$ contain more area if they correspond to larger $\theta$. In the same time, rings with equal $\Delta \cos(\theta)$ contain equal area for any value of $\theta$. For the particular case of the isotropic distribution, the cosine representation leads to constant ODF (equal to $1/4\pi$), whereas the
representation through $\theta$ have to include the factor $d(cos\theta)=sin(\theta)d\theta$ to provide a proper normalization.

![Diagram](image)

Fig 2.5 Rings around sphere with equal $\Delta \theta$ contain more area if they correspond to larger $\theta$. Rings with equal $\Delta cos(\theta)$ contain equal area for any $\theta$. The orientation probability for isotropic orientation distribution $U$ is proportional to surface element $sin\theta\Delta\theta=\Delta cos(\theta)$ while it is constant if $U$ expressed as a function of $cos(\theta)$.

It will be shown in the following section that in the case of NMR analysis it is often more convenient to use the representation of the ODF via series of the «moments», for example the generalized spherical harmonics [II.11].

$$W(\theta, \varphi, \psi) = \sum_{n=0}^{\infty} \sum_{m=-1}^{+1} \sum_{k=-1}^{+1} w_{nmk} Y_{nmk}(cos(\theta)) e^{-im\varphi} e^{-imp}$$ (2.5)

In many cases, yet, the one or more Eulerian angles are not relevant. For example the bulk polymers in a shape of film or a fiber have overall orthorhombic or hexagonal symmetry, respectively. For different types of liquid crystals, at least an axially symmetrical ordering has to be always assumed. Therefore, depending on the type of system symmetry the dimensionality of the ODF can be reduced to one or two dimensions. Some examples of the ODF’s which can be found in real mesogenic and other partially ordered systems are demonstrated on Fig 2.6. The two-dimensional orientation distribution function is denoted here like a $V(\varphi, cos(\theta))$. For the particular case when only one (usually azimuthal) angle is relevant the one-dimensional function $U(cos(\theta))$ will be used.

![Diagram](image)

Fig 2.6 The examples of the orientation distribution functions.
2.2.2 Methods of ODF examination by NMR lineshape analysis.

As it was shown in previous section, the anisotropic spin interaction by itself leads to specific pattern of the NMR lineshape. The form of the pattern is different depending on the type and the parameters of the interaction. The orientation distribution function enters the shape of the wideline spectrum in some hidden manner [II.6, 12-14]. The angular dependence of the NMR resonance frequency is given by the Eqn. 2.2 via the orientation of the magnetic field in principal axis system of the spin interaction tensor. Obviously, when some specific orientation distribution is present in the system, some of the angular areas and therefore the corresponding spectral position are more abundant. This leads to the changing of the lineshape function. It is argued that amount of interaction tensor main axes in the interval \(\cos(\theta) \ldots \cos(\theta) + d(\cos(\theta))\), \(\varphi, \varphi + d\varphi\) the number of which is \(V(\varphi,\cos(\theta))\) contribute to the resonance position \(\sigma.\sigma + d\sigma\) with intensity \(S(\sigma)\).

\[
S(\sigma)d\sigma = V(\cos(\theta),\varphi)d\cos(\theta)d\varphi
\] (2.6)

The wideline NMR spectrum can be written as the convolution of resonance frequency offset with the orientation distribution function \(V(\varphi,\cos(\theta))\).

\[
S(\sigma) = \int_{\sigma_{\min}}^{\sigma_{\max}} f(\sigma) \int_{0}^{2\pi} f(\sigma_{\varphi} - \sigma(\cos(\theta),\varphi))V(\cos(\theta),\varphi)d\cos(\theta)d\varphi
\] (2.7)

Here \(f(\sigma)\) denotes the intrinsic shape of the individual NMR line. In ideal case \(f(\sigma)\) can be considered as \(\delta\)-function. In practice, different broadening factors leads to the approximately Lorentz or Gaussian pattern for \(f(\sigma)\). It was shown in Chapter I that for the uniaxial spin interaction (dipolar, quadrupolar or CS with \(\eta=0\)) the resonance frequency position depends only on azimuthal angle \(\theta\). In this case the information about only the one-dimensional variant of the orientation distribution function \(U(\cos(\theta))\) can be extracted from lineshape analysis [II.6,13,14].

One of the frequently used ways of estimation of the ODF is using the specific model function with parameters to be found from the experiments. A number of works are devoted to the developing of the different models of the orientation distribution [II.15-19]. On the other hand, the model approach needs either strong theoretical background to build the realistic sample function with reasonable amount of unknown parameters. Another way round is a “brute force” method of the molecular dynamics simulation which costs a lot of time and computer resources. Therefore, we concentrate in our work on the model free approaches to the orientation distribution, trying to make the experimental results interpretation in the direct way and using only the most common a priori suggestions about the system to be studied.
2.2.3 Model Free approaches to ODF estimation using the NMR

There are basically three main “model free” possibilities of the $U(\cos \theta)$ estimation which can be found in literature on this subject:

1. Comparison of the lineshape of oriented and fully disoriented sample.

For one dimension of the ODF, the 2.6 can be rewritten as:

$$S(\sigma)d\sigma = U(\cos(\theta))d\cos(\theta)$$  \hspace{1cm} (2.8)

For the isotropic orientation distribution, when $U(\cos(\theta))=1/4\pi$ the isotropic lineshape can be obtained as a «reference spectrum» from the same sample in disordered state.

$$S_{iso}(\sigma) = \frac{1}{4\pi^2} \frac{d \cos(\theta)}{d\sigma}$$  \hspace{1cm} (2.9)

Therefore $U(\cos(\theta))$ can be estimated from the corresponding spectral lineshape of oriented sample by dividing it on reference spectrum $S_{iso}(\sigma)$ [II.20-22].

$$U(\cos(\theta)) = 4\pi^2 \frac{S(\sigma)}{S_{iso}(\sigma)}$$  \hspace{1cm} (2.10)

The obvious disadvantages of this method are (i) high sensitivity to the unavoidable experimental error (noise, phase distortions) and (ii) necessity to be able to get the spectrum of the isotropic sample (that is not always possible).

2. Deconvolution procedure can be applied to the spectrum lineshape (or, sometimes, the set of lineshape for different sample orientation with respect to external magnetic field) described by Eqn. 2.7 to get the orientation function from the integral. In general, case this leads to the integral equation which solution is the so-called «Fredholm problem of the first kind». In general, it provides only the approximate and often unstable numerical solution for the subintegral function to be found. Nevertheless, using the specially adopted algorithms in some cases it is possible to restore the ODF from spectrum in the form of discrete histogram with reasonable solution stability and error [II.22, 23].

3. Method of the ODF «moments» determination [II.6] extensively developed by Hentschel, Sillescu and Spiess [II.11-14]. For one-dimensional ODF $U(\cos(\theta))$ the spherical harmonics of the expansion series in Eqn 2.5 becomes Legendre polynomials.

$$U(\cos(\theta)) = \sum_{n=0} u_n P_n(\cos(\theta))$$  \hspace{1cm} (2.11)

The orthogonality of the $P_n$ permits the calculation of the expansion coefficients as

$$u_n = \frac{2n+1}{2} \int_{-1}^{1} U(\cos(\theta)) P_n(\cos(\theta)) d(\cos(\theta)) = \frac{2n+1}{2} \langle P_n \rangle$$  \hspace{1cm} (2.12)
and can be treated like the «moments of the n-th order» of the orientation distribution function $U(\cos(\theta))$. For an isotropic distribution $\langle P_0 \rangle = 1$ and $\langle P_n \rangle = 0$ for $n>1$. For completely ordered sample $\langle P_n \rangle = 1$. Clearly, zero-moment $\langle P_0 \rangle$ quantifies the isotropic part of the orientation distribution. $\langle P_2 \rangle$ is the second moment also known as the orientation degree or macroscopic orientation order parameter. For weakly ordered samples usually the moments higher than 4 are not relevant for the ODF description. In the same time, with the sample ordering increase the higher moments become more significant. Because the expansion treats molecular order like a perturbation of the isotropic state, it converges for weak order. To achieve converges for high order the ODF may be expanded, for instance, into planar or conical distributions (see Fig 2.6).

Because $\cos(\theta)$ enters only by its square into all the types of anisotropic spin interaction tensor constants (see section 2.1) a negative and positive $\cos(\theta)$ which means $\theta$ and $\pi - \theta$ cannot be distinguished by this method and $U(\cos(\theta))$ represents the only symmetrical part of the ODF. Therefore, only the coefficients $u_n$ with even power of $\cos(\theta)$ survive in the series (2.11).

Turning to the one–dimensional ODF in expression 2.7 for spectral lineshape and substituting the Legendre series representation for $U(\cos(\theta))$ the Legendre subspectra analysis can be determined:

$$S(\sigma) = \sum_{n=0}^{\infty} \frac{2n+1}{2} S_{2n}(\sigma)$$

(2.13)

$$S_{2n}(\sigma) = \langle P_{2n} \rangle \int_{-\sigma}^{\sigma} P_{2n}(\cos(\theta)) f(\sigma - \theta) d\cos(\theta)$$

Here $S_{2n}(\sigma)$ represents the subspectra corresponding to different moments $\langle P_{2n} \rangle$ of the orientation distribution function. Formula 2.13 demonstrates a general approach to the Legendre subspectra analysis. The following steps may depend on many practical aspects of the system to be studied. The application of this approach is restricted by the symmetry requirements mentioned above, that is to cylindrical molecules, macroscopically uniaxial samples and uniaxial tensors of anisotropic spin interactions. For many samples this conditions are fulfilled when using dipolar interaction between protons, deuterons in aliphatic bonds or axially symmetric chemical shift of $^{13}$C nuclei [II.7,14, 25]. In simplest variant when the principal axis of the spin interaction tensor is oriented along the molecular segment which orientation is studied, the
determination of the ODF moments according to 2.13 can be performed by direct fitting of the

Legendre subspectra analysis

ODF Legendre expansion $<P_{2n}>$ weighted spectra

$P_0(\cos(\theta))$

$P_2(\cos(\theta))$

$P_4(\cos(\theta))$

$U(\cos(\theta)) = P_0 + <P_{2n}> P_2(\cos(\theta)) + <P_{4n}> P_4(\cos(\theta))$

$S_0 + S_2 + S_4$

$S_0$

$S_2$

$S_4$

Fig 2.7. Method of the Legendre subspectra analysis for axial symmetric CS tensor. Left column: expansion terms of the ODF $U(\cos(\theta))$. Right: corresponding $<P_{2n}>$ weighted subspectra. It should be noticed that the roots of the Legendre polynomial are directly reflected as zero-crossing in corresponding subspectra.

experimental spectra with the Legendre subspectra combination varying the $<P_{2n}>$ parameters (see Fig 2.7). This method can be especially effective for moderate and weak ordering when the higher order moments of the ODF are not relevant.

The examples of Legendre subspectra analysis for the wideline NMR lineshape caused by the uniaxial CS tensor is shown on Fig 2.7. The resonance frequency offset due to anisotropic chemical shift with asymmetry parameter $\eta = \theta$ according to consideration in section 2.1 can be written as:

$$\sigma(\theta) = \sigma_{iso} + \frac{2}{3} \Delta \sigma P_2(\cos(\theta))$$

(2.14)

where $\Delta \sigma$ is CS anisotropy parameter and $\theta$ is the angle between the external magnetic field and CS tensor main axis. The intrinsic lineshape function $f(\sigma - \sigma_{iso})$ can be recovered from the spectrum of powder (isotropic) sample:

$$S_0(\sigma) = \int_0^1 f(\sigma - \sigma_{iso} - \frac{2}{3} \Delta \sigma P_2(\cos(\theta))) d\cos(\theta)$$

(2.15)

by the deconvolution procedure or using the one-parametrical fitting with some sample function (normally Gaussian or Lorentz form) in the manner described in 2.1. The coefficients $<P_{2n}>$
can be chosen to provide the best fit of the analyzed spectra with the result of the Legendre subspectra summation according to 2.13. Fitting may be done «by-eye» or numerically using the appropriate algorithms for minimization of the residuals between calculated and experimental spectrum. The last variant, being more precise, requires a significant amount of the computation recourses, especially for the case of low signal-to-noise ratio in experimental data.

2.2.4. Relationship between NMR-concerned coordinates frames.

In general, the situation with the angular dependence of spin interactions in NMR is rather complicated. While the orientation dependence of a resonance line position which enters into 2.13 as \( f(\sigma_0, \sigma(\theta)) \) is given via the interaction tensor axes orientation with respect to external magnetic field \( B_0 \), the orientational distribution function specifies a distribution of the preferential direction \( N \) in molecule-fixed coordinate frame. Generally, for the description of the orientation distribution of the molecular segments with arbitrary mutual orientation of molecular and spin interaction tensor axes, the one Eulerian angle is not sufficient.

Fig 2.8 shows the relationship between the different coordinate frames and the definitions of the mutual orientation angles. The first Euler angle \( \alpha \) describes the azimuthal direction in which segment \( u \) is tilted. For the axially symmetric orientation (that is usually assumed for the oriented polymers and mesogenic samples) \( \alpha \) is isotropically distributed and can be excluded from consideration by the integration over it. The polar angle \( \beta \) describes the tilt of the segment long axis with respect to the local director \( N \). Angle \( \gamma \) describes the rotation of the segment around its long axis. The main axis of the spin interaction tensor is connected with the orientation of molecular segment by the angle \( \varepsilon \). The spin interaction intensity, however, depends on the angle between the main tensor axis and the external magnetic field \( B_0 \) that gives the laboratory frame in addition to the molecular and spin interaction axes frames. The orientation of the sample (by its local director) in the laboratory frame is described by the angle \( \delta \). The general scheme of the frames interconnections is shown on Fig 2.9 [II.25].
Fig 2.9. The set of angles describing mutual orientation of laboratory (B₀), local director (N) and molecular frames (u, CS). The polar angle \( \beta \) gives the tilt of the segment long axis with respect to the local director N. Angle \( \gamma \) describes the rotation of the segment around its long axis. The main axis of spin interaction tensor is connected with the orientation of the molecular segment by angle \( \epsilon \). The dependence on angle \( \alpha \) is not relevant in axially symmetric systems and can be averaged by the integration.

That way, to apply the methods of the Legendre subspectra analysis, it needs to develop the special approach in each specific case depending on the kind of the spin interaction tensor, which is used to probe the orientation distribution and the relationships between the relevant coordinate frames in sample. Basing on the approach described above the NMR spectrum lineshape can be analyzed also in somewhat different manner to get the necessary information. Instead of the expanding into subspectra, the wideline NMR pattern can be decomposed into their moments:

\[
M_n = \int (\sigma - \sigma_u)^n S(\sigma) d\sigma
\]  

(2.16)

It was shown by the Hentschel at al [II.13] that similar to expansion of the lineshape via the Legendre subspectra (2.9), the moments of spectral line can be expressed via the linear combination of the ODF’s Legendre polynomial moments \( <P_n> \). By reversing of this dependence, the moments of the orientation distribution functions can be determined. The application of this procedure for the investigation the orientational order in the side-chain liquid crystalline polysiloxanes using the \(^{29}\text{Si}\) NMR will be considered in the following section.

2.3 Main-chain molecular segments orientation investigation using \(^{29}\text{Si}\) NMR spectra.

2.3.1. Method of the spectral lineshape analysis based on CS- tensor orientation.

As it was mentioned in Chapter I, the \(^{29}\text{Si}\) NMR has significant advantages for investigation of the investigation of the main-chain orientation in polysiloxanes. Particularly, it seems to be quite effective method because the main contribution to the spectrum comes from the main chain silicon nuclei. The only other line, which could be detected, arises from the end group -\( \text{Si-(CH}_3\text{)}_3 \)
with intensity about less than 5% compared to the main resonance. The orientation of siloxane segment can be therefore monitored by means of anisotropy of the chemical shift tensor. It was experimentally established, that for polyalkylsiloxane chains the chemical shift tensor is axially symmetrical with good accuracy, i.e two of three main values have equal shift $\sigma_{\perp}=(-16\pm1)$ ppm and the third value is shifted by $\sigma_{\parallel}=(32\pm1)$ ppm with respect to isotropic position $\sigma_{\text{iso}}=(\sigma_{\parallel}+2\sigma_{\perp})/3$.[[II.25]. The difference between two positions gives the CS anisotropy value of $\Delta\sigma=(48\pm1)$ ppm. The mutual orientation of the CS-tensor main axis ($\sigma_{\parallel}$), siloxane molecular segment ($u$), local director ($N$) as well as the relevant angles (particularly, the orientation of tensor axis with respect to external magnetic field $B_0$) are shown in Fig 2.10.

![Fig 2.10](image)

**Fig 2.10** Relation between characteristic angles of different coordinate frames applied to the polysiloxane molecular unit. The molecular segment direction $u$ corresponds to Si-Si interconnection vector. The chemical shift main axis coincides with direction of the CH$_3$-CH$_2$ bond. Local director $N$ is given by the preferable orientation of side-chain mesogenic units.

The experimental $^{29}$Si spectrum of fully disordered polysiloxane sample ([Fig 2.11](image)) is, of course, somewhat broadened as compared to the theoretically predicted pattern ([Fig 2.2](image)). The reason is mainly in distribution of CS tensor main values arising from conformational and structural disorder (for instance the distribution of intermolecular distances). The intrinsic lineshape $f(\sigma)$ of the individual resonance line recovered from the experimental spectrum by deconvolution procedure according to Eqn 2.15 can be fitted by the Gaussian function with satisfying accuracy (see [Fig 2.12](image)).[[ II.24]

![Fig 2.11](image)

**Fig 2.11** Experimental $^1$H decoupled $^{29}$Si NMR spectrum of disoriented (powder-like) polysiloxane M6 sample. The lineshape is determined by the axially symmetric CS tensor with $\Delta\sigma=48$ ppm.
Deconvolution of the wideline $^{29}\text{Si}$ NMR spectrum of disoriented PLC M6

Fig 2.12. The example of the powder polysiloxane $^{29}\text{Si}$ CS NMR spectral pattern deconvoluting in order to obtain the intrinsic lineshape. Deconvoluted line (right) can be fitted with the Gaussian function that is typical for the polymer samples. The broadening parameter and the lineshape characterize the thermal motion and tensor parameters variety because of the conformation distribution.

In oriented sample, where some orientations of CS-tensor $\sigma$ axes is more probable than others, the deformation of the lineshape pattern from the isotropic one takes place according to more or less abundant spectral positions corresponding to specific angular directions. The clear evidence of the non-isotropic ordering of $\sigma$ main axes in the sample comes when the CS-spectral patterns are recorded with different orientation of the sample local director $N$ with respect to external magnetic field. Varying angle $\delta$ the maxima of orientation distribution function $U(\theta)$ and therefore the maxima of the spectral intensity $S(\sigma(\theta))$ (eqn 2.8) can be shifted to different positions (see Fig 2.13.)

In our case we are interested in the distribution of orientations of the main-chain segments $u$, which have a perpendicular orientation with respect to the CS tensor main axis ($\epsilon=90^\circ$). Hence, when $\delta=0^\circ$, $u$ can particularly has either parallel or perpendicular orientation to $B_0$. In first case the $\sigma$ main axis is preferably perpendicular to $B_0$ which leads to strong enhancement of $\sigma=\sigma_\perp$ spectral position intensity. In the other case all angles between $\sigma$ and $B_0$ are possible. Due to the
axial symmetry of the $^{29}$Si CS-tensor the wideline NMR spectrum provides only one-dimensional information about the distribution of the polar angles of CS main axis orientation $\theta$, denoted as orientation distribution function $U(\theta)$.

In principle, $U(\theta)$ could be obtained by the direct dividing procedure of the spectra of oriented and unoriented samples (2.10) or by the method of Legendre subspectra analysis described in previous section. However, the spectra of polysiloxanes have a strong inhomogeneous broadening of the intrinsic lineshape $f(\sigma)$ and, therefore, the rounding-off of the wideline spectrum $S(\sigma)$. This makes the direct analysis of the spectral pattern very complicated. Therefore, the method of the spectral line moments and their connection to the moments of the $U(\theta)$ Legendre expansion seems to be most appropriate in this case.

Replacing the integrand of Eqn 2.16 by 2.8 and 2.14 we get

$$M_n = \left(2\Delta \sigma / 3\right)^n \langle P_2^n \rangle$$

entering the notation:

$$m_n = \frac{M_n}{\left(2\Delta \sigma / 3\right)^n}$$

The powers of the $P_2 (\cos(\theta))$ can be expanded according to (2.12) via the finite sum of the Legendre polynomials of even order.

$$m_1 = \langle P_2 \rangle_{CS}$$

$$m_2 = \frac{11}{35} \langle P_4 \rangle_{CS} + \frac{2}{7} \langle P_6 \rangle_{CS} + \frac{1}{5} \langle P_8 \rangle_{CS}$$

$$m_3 = \frac{18}{77} \langle P_6 \rangle_{CS} + \frac{108}{385} \langle P_8 \rangle_{CS} + \frac{3}{7} \langle P_{10} \rangle_{CS} + \frac{2}{35} \langle P_{12} \rangle_{CS}$$

Because of the normalization conditions, $\langle P_0 \rangle_{CS}$ has the value $\frac{1}{2}$ if $\cos(\theta)$ has its full range from -1 to +1 ($\theta = [\pi..0]$) and 1 if the interval is restricted to $[0..1]$ ($\theta = \pi/2 ..0$).

$$\langle P_2 \rangle_{CS} = m_1$$

Relations 2.19 can be inverted as:

$$\langle P_4 \rangle_{CS} = \frac{35}{18} m_2 - \frac{10}{18} m_1 - \frac{7}{18}$$

$$\langle P_6 \rangle_{CS} = \frac{77}{18} m_3 - \frac{7}{3} m_2 - \frac{7}{6} m_1 + \frac{2}{9}$$

The moments $m_n$ can be obtained directly according to (2.18) and (2.16) using the wideline $^{29}$Si spectrum. To get the Legendre moments $\langle P_{2n} \rangle$, unambiguously characterizing the orientation distribution function $U(\theta)$, the equation 2.20 is then applied. In practice, an additional step is required due to the problem of the accuracy of the reference point determination which has to be chosen so that $m_1 = 0$. Theoretically, $m_1$ represents the shift of the gravity center between the
spectrum of oriented and disoriented sample. For a weak orientation order degree, which is
typical for polysiloxanes, this shift is comparable to the experimental error. Therefore, the
wideline $^{29}$Si spectrum lineshape was recorded at different values of angle $\delta$ which describe the
tilting of the sample local director with respect to external magnetic field $B_0$ (see Fig 2.13).
Because of the axial symmetry of sample orientation, the angular dependence of the Legendre
moments will be given by:

$$\left\langle P_{2n} \right\rangle_{CS} (\delta) = \left\langle P_{2n} \right\rangle_{CS} (0) \cdot P_{2n} (\cos(\delta))$$  \hspace{1cm} (2.21)

It is now possible to get the $\left\langle P_{2n} \right\rangle (0)$ either by fitting of the $\left\langle P_{2n} \right\rangle (\delta)$ curve using relations
(2.20). The alternative variant is to use the orthogonality conditions of the Legendre
polynomials:

$$\int_{-1}^{1} P_l (x) P_k (x) dx = \frac{2l+1}{2} \delta_{lk}$$

which allows one to select from the linear combinations (2.19) one by one all the moments
$\left\langle P_{2n} \right\rangle$ to be found just by the integration with corresponding Legendre polynomial. This can be
done with higher accuracy than by using of gravity center shift of the wideline pattern.

2.3.2 ODF ambiguity caused by transversal anisotropy and CS tensor
symmetry

It should be recollected that $U(\cos(\theta))$ is still only an intermediate result. The purpose is to
get the orientation distribution of the molecular segments $u$ with respect to local director $N$. The
determination of latter is only possible using some additional information about the distribution
of CS tensor axes in a plane perpendicular to $u$. In the case of transversal isotropy [II.25] of the
CS tensor main axes distribution, (i.e the equal probability for all of their orientations in the
plane perpendicular to the segment $u$) the estimation of segment orientation degrees $\left\langle P_{n} \right\rangle_S$ will
be possible simply by means of the multiplication with the corresponding Legendre polynomial
of the cosine of interconnection angle $\varepsilon$.

$$\left\langle P_{n} \right\rangle_{CS} = \left\langle P_{n} \right\rangle_{S} \cdot P_{n} (\cos(\varepsilon))$$  \hspace{1cm} (2.22)

Nevertheless, for the backbone segments of LCSP, the essential deviation from transverse
isotropy can take place. A rotation of the main-chain segments around own axis requires
different conformations of the spacer and different excluded volume space (see Fig 2.14)

Therefore, a violation of the transverse isotropy has to be expected leading to the
$\gamma$ dependent correction terms. In extreme cases, it can be not only a minor correction, but also
even reversing of the sign of the orientation order degree. Consequently, because of the possible
transversal anisotropy of the tensor axes distribution, the comprehensive approach demands
considering a two-dimensional distribution function \( V(\cos(\beta), \gamma) \) to determine the orientation of the molecular segment \( u \) from the orientation of the CS-tensor. In the same time, the axially symmetric CS-tensor of \( ^{29}\text{Si} \) in polysiloxanes, in generall, provides only one-dimensional information about the own orientation. To overcome this problem some \textit{a priori} suggestions about the type of \( \gamma \)-dependent correction for the \( U(\cos(\beta)) \), have to involved into consideration. For example, the analysis of two-dimensional ODF \( V(\cos(\beta), \gamma) \) and the corresponding moments of the orientation order can done if to suggest that the correction term can be separated on the \( \gamma \)-dependent and independent parts:

\[
V(\cos(\beta), \gamma) = \frac{1}{2\pi} U_0(\cos(\beta)) + U_1(\cos(\beta)) g(\gamma)
\]

(2.23)

Where \( U_0(\cos(\beta)) \) is transversally independent part of \( V \), and \( U_1 \) represents the amplitude of the \( \gamma \)-dependence. The detailed analysis of this specific case can be found in [II.25]. Thus, to prove the correctness of different model approaches and simplifications some independent information about the orientation of the molecular segments is required. Such information can be obtained by using a method directly sensitive to the orientation of the molecular segment. This allows one avoiding the problems of the ambiguity of the data interpretation discussed above. Moreover, if the moments of the segments ODF \( <P_{2n}> \), could be determined directly by the method different from the \( ^{29}\text{Si} \) CS-spectrum analysis, the correction terms in Eqn 2.23 caused by the transversal anisotropy can be estimated. The possibility for such an alternative method employing will be considered in the following section.

2.3.3 Using direct dipolar interaction of \(^{29}\text{Si} \) pairs for main-chain segment orientation study.

To get information about the orientation of the molecular segment independently from the methods of the CS-tensor orientation, some alternative tensor spin interaction should be used.
It can be seen on Fig 2.10 that the orientation of the segment $u$ coincides with the interconnection vector of two silicon atoms. Therefore, the most natural decision is to use the angular dependence of direct dipolar interaction to probe the orientation distribution of these vectors. The dipolar interaction leads to the splitting of each energy levels (and therefore the resonance line) on two and the value of the splitting depends on the angle between the vector, which connects the involved nuclei, and the external magnetic field. In time domain NMR signal it appears like amplitude and, generally, the phase modulation of the resonance signal with the dipolar splitting frequency. The angular dependence of the dipolar splitting frequency is represented via the second Legendre polynomial that makes natural to perform the analysis of the ODF in terms of the moment expansion, as well as in the case of the CS-tensor spectrum. For example, the method of moment expansion similar to the one described for the $^{29}\text{Si}$ CS-spectrum can be applied to determine the orientation order in low-molecular liquid crystals using the second moment of the wide-line $^1\text{H}$ spectrum mainly determined by the direct dipolar coupling [II.19]. For the polysiloxane LCSP samples the dipolar interaction of the protons in phenyl ring was used to get the information about the ordering of the side-chain mesogenic units which determine the macroscopic orientation of whole sample (local director $N$)[II.26]. In the case of $^{29}\text{Si}$ NMR in polysiloxanes, yet, a sufficient difficulties can be foreseen, which makes problematic the employing of dipolar interaction for the orientation distribution studies.

The first problem is concerned with natural abundance of the $^{29}\text{Si}$ nuclei that is 4.7% of total amount of the silicon atoms in any sample. The rest of the atoms contain the $^{28}\text{Si}$ nuclei which have zero spin ($I=0$) and, therefore, do not contribute to the NMR signal. The enrichment with the $^{29}\text{Si}$ nuclei is technologically very problematic and expensive and applicable not to all the sort of the samples, especially in the case of polymers. That way, the NMR signal from the $^{29}\text{Si}$ is intrinsically low that leads to the essentially long measurement period to get reasonable signal-to-noise ratio in experiment. Situation becomes more difficult when the dipolar interaction between two $^{29}\text{Si}$ nuclei needs to be observed. Obviously, at natural abundance only less than 10% of all the $^{29}\text{Si}$ nuclei (or $\approx 0.005\%$ of total silicon amount) in the sample establish the coupling pairs (see Fig 2.15). Thus, the 90% of the NMR signal comes from non-coupled spins and does not give any information about the $^{29}\text{Si}$-$^{29}\text{Si}$ dipolar interaction. Therefore, the useful signal (i.e. signal of coupled spins) has to be separated, in some way, from the significantly higher signal of non-coupled $^{29}\text{Si}$. The second problem arises from the low strength of the dipolar interactions between two $^{29}\text{Si}$ as compared to the interaction caused by other anisotropic terms of nuclear Hamiltonian, particularly the chemical shift. From the quantum, chemistry calculations the dipolar splitting frequency for coupled $^{29}\text{Si}$ can be roughly estimated as $200...300 \text{ Hz}$. In the same time, it was shown in previous section that the total width of the CS–
pattern is of the order of CS anisotropy constant value (about 48 ppm for polysiloxanes). For the external magnetic field 9.4T, using to measure the spectra, this gives the value about 3000Hz, that is on one order of magnitude higher than dipolar splitting. In addition, the intrinsic line (obtained from the $^{29}$Si wideline spectrum deconvolution) is broadened up to 500Hz because of the structural conformation inhomogeneity or CS parameters distribution.

These factors cover the dipolar splitting in the $^{29}$Si NMR spectrum and do not allow observing it directly. For this reason, the special technique has to be developed and applied to (i) separate the signal of coupled and non-coupled spins and (ii) to get the information about the dipolar coupling in presence of the resonance line inhomogeneous broadening (which may exceed the dipolar coupling in a factor of 10 ) due to another types of nuclear spin interactions. The solution of the theoretical and practical aspects of the mentioned above problems represents the main subject of current work and will be considered in the following chapters.

Fig 2.15 Only 5% of nuclei are $^{29}$Si spins, which contribute to NMR signal. The rest are $^{28}$Si (95% of whole Si in the sample at natural abundance) which give no signal. The non-coupled spins are, therefore, give 90% of whole signal and the coupled ones only 10%.