Orientation distribution function and order parameters of oriented spin probe as determined by EPR spectroscopy

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ABSTRACT

Two methods for determination of molecular orientation distribution from angular dependence of EPR spectra are compared. One of these methods is based on direct expansion of the orientation distribution function in a series of generalized spherical harmonics, in another method the mean field potential is used. The limitations of these approaches as well as their capabilities and advantages are considered

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1. Introduction

It is well known that molecular orientational alignment is an important feature of liquid crystals, oriented polymers, biopolymers and other materials. The most comprehensive description of molecular orientational order is an orientation distribution function (ODF) $\rho(\alpha, \beta, \gamma)$, where α, β, γ are Euler angles defining the relative orientation of the molecular reference frame and the sample frame. ODF gives the probability density of particles orientation with angles α, β, γ, so that $dN = \rho(\alpha, \beta, \gamma) \sin\beta d\alpha d\beta d\gamma$. The orientation distribution function can be presented as an expansion in a series of generalized spherical harmonics (elements of Wigner D-matrix):

$$\rho(\alpha, \beta, \gamma) = \sum_{j,m',m} \frac{2j+1}{8\pi^2} \left\langle D^{j}_{m'm}{}^* \right\rangle D^{j}_{m'm}(\alpha, \beta, \gamma) \quad (1)$$

In case of uniaxial sample the series Eq. (1) can be simplified using Legendre polynomials $P_j(\cos\beta)$ and associated Legendre polynomials $P_{jm}(\cos\beta)$:

$$\rho(\beta, \gamma) = \frac{1}{2\pi} \sum_{j=0}^{\infty} \left(\frac{1}{2} a_{j0} P_j(\cos\beta) + \sum_{m=1}^{j} P_{jm}(\cos\beta) \left[a_{jm} \cos m\gamma + b_{jm} \sin m\gamma \right] \right) \quad (2)$$

The expansion coefficients $\langle D^{j}_{m'm}{}^* \rangle$ (or a_{jm}, b_{jm}) provide a set of order parameters. The concept of order parameters is considered in detail in [1]. To characterize order parameters of uniaxial system in real numbers the following expressions are used:

$$A^{j}_{m} \equiv S_{jm} = \frac{\left\langle D^{j}_{0m}{}^* \right\rangle + \left\langle D^{j}_{0-m}{}^* \right\rangle}{2} = \frac{a_{jm}}{2j+1} \sqrt{\frac{(j+m)!}{(j-m)!}}$$

$$B^{j}_{m} = \frac{\left\langle D^{j}_{0m}{}^* \right\rangle + \left\langle D^{j}_{0-m}{}^* \right\rangle}{2i} = \frac{b_{jm}}{2j+1} \sqrt{\frac{(j+m)!}{(j-m)!}} \quad (2a)$$

Orientational order can be described using orientation factors and elements of Saupe orientation matrix as well. Different sets of orientation characteristics are convenient for description of different systems and experiments. However, all these characteristics can be easily transformed from one form to another one. The brief comparison of the orientation characteristics is presented, for example, in [2].

Specification of all order parameters gives a complete specification of orientation distribution function. Unfortunately, at present time there is no technique available for complete experimental determination of orientation distribution function for soft matter. Only second moments of ODF (order parameters of rank 2) are determined usually since they can be obtained using one-photon optical methods. The orientation characteristics of rank 4 are determined experimentally rather rarely. EPR spectroscopy combined with spin probe and spin label techniques provides, in principle, the possibility of more complete determination of an orientation distribution function. This aim can be achieved by numerical simulation of EPR spectra, recorded at different orientations of examined sample in magnetic field of the spectrometer. Obvious limitation of this technique is the symmetry of the spin Hamiltonian with respect to inversion of coordinate system. It means that EPR spectra recorded at direct and opposite directions of magnetic field are quite the same. As a result of this feature even order parameters (coefficients of expansion Eq. (1)) can be determined only. Other limitations, imposed on extractable characteristics of orientational

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distribution by symmetry of sample, probe molecule and spin Hamiltonian are considered in details elsewhere [2,3].

The most widespread method of simulation of EPR spectra with determination of orientation distribution function is the method, described in [4–6]. In this approach the orientational order of spin probe (or label) is described using mean force approximation. The molecular orientational alignment is considered as a result of action of mean field potential $U(\alpha, \beta, \gamma)$ at the conditions of Boltzmann equilibrium as follows:

$$\rho(\beta, \gamma) = \frac{e^{-U(\beta, \gamma)/k_b T}}{\int e^{-U(\beta, \gamma)/k_b T} \sin \beta d\beta d\gamma} \tag{3}$$

where the orienting potential is expanded in a series of spherical Wigner D-functions:

$$\frac{U(\beta, \gamma)}{k_b T} = -\sum_{j,m} c_{jm} D^j_{0m}(\beta, \gamma) \tag{4}$$

Eq. (4) is used commonly in the following form:

$$\frac{U(\beta, \gamma)}{k_b T} = -\sum_j c_{j0} D^j_{00}(\beta, \gamma) - \sum_{j,m} c_{jm} \left[D^j_{0m}(\beta, \gamma) + D^j_{0-m}(\beta, \gamma) \right] \tag{4a}$$

where j, m = 2, 4.

This approach was developed in the 1970s (see, for example, [7]). There is extensive literature, describing applications of this approach. In the earlier works the parameters of ODF were determined by means of trial-and-error way [8–10]. Now the nonlinear least-squares minimization of discrepancies between calculated and experimental spectra is used [11,12]. The different fitting algorithms are considered in [13]. The most widespread software realization of the approach is described in [4–6]. The program is based on the stochastic Liouville equation (SLE) and, thus, it is intended for calculation of EPR spectra of rotating particles. The similar method is incorporated in integrated software *E-SpiReS* aimed at interpretation of EPR spectra in fluids [14,15]. A lot of useful and interesting results were obtained using this approach with available software. This model will below be referred to as OP (orienting potential) approach. An alternative approach is based on determination of an orientation distribution function immediately in form of Eq. (1) or Eq. (2) (OD approach) [16–21]. Comparison of these two approaches and determination of their applicability are subjects of this contribution.

2. Qualitative consideration

The reference frames used are shown in Fig. 1. Sample frame (SF) is associated with the macroscopic director of oriented medium. At every point of the oriented medium there is local orientational alignment with local main direction fixed with local frame (LF). The paramagnetic molecule, located in the medium, is characterized by molecular orientation axes, which form the molecular orientation frame (MOF). Tensor of rotational diffusion, g-tensor and hfi-tensor are diagonal in their own molecular frames RF, gF, AF accordingly. The set of Euler angles that transforms one frame to another one is designated by Ω.

2.1. Some features of OP and OD approaches

1. In accordance with OP let us assume, that the local director in all points of the medium coincides with macroscopic sample director ($\Omega_{SF \to MOF} \equiv \Omega_{LF \to MOF} \equiv \Omega$), and orientational order of paramagnetic molecules is induced by the orienting potential (Eq. (3)) at the temperature T_0:

$$\rho_o(\Omega) = \frac{1}{N} e^{-U(\Omega)/k_b T_0} \tag{5}$$

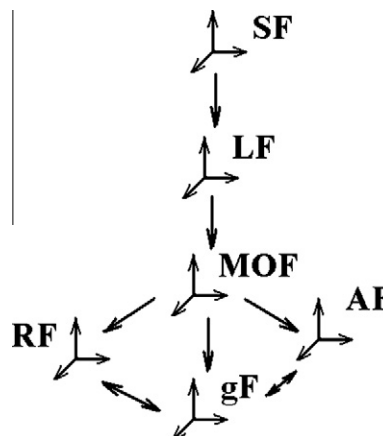where $N = \int e^{-U(\Omega)/k_b T} d\Omega$ is normalization factor.

Fig. 1. Reference frames used in the text.

When the temperature of the sample is changed, the relaxation processes, directed to the new Boltzmann equilibrium, take place. The evolution of the orientation distribution function can be presented as:

$$\rho(t) = \frac{1}{N} [\rho_1 + ((\rho_0 - \rho_1) f(t)] \tag{6}$$

where ρ_1 is the equilibrium orientation distribution function at new temperature T_1; function $f(t)$ describes kinetics of relaxation.

In the simplest case $f(t)$ is the exponential decay function. In general case relaxation kinetics is defined by one or more characteristic times τ. Taking into account the anisotropy of rotation we should conclude, that characteristic time is angular dependent:

$$f(t) = f\left[\frac{t}{\tau(\Omega)} \right] \equiv \xi(t, \Omega) \tag{7}$$

If the cooling of the sample is sufficiently rapid and deep, the overcooled glassy state is achieved, where the relaxation is not finished within the time of experiment t_{exp}. It means, that $f(t_{exp}) = \xi(t_{exp}, \Omega) \neq 0$. In this case the orientation distribution function state is as follows:

$$N\rho(\Omega) = \exp\left(-\frac{U(\Omega)}{k_b T_1} \right) + \left[\exp\left(-\frac{U(\Omega)}{k_b T_0} \right) - \exp\left(-\frac{U(\Omega)}{k_b T_1} \right) \right] \xi(t_{exp}, \Omega) \tag{8}$$

One can see, that the orientation distribution function (Eq. (8)) does not meet the Boltzmann form (Eq. (3)). Thus, the non-equilibrium glassy state cannot be described using the OP approach.

2. The local director in general does not coincide with the sample director. It is known, that liquid crystals, membranes and other partially oriented systems often have domain structure. The orientation distribution of a sample, consisting of two domains with slightly different directors, should be described as a sum of two Boltzmann exponents. When the poly-domain sample is studied, the orientation distribution is expressed as a sum of molecular orientation distributions over all domains. It is evident, that molecular orientation in a poly-domain sample cannot be described in the framework of the distribution (3, 4) solely. The additional distribution function for domain directors is necessary. Particular case of the random local director distribution is known as MOMD model (Microscopic Order Macroscopic Disorder) [4–6]. Other examples of *a priori* assumed director distributions are described in [8,22].

The presented consideration shows, that approach (3, 4) is not valid, when the molecular orientational equilibrium has not been reached. It is rather trivial statement, but we underline it here, as the orientational degree of freedom is a very specific one. For