Extended Czjzek model applied to NMR parameter distributions in sodium metaphosphate glass

Filipe Vasconcelos¹, Sylvain Cristol¹, Jean-François Paul¹, Laurent Delevoye³, Francesco Mauri², Thibault Charpentier³ and Gérard Le Caër⁴

¹ Unité de Catalyse et Chimie du Solide, UMR CNRS 8181, École Nationale Supérieure de Chimie de Lille, Université de Lille, BP 108, F-59652 Villeneuve d’Ascq Cedex, France
² Institut de Minéralogie et Physique des Milieux Condensés, Université Paris 6, CNRS, 4 Pl. Jussieu, 75005 Paris, France
³ CEA, IRAMIS, SIS2M, CEA/CNRS UMR 3299—Laboratoire de Structure et Dynamique par Résonance Magnétique, F-91191 Gif-sur-Yvette cedex, France
⁴ Institut de Physique de Rennes, UMR U1-CNRS 6251, Université de Rennes 1, Campus de Beaulieu, Bâtiment 11A, Avenue du Général Leclerc, F-35042 Rennes Cedex, France

E-mail: filipe.vasconcelos@cea.fr and laurent.delevoye@enscl-lille.fr

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Abstract

The extended Czjzek model (ECM) is applied to the distribution of NMR parameters of a simple glass model (sodium metaphosphate, NaPO₃) obtained by molecular dynamics (MD) simulations. Accurate NMR tensors, electric field gradient (EFG) and chemical shift anisotropy (CSA) are calculated from density functional theory (DFT) within the well-established PAW/GIPAW framework. The theoretical results are compared to experimental high-resolution solid-state NMR data and are used to validate the considered structural model. The distributions of the calculated coupling constant \( C_Q \propto |V_{zz}| \) and the asymmetry parameter \( \eta_Q \) that characterize the quadrupolar interaction are discussed in terms of structural considerations with the help of a simple point charge model. Finally, the ECM analysis is shown to be relevant for studying the distribution of CSA tensor parameters and gives new insight into the structural characterization of disordered systems by solid-state NMR.

(Some figures may appear in colour only in the online journal)

1. Introduction

It is generally accepted, since the early work of Zachariasen [1], that oxide glasses are built up from polyhedra randomly organized in such a way however that the local short-range order that prevails in the corresponding crystalline compounds is preserved. This seminal model, named the continuous random network (CRN), evolved slightly with time and was extended to covalent glasses such as amorphous silicon ([2, 3] and references therein). Its validity appears to be reinforced by diffraction techniques from which radial distribution function (RDF) can be determined and compared to the radial distribution associated with the local arrangements of polyhedra in a CRN model. However, conclusions about the structures of amorphous materials are questionable when they are obtained solely from pair correlations as they suffer from a lack of uniqueness beyond very short-range structure [2]. Other techniques that are more sensitive to topological or medium-range order are needed to constrain structural models as advocated very recently for amorphous silicon [2, 3]. Complementary techniques are then needed to provide additional input data which...
constrain models determined for instance by reverse Monte Carlo methods. Among the various spectroscopic techniques that can be used (Raman, infrared, EXAFS for instance), solid-state nuclear magnetic resonance (NMR) spectroscopy can be seen as one of the most promising tools to characterize oxide glass structure.

In solid-state NMR, the structural information is carried by the different interactions, i.e. chemical shift, quadrupolar, dipolar coupling, indirect spin–spin coupling, which are deduced either directly by a one-dimensional experiment or indirectly through the use of multiple-dimensional experiments (homo- and hetero-nuclear correlations). These interactions being orientationally dependent, they often contribute to a line broadening of NMR spectra. All these interactions can be described by tensors, i.e., the chemical shift anisotropy tensor (CSA), the electric field gradient tensor (EFG). If the anisotropic parts of NMR interactions have been, for a long time, considered as a major drawback for the NMR investigation of solids, the development of the magic angle spinning (MAS) technique has opened up new perspectives by significantly improving the spectral resolution, especially for those nuclei with a spin half value \( I = 1/2 \). For nuclei with higher spin values \( I > 1/2 \), which are subjected to the quadrupole interaction, the MAS technique alone is unable to average out completely the quadrupolar interaction. Over the last twenty years, several methods were proposed to get rid of the second-order anisotropic quadrupolar interactions: double orientation rotation (DOR), [4] dynamic angle spinning (DAS), [5] multiple-quantum-MAS (MQMAS), [6, 7] or satellite-transition MAS (STMAS) [8]. The most versatile and most widely used MQMAS method is a high-resolution experiment designed for half-integer quadrupolar nuclei and routinely used to average out the anisotropic second-order quadrupolar interactions by correlating the multiple-quantum transitions with the single-quantum transitions. These methods, among others, allow the observation of many nuclei from the periodic table and the characterization of their anisotropic interaction tensors.

In crystalline solids, the broadening of NMR spectra of powdered samples is the result of different orientations of the crystallites relative to the external field. In such a case, the structural characterization can be done without ambiguity from the principal components of the tensors alone. In the case of an amorphous system, the distribution of chemical environments results in an intrinsic distribution of all the components of the interaction tensor. This additional distribution is then responsible for the broadening of the spectra observed experimentally in glasses. The challenging problem in solid-state NMR analysis of disordered materials is to interpret this spectral broadening in structural terms. First, the extraction of NMR parameter distributions from NMR data can be rather difficult. It is clear that the availability of analytical models can facilitate this task. Second, the relationships between NMR parameter distributions and the structural and chemical disorder has to be established.

Structure elucidation by solid-state NMR suffers from a fundamental drawback: the assignment of NMR spectra to chemical environments is an indirect process. Thereby, except for some cases where the chemical environments belong clearly to very different families, the assignment needs a structural model to remove possible ambiguities. The development of methods to calculate NMR parameters from the atomic scale during the last decade is of this view as they allow the assignment of similar chemical environments and confirm the sensibility of NMR parameters to structure. In particular, the now routinely used DFT-PAW/GIPAW (projector augmented wave and gauge including projector augmented wave respectively) [9, 10] combined approach accounts very accurately for the CSA and EFG tensors of a large amount of crystalline organic [11, 12] or inorganic [10, 13–16] compounds. However, this theoretical approach to assign resonances is still an indirect process. Indeed, for crystalline compounds, a known structure, deduced from diffraction techniques, is mandatory to be used as an input in ab initio and DFT codes and to be further compared to experimental NMR results. Similarly, for amorphous or disordered compounds, a structural model must be built to confirm the interpretation of NMR spectra. Recently, the combination of molecular dynamics (MD) and solid-state NMR has shown a great ability to interpret experimental spectra and to propose structural glass models for different oxide glasses [17–23]. This approach has the advantage of giving access to the distributions of all the NMR interaction tensors (CSA, EFG).

The case of EFG tensor distribution has recently been subject to some new considerations in the context of solid-state NMR. Indeed, d’Espinose de Lacaillerie et al [24] examined the fields of applications of the Cžižek model [25, 26], also called the Gaussian isotropic model (GIM) that is summarized in the background section (section 2). The GIM is the first analytical model for the analysis of NMR line shapes observed in the MAS NMR spectra of quadrupolar nuclei in disordered solids. Apart from its application in other spectroscopies (ex. in Mössbauer spectroscopy [26, 27] and references therein), this model was successfully applied to the NMR study of amorphous systems, to different nuclei such as aluminum-27 [28, 24, 29], gallium-71 [30–33], arsenic-75 [32] and should be applicable to other nuclei (sodium shows characteristic isotropic distributions see ex. figure 2 of [34]). In particular, this model is able to describe the asymmetric broadening observed at low chemical shift [24, 33]. Since a quadrupolar nucleus in an amorphous system presents also a distribution of the isotropic chemical shift, the GIM gives the means to better separate and quantify these two contributions within the resonance broadening. However, the specific two hypotheses defining the GIM (i.e., rotational invariance and central limit theorem) [26, 35] are unable to provide structural considerations from the analysis of the NMR lineshape distribution. As discussed by Le Caër et al. [35] the GIM, which results in fine from the application of a central limit theorem to the EFG tensor (section 2.2), can thus be seen as a kind of ‘black hole’ from which no information about the specific structural features of the investigated solid and about the physical origins of the EFG can come.

The introduction of the extended Cžižek model (ECM), [36, 26, 35] also summarized in section 2, is currently
the simplest but most useful way to generalize the GIM. In a recent contribution, one of us showed that this ECM could be seen as the introduction of physical (i.e., structural) contribution to the GIM. Indeed, the ECM is intended to mimic the EFG contribution of a well-defined neighbourhood of a given atomic species modified by the effect of more remote atomic shells. In practice, this well-defined first atomic shell and the remote atomic shells are modelled by a fixed ‘local’ contribution and a distributed Czjzek contribution, respectively. Therefore, depending on the relative weight of the local contribution, the ECM is able to include some direct structural effects in the Czjzek model. Indeed, for a given EFG tensor, the relation between structural data and the quadrupolar interaction can be easily determined from ab initio calculations of the EFG [24]. Then, the observation of an ECM distribution with a predominant local contribution can be interpreted through structural considerations.

In this paper, we present a general approach to study the EFG distribution of a simple glass model, namely the sodium metaphosphate glass (NaP03), generated by molecular dynamics (MD). In a previous work, the NMR signature of the non-bridging oxygen (NBO) of this compound was interpreted, to some extent, with a continuous random network model [37]. Indeed, the observed narrow distribution of the quadrupolar parameters, the mean value of which is comparable to those observed in related crystalline compounds, was interpreted as the conservation of the local structure. In addition, the large distribution of the isotropic chemical shift was interpreted as the signature of long-range disorder. For bridging oxygens (BO), some correlation between the quadrupolar parameters and simple structural properties appeared to be close to those observed in silicates [38]. This glass system can thus be seen as a good candidate for the application of the ECM to 17O environments. In a second step, the use of the ECM to describe sodium NMR lineshapes will show the ability of such models to reveal a pure isotropic tensor distribution as defined in the GIM.

This paper is organized as follows. In section 2, we recall the basic characteristics of the distributions of the main EFG parameters in the frame of the GIM and ECM. In section 3, we present the methodology used to generate different configurations of the sodium metaphosphate glass and to calculate the NMR parameters for all nuclei in the corresponding glass structure. In section 4, the results are compared to experimental 17O and 31P high-resolved NMR spectra to validate the structural model. In the same section, we present a detailed analysis of the calculated EFG distribution within the ECM. In section 5, we analyse the distributions of the EFG tensor parameters and their link with the structure of the glass. In particular, we show that a simple point charge model analysis is able to explain the distributions related to the EFG tensor for the different sites. In section 6, we introduce a preliminary application of the ECM to the distribution of the chemical shielding anisotropy tensor.

2. Distribution of the EFG tensor: background

2.1. EFG related definitions

In solid-state NMR, the quadrupolar interaction is characterized by two parameters: \( Q \) and \( \eta_0 \) (respectively the quadrupolar coupling constant, and the quadrupolar asymmetry), which are both defined from the three principal components of the diagonal EFG tensor (V), by the following relations:

\[
Q = \frac{e|Q|}{h}|V_{zz}|, \quad \eta_0 = \frac{V_{yy} - V_{xx}}{V_{zz}}
\]

where \( e \) is the elementary charge, \( h \) is the Planck’s constant, \( Q \) is the quadrupolar moment and the principal components \( V_{ii} \) (\( i = x, y, z \)) are sorted such that \( |V_{zz}| \geq |V_{xx}| \geq |V_{yy}| \). In the present work, we used \( Q = -25.58 \times 10^{-31} \text{ m}^2 \) and \( Q = 100.54 \times 10^{-31} \text{ m}^2 \), respectively for the oxygen and the sodium quadrupolar moment as tabulated by Pyynko [39].

Thereafter, we only consider the parameters \( V_{zz} \) and \( \eta_0 \) to represent the principal components of the diagonal EFG tensor. Even if NMR experiments at room temperature are unable to provide the sign of the largest principal component [40], it is explicitly available by DFT calculations and is important to characterize the distribution as demonstrated below.

The EFG tensor, whose components are \( v_{ij} \) with \( (i,j = x, y, z) \), is usually not diagonal, and three others parameters defining the orientation of the tensor in a fixed reference frame are required. Consequently, the EFG tensor is completely defined by five independent quantities as expected for a traceless symmetric second-rank tensor. Following Czjzek et al [25], we define five real parameters \( U \) from the Cartesian components of the EFG tensor:

\[
U_1 = v_{zz}/2, \quad U_2 = \frac{v_{zz}}{\sqrt{3}}, \\
U_3 = \frac{v_{zz}}{\sqrt{3}}, \quad U_4 = \frac{v_{xy}}{\sqrt{3}}, \\
U_5 = \frac{(v_{xx} - v_{yy})}{2\sqrt{3}}.
\]

The five-dimensional vector \( U = (U_1, \ldots, U_5) \) constitutes a random vector representative of the EFG tensor of an amorphous solid in the same fixed reference frame for all the sites. The distribution of \( U \) fulfils a number of conditions for disordered solids which are statistically invariant by any rotation. This invariance does not imply any kind of local geometrical symmetry. In other words, ‘statistical isotropy’, which is a global property, and ‘geometrical anisotropy’, which is a local property, are not contradictory characteristics and are most often the rules for amorphous solids. Statistical isotropy simply means that the distribution of \( U \) remains unchanged when any fixed, but arbitrary, frame of reference is chosen to calculate the EFG’s of all atoms of the selected isotope. It implies nothing about possible symmetries of local clusters centred on these atoms. The essential conditions, which are needed in the discussion of the results of the present paper, are derived by a simple method in [26]. They are:
The distribution of \( U \) is such that \( \langle U_i \rangle = 0 \) and \( \langle U_i U_j \rangle = \sigma^2 \delta_{ij} \) with \( (i, j = 1, \ldots, 5) \) where \( \sigma^2 \) is the common variance of the five components of \( U \). The latter conditions are true for any distribution of \( U \) as soon as means and variances do exist.

- The marginal distribution \( P(U_1) \) is a priori asymmetric and different from the marginal distributions \( P(U_i, i > 1) \) which are all identical and symmetric.

When structural models are available, theoretical distributions \( P(U_i) \) can be used to check if the previous conditions of statistical isotropy hold or not. In addition, when the distribution of \( U \) is multivariate Gaussian, as in the Czjzek model, then the \( U_i \) are independent random variables and the five distributions \( P(U_i) \) are identical Gaussians.

2.2. The Gaussian isotropic model (Czjzek model)

The Czjzek model [25] is used for the analysis of the joint distribution of the components of the previous vector \( P(U_1, \ldots, U_5) \) in the context of an isotropic distribution of the EFG tensor. At the thermodynamic limit (i.e. an infinite number of sites), or at least when the physics that determine the distribution of the EFG tensor meets the quite general requirements of the multidimensional central limit theorem, the random variables \( U_i \) become independent and identically distributed according to a Gaussian distribution with a zero mean. With these two assumptions, the Czjzek model is summarized by the following analytical expression for the bivariate distribution \( P(V_{zz}, \eta_Q) \):

\[
P(V_{zz}, \eta_Q) = \frac{1}{(2\pi)^{1/2} \sigma^5} V_{zz}^4 \eta_Q (1 - \eta_Q^2 / 9) \exp \left( - \frac{S^2}{2\sigma^2} \right)
\]

where \( S \) is the norm of the tensor \( S^2 = V_{zz}^2 (1 + \eta_Q^2 / 3) \). This model is fully defined by a single parameter, namely the standard deviation \( \sigma \) of the Gaussian distribution of every component \( U_i \). In this paper, we only consider some properties of the marginal distributions \( f(\eta_Q) \) and \( f(V_{zz}) \). For a further description of the GIM properties, the reader is referred to the following articles [24–26, 35].

2.3. The extended Czjzek model

2.3.1. Model presentation. The extended Czjzek Model (ECM) allows the introduction of an anisotropic part in the total EFG tensor. In this model, the total observed EFG tensor \( \mathbf{V}(\epsilon) \) is defined as the sum of two distinct contributions as follows:

\[
\mathbf{V}(\epsilon) = \mathbf{V}_0 + \rho \mathbf{V}_{\text{GIM}}
\]

where \( \mathbf{V}_0 \) represents the local anisotropic tensor due to a close neighbourhood of the considered atom and \( \mathbf{V}_{\text{GIM}} \) is the global isotropic distribution modelled by a GIM tensor weighted by a parameter \( \rho \) due to more remote atomic shells. The choice of a Czjzek contribution to express the effect of noise is justified by two very general assumptions, statistical isotropy and Gaussianity, which unavoidably lead to the Czjzek model. In equation (5) the tensor \( \mathbf{V}_{\text{GIM}} \) is obtained from a vector \( \mathbf{U} \) (equation (2)) whose components are standard Gaussians with means equal to zero and variances equal to 1. All tensors in equation (5) are expressed without loss of generality in the local frame of reference in which \( \mathbf{V}_0 \) is diagonal (see appendices A and B). Thus, the distribution of \( \mathbf{V}(\epsilon) \) is not statistically isotropic. If needed, \( \mathbf{V}(\epsilon) \) can be transformed into a tensor \( \mathbf{V}'(\epsilon) \) which is statistically isotropic (appendix A). The tensors \( \mathbf{V}(\epsilon) \) and \( \mathbf{V}'(\epsilon) \) have identical distributions of principal values (appendix B). The

Figure 1. Characteristic shapes of the marginal distributions of (a) \( \eta_Q \) and (b) \( V_{zz}/\sigma \) in the case of a Czjzek distribution of the EFG tensor (GIM). (a) The distribution \( f(\eta_Q) \) is independent of \( \sigma \), the single free parameter of the bivariate distribution of \( V_{zz} \) and \( \eta_Q \); the mean asymmetry parameter is 0.6098. (b) The \( V_{zz} \) distribution is symmetric about zero. The ratio \( \rho \) (see equation (7)) is independent of sigma, being \( \sim0.326 \).

Figure 1 presents the characteristic shapes of the marginal distributions \( f(\eta_Q) \) and \( f(V_{zz}) \) obtained from the distribution (3). These distributions have the following properties:

(A) The shape and the mean value of the \( f(\eta_Q) \) distribution are independent of \( \sigma \) (figure 1(a)). The latter distribution is given by

\[
f(\eta_Q) = 3\eta_Q \frac{1 - \eta_Q^2}{(1 + \eta_Q^2)^{3/2}}.
\]

(B) The marginal distribution \( f(V_{zz}) \) is symmetric about zero (figure 1(b)) and \( f(V_{zz}) \propto V_{zz}^4 \) for small values of \( V_{zz} \).
distributions of the components of $V_0$ are further discussed in appendix B.

The total EFG tensor is now a function of $\epsilon$, with $\rho$ defined by:

$$\rho = \frac{\epsilon \|V_0\|}{\|V_{\text{GIM}}\|}$$

which corresponds to the ratio of the norm of the different contributions. This $\epsilon$ parameter permits one to study the influence of each contribution independently of the value of the fixed tensor. The principal values of the fixed diagonal tensor $V_0$ are fully characterized by $V_{zz}(0)$ and $\eta_Q(0)$. In summary, the ECM is defined by three parameters: $V_{zz}(0)$ and $\eta_Q(0)$ for the local contribution and $\epsilon$ for the weight of the noise in the total EFG tensor. Hereafter, $V_0$ will be consistently named the ‘local’ contribution to the EFG tensor $V(\epsilon)$ while the name ‘noise’ (or Czjzek or background) will be used to designate the second contribution.

The main simplification of the ECM is to consider that $\eta_Q(0)$ and $V_{zz}(0)$ are not distributed, being the same for all atoms of a given family. By family, we mean the set of all local clusters, centred on atoms of a given species, which can be put in coincidence by some rotation, within very small atomic displacements (see sections 3 of [26] and 3.1 of [35]). This simplification aims at restricting the number of free parameters to a minimum value while mimicking the essential structural effects of the local atomic configurations. A disordered solid, for which the ECM is relevant, does not necessarily include a single family of sites. Many families may be necessary to describe the whole set of sites occupied by a given atomic species. A finite collection of extended Czjzek families may be sufficient to describe the EFG properties of some solids while others need to be described by a continuous distribution of families (section B.3).

2.3.2. $\eta_Q$ and $V_{zz}$ distributions within the ECM. We restrict the following discussion to the characteristics of the distributions of $\eta_Q$ and $V_{zz}$ in the ECM model and we compare them to the related distributions in the Czjzek model as summarized by the previous points (A) and (B). For a detailed description of all the ECM properties, the reader is referred to [35].

Figure 2(a) presents the evolution of the distribution $f(\eta_Q)$ of $\eta_Q$ with $\epsilon$ for $\eta_Q(0) = 0.2$. For small values of $\epsilon$ (i.e. large local contribution), the distribution of $\eta_Q$ is narrow and concentrated around $\eta_Q(0)$. For increasing $\epsilon$ (i.e. increase of the global isotropic contribution) the distribution $f(\eta_Q)$ converges to the $\eta_Q$ distribution of the Czjzek model (equation (4)). For all pairs $(\eta_Q(0), \epsilon)$, the $f(\eta_Q)$ distribution is accurately approximated by a closed-form expression (equation (22) of [35]). For a given value of $\epsilon$, the $\eta_Q$ distributions allow a determination of the parameter $\eta_Q(0)$ of the ECM.

Figures 2(b) and (c) present the evolution with $\epsilon$ of two characteristics of the $V_{zz}$ distributions. Figure 2(b) presents the variation with $\epsilon$ of the probability of occurrence of positive values of $V_{zz}$ (i.e. $P(V_{zz} > 0)$). A given probability $p = \max(P(V_{zz} > 0), P(V_{zz} < 0))$, with $0.5 \leq p \leq 1$ is not in a one-to-one correspondence with $\epsilon$ (see for instance figure 6 of [35]). It is thus necessary to select another parameter for an unambiguous determination of $\epsilon$. A convenient parameter, which characterizes the $V_{zz}$ distribution while being scale independent, denoted $\rho_z$, is defined as follows:

$$\rho_z = \frac{\sigma(|V_{zz}|)}{|\langle V_{zz} \rangle|}$$

where $\sigma(|V_{zz}|)$ and $|\langle V_{zz} \rangle|$ are respectively the standard deviation and the average value of $|V_{zz}|$. Distribution. Figure 2(c) presents the evolution of $\rho_z$ with $\epsilon$. The ratio $\rho_z$ is accurately approximated the relation given in (i) below. The previous ratio allows an unequivocal determination of $\epsilon$.

We propose now a simple procedure to analyse, within the ECM, a given distribution of $V_{zz}$ and $\eta_Q$. Indeed, as on the one hand the distribution of $V_{zz}$ is practically independent of $\eta_Q(0)$ and depends largely on the $V_{zz}(0)$ value and on the other hand $\epsilon$ is completely defined from the $V_{zz}$ distribution, only three steps are needed to determine all the ECM parameters:
Using the previous parameters, the sodium metaphosphate glass system as schematized in figure 3. In the present work, we used a combination of classical 3.1. Sodium metaphosphate structural glass model

Theoretical approach

(i) $\epsilon$ is determined from $\rho_Z$ using the expression (equation (20) of [35])

$$\rho_Z = 0.32607(1 - \exp(-2.097\epsilon^{1.151}))$$

valid for any $\eta_Q(0)$, where 0.32607 is the value for the Czjzek model.

(ii) $\eta_Q(0)$ is first determined from the $\eta_Q$ distribution using the approximation (equation (22) of [35])

$$f(\eta_Q) \propto \eta_Q^a \exp(-k\eta_Q^\beta) + (2 - \eta_Q)^a \exp(-(2 - \eta_Q)^\beta)$$

with $0 \leq \eta_Q \leq 1$ and where $k, \alpha, \beta$ are tabulated in function of $\epsilon$ and $\eta_Q(0)$ [35].

(iii) Using the previous parameters, $|V_Z(0)|$ is finally well approximated by:

$$|V_Z(0)| \propto \frac{\sqrt{1 + (\eta_Q)^2}}{\sqrt{1 + \tau(\epsilon)\eta_Q(0)^2/3}}$$

where $\tau(\epsilon)$ is a function given by equation (15) of [35].

The method described above involves only simple desk calculations. We notice that the deconvolution program of solid-state quadrupolar NMR spectra of Grimminck et al [41] uses a more precise method based on the bivariate distribution of the ECM expressed in the form of a triple integral.

3. Theoretical approach

3.1. Sodium metaphosphate structural glass model

In the present work, we used a combination of classical molecular dynamics (MD) simulations and DFT calculations to generate a configuration manifold of the sodium metaphosphate glass system as schematized in figure 3.
3.2. The force field and thermal quenching procedure

Amorphous sodium metaphosphate configurations were generated using the effective force field proposed by van Beest, Kramer and van Santen (BKS) [48, 49]. This force field, which is only based on a two-body potential, is formalized by the following equation:

$$V_{\alpha\beta} = \frac{q_{\alpha}q_{\beta}}{r} + A_{\alpha\beta} \exp\left(-\frac{r}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r^6}$$  \hspace{1cm} (8)

where the first term is the electrostatic interaction with partial charges $q_{\alpha}$. The following two terms correspond to the Buckingham potential, which is composed by an exponential repulsive part and an $r^{-6}$ attractive term. Table 1 summarizes the values of the set of parameters ($q_{\alpha}, A_{\alpha\beta}, \rho_{\alpha\beta}$ and $C_{\alpha\beta}$) used in the classical step of our procedure for each $\alpha, \beta$ atomic pair. The short-range part of the potential was truncated at 6.1 Å and the Ewald sum method was used to deal with the long-range electrostatic forces. The form A of NaPO$_3$ crystalline compound [50] was chosen as an initial configuration for the MD simulation. We used a 2 × 2 × 1 super-cell containing 160 atoms (32 $^{23}$Na, 32 $^{31}$P and 96 $^{17}$O sites) with cell parameters set to $a = 12.20$ Å, $b = 12.48$ Å and $c = 14.07$ Å to match to the experimental density of the glass system with the same stoichiometry (2.53 g ml$^{-1}$).

The configurations are obtained by quenching different configurations extracted from a long well equilibrated high-temperature trajectory ($\sim$1 ns at 3500 K) to low-temperature configurations (300 K). The classical quench was obtained by 20 temperature steps in the NVE ensemble (equilibrating for 2 ps at each step). The former quench procedure corresponds to a quenching rate of $\sim$4 K ps$^{-1}$. The chosen quench rate is slow enough to reproduce final structures that provide NMR parameters in reasonable agreement with experiments and fast enough to be tractable in terms of computation time. Classical trajectories were obtained using the academic code DL_POLY [51]. Hundreds of configurations have been obtained by this procedure. Then, the atomic positions were optimized (e.g. energy minimization) with DFT calculations using the VASP code (Vienna Ab initio Simulation Package) [52–55]. These calculations were done at DFT-GGA (PW91) [56–58] level of theory using standard PAW [59] to describe the electron–ion interactions. Plane-wave basis cut-off was set to $\sim$44 Ryd (600 eV) and only the $\Gamma$-point was used in the Brillouin integration. The geometry was considered as converged when the forces acting on the atoms were below 0.01 eV Å$^{-1}$. This last step of the procedure being more time consuming, only a limited number of configurations could be generated. We finally generated 17 configurations of metaphosphate glass (NaPO$_3$) by this complete procedure giving us a statistical sampling of 544 sodium and phosphorus sites and 1632 oxygen sites.

3.3. NMR tensor calculations

NMR tensor calculations were performed on the obtained configurations using the PARATEC code at a DFT level of theory [62, 63]. We used the PBE [64] functional for the generalized gradient approximation (GGA) of the exchange–correlation functional. The potentials due to the ions are represented by norm-conserving Trouillier–Martins pseudo-potentials [65]. The electronic configuration involved in the construction of the pseudo-potentials for the different nuclei $^{23}$Na, $^{31}$P and $^{17}$O are respectively [2p$^2$ 2p$^6$ 3d$^0$], [3s$^2$ 2p$^3$ 3p$^3$ 3d$^0$2] and [2s$^2$ 2p$^3$] with respective core radii (in atomic unit) [1.8 1.49 1.8], [2.0 2.0 2.0] and [1.45 1.45].

The electronic structure gives access to the EFG tensor through the reconstruction of the all-electron wavefunction that is obtained with the PAW approach [66, 10]. The non-diagonalised EFG tensor $V$ is used to calculate the five real components $U_{ij}$ (equation (2)), whereas the principal components $V_{xx}, V_{yy}$ and $V_{zz}$ of the diagonal tensor are used to calculate the quadrupolar coupling constant $C_Q$ and the asymmetry parameter $\eta_Q$ (defined by relation (1)). However, as mentioned above, $V_{zz}$ will be used in the distribution analysis.

The calculation of the chemical shielding tensor was performed using the linear-response method [67] using the GIPAW reconstruction developed by Pickard and Mauri [9]. Experimental isotropic chemical shifts $\delta_{cs}$ and absolute isotropic chemical shielding $\sigma$ are related through the definition of an isotropic reference shielding $\sigma_{\text{ref}}$ defined by $\delta_{cs} = \sigma_{\text{ref}} - \sigma$. In the NMR community, it is commonly accepted to use a liquid as an external chemical shift reference. In the present work, we set the absolute chemical shift value to an unambiguous isolated resonance of a crystalline site studied previously [37].

For both EFG and CSA tensor calculations, we used an energy cutoff of 100 Ryd, according to convergence tests previously performed on crystalline compounds [37, 68]. Owing to the size of the unit cell, only one $k$-point was used for the integration of reciprocal space.
Table 2. A comparison between some structural properties of our MD configurations and published data. (Top) Position \( R \) of the first peak of the radial distribution function. (Bottom) Phosphate coordination \( Q^p \) composition. Distances \( R \) are given with an uncertainty of \( \pm 0.02 \text{ Å} \) for the neutron study [60] and of \( \pm 0.025 \) for this work.

| Atomic pair | MD\(^a\) | Neutron\(^b\) | This study |
|-------------|----------|-------------|------------|
| P–NBO       | 1.50     | 1.48        | 1.45       |
| P–BO        | 1.59     | 1.61        | 1.65       |
| P–P         | 3.18     | 2.93        | 2.95       |
| O–O         | 2.51     | 2.52        | 2.55       |
| Na–Na       | 3.10     | 3.07        | 3.35       |
| Na–O        | 2.31     | 2.33        | 2.35       |

Coordination (\%) 

| \( Q^1 \) | 25  | —  | 4  |
| \( Q^2 \) | 50  | 100\(^c\) | 92 |
| \( Q^3 \) | 25  | —  | 4  |

\(^a\) From [61].
\(^b\) From [60].
\(^c\) By definition of the metaphosphate structure.

4. Results

4.1. Validation of the structural model

4.1.1. Local order and medium-range order. Table 2 compares the short (i.e. the position of the maximum of the first peak of the radial distribution function, \( R \)) and medium-range order parameters (relative concentration of \( Q^p \)) of the NaPO\(_3\) MD configurations obtained with the procedure described above. We also present a previous attempt by Speghini et al [61] to reproduce sodium metaphosphate glass structure from classical molecular dynamics. Experimental neutron diffraction data from [60] are also included for comparison. First, our glass model is seen to reproduce accurately the local structure, as represented through simple geometrical parameters such as \( R \). Our structural parameters are in better agreement with the experimental ones than are those of Speghini et al which were calculated only with a classical procedure. This is essentially due to the ab initio step in our calculation scheme. However, as discussed above, an accurate structural glass model for phosphorous compounds cannot be restricted to the sole aim of reproducing the local structure. It should also describe the medium-range structure. Our procedure provides a way to keep the ratio of \( Q^1 \) and \( Q^3 \) at a low level to fit the experimental data, whereas for example, the relative concentration of \( Q^6 \), is not accurately reproduced in the work of Speghini et al (see table 2).

4.1.2. Validation through \( ^{31}\text{P} \) and \( ^{17}\text{O} \) NMR. Figure 4 exhibits the experimental \( ^{31}\text{P} \) MAS NMR spectrum of NaPO\(_3\) glass together with the one obtained from DFT-GIPAW calculation of NMR chemical shifts. The latter was obtained with 544 phosphorous sites. As expected, the main contribution occurs around \( -20 \text{ ppm} \), a chemical shift usually assigned to \( Q^2 \) groups. The experimental spectrum shows some very small resonances in the region of \( Q^1 \) phosphorous, revealing a small excess of sodium in the chemical composition as compared to the stoichiometric composition. On the simulated spectrum, the small resonances around 0 ppm and \( -40 \text{ ppm} \) are due respectively to the \( Q^1 \) and \( Q^3 \) coordinations present in our statistical sampling. A close look at the simulated spectrum additionally reveals an overestimation of the \( ^{31}\text{P} \) \( Q^3 \) linewidth as well as a small shoulder around \( -30 \text{ ppm} \), revealing some limitations of our structural model.

Figure 5 compares experimental and simulated MQMAS spectra of NaPO\(_3\) at 18.8 T. It is important to recall that a MQMAS spectrum of an amorphous material gives the means to separate the chemical shift distribution from the distribution of quadrupolar parameters. Indeed, these distributions lead to a broadening of the two-dimensional site along two different axis, as evidenced in figure 5(a). In the NBO region, we interpreted recently the broad distribution of chemical shift as a consequence of long-range disorder in contrast to the conservation of the local structure observed through the small spreading along the quadrupolar distribution axis [37]. The NBO and BO sites are experimentally clearly separated by their chemical shifts, quadrupolar coupling constants and to a lesser extend by their asymmetry parameters.

The NBO sites present a broad distribution in chemical shifts, which is well reproduced by the MD configurations that permit one to reproduce the resonance asymmetry observed in the MAS dimension. On the other hand, for the BO, the line broadening in the MD spectrum reveals a broad distribution of chemical shift which seems to be overestimated with respect to the one observed experimentally. Overall, the main NMR parameters are well accounted for by the MD configurations for both BO and NBO sites.

![Figure 4](image-url)
Figure 5. (Left) Experimental and (right) theoretical $^{17}$O MQMAS (calculated using MD configurations). BO and NBO oxygens are respectively represented in blue (top contour plots) and red (bottom contour plots). Chemical shift (CS) and quadrupolar isotropic shift (QIS) lines are represented by dashed lines.

Table 3. Statistical properties of the MD configurations together with the ECM parameters obtained from the EFG distribution analysis.

|                  | MD statistics | ECM parameters |
|------------------|---------------|----------------|
|                  | $N$ sites     | $P(V_{zz} > 0)$ (%) | $\rho_z$ | $\epsilon$ | $V_{zz}(0)$ | $\eta_Q(0)$ |
| $^{23}$Na        | 544           | ~46             | 0.349    | —            | 0.148       | —            |
| $^{17}$O NBO     | 1088          | 100             | 0.041    | 0.093        | 0.853       | 0.15         |
| $^{17}$O BO      | 544           | 100             | 0.061    | 0.135        | 1.387       | 0.43         |

4.2. ECM analysis of the EFG distribution

Table 3 gathers results obtained from the previous MD calculations and the ECM parameters deduced from the procedure described in section 2.3.2.

Sodium atoms in our MD configurations have $P(V_{zz} > 0) \approx P(V_{zz} < 0)$ as expected if the GIM holds. This suggests that the EFG distribution of these sites is a Czjzek distribution. However the ratio $\rho_z (0.3487)$ is slightly larger than the Czjzek value of 0.32607. This difference is probably non-significant and related to the statistical fluctuations because of the low number of sites used to calculate it. In any case, the ECM analysis of sodium sites leads to the same parameters as those of the Czjzek model.

The calculated EFG tensors of the oxygen atoms show a clear difference between BO and NBO through the calculated ECM parameters, $V_{zz}(0)$ and $\eta_Q(0)$, as expected from the MD structures. The important element here is that oxygen sites present only positive values of $V_{zz}$, differing strongly from the essentially equal weights of the positive and negative parts of the $V_{zz}$ distribution which hold for the GIM. Furthermore, the $\epsilon$ values which are found to be small, being 0.09 and 0.13 for the NBO and BO, respectively, reflect a large local contribution in the ECM. Figure 6 presents the MD distributions of $\eta_Q$ and $V_{zz}$ parameters compared to the corresponding ECM distributions calculated with the parameters given in table 3. Small deviations between MD distributions and ECM analyses are observed for $\eta_Q$. This point will be addressed specifically in section 5. Finally, it is worth noting that such an overall agreement is obtained with a model based on three parameters only (i.e. $V_{zz}(0)$, $\eta_Q(0)$ and $\epsilon$).

5. Structural interpretation of the distributions

The previous discussion concentrates on the distributions of the principal values of the EFG as calculated from our structural models. In this section, we focus on the distributions of the components of the EFG vector $\mathbf{U}$ (equation (2)). These distributions are characterized and compared with some simple model predictions for the oxygen and sodium sites.

5.1. The case of oxygen ($^{17}$O)

The calculated EFG distribution can be explained in terms of the local structural features of BO and NBO sites. Indeed, the ECM analysis unveils the existence of a strong local contribution, consistent with the small coordination number of oxygen atoms. Intuitively, we understand that the electrostatic field felt locally by oxygen atoms is principally due to the variation of charge density induced by the chemical bonds shared with phosphorus. All other contributions can be considered as small perturbations to this ‘localized’ anisotropy in the charge distribution. As a consequence, it
makes sense to analyse the calculated $^{17}$O EFG distribution with a simple model of effective point charges, as discussed for instance in [26]. This model describes the probability distribution of the EFG created at the centre of a sphere by a random repartition of $n$ point charges on its surface. For this purpose, we analyse the distribution of $U$, the vector whose components are related to the elements of the EFG tensor through equation (2). In practice, the discrete charge model is equivalent to the calculation of the five components of $U$ by the following classical relations:

\[
\begin{align*}
U_1 &= \frac{1}{2} \sum_n (q_n/r_n^3) (3\cos^2(\theta_n) - 1) \\
U_2 &= \sqrt{3} \sum_n (q_n/r_n^3) \sin(\theta_n) \cos(\phi_n) \\
U_3 &= \sqrt{3} \sum_n (q_n/r_n^3) \sin(\theta_n) \cos(\phi_n) \\
U_4 &= \frac{\sqrt{3}}{2} \sum_n (q_n/r_n^3) \sin^2(\theta_n) \sin(2\phi_n) \\
U_5 &= \frac{\sqrt{3}}{2} \sum_n (q_n/r_n^3) \sin^2(\theta_n) \cos(2\phi_n)
\end{align*}
\]

(9)

where $q_n$ and $r_n$, $\theta_n$, $\phi_n$ are respectively the charge and the positions in spherical coordinates of the $n$th point charge.

Le Caër and Brand used this simple problem to exemplify the convergence of the distributions of the $U_i$ ($i = 1, \ldots, 5$) to the GIM distributions, that is to identical Gaussian distributions with variance $\sigma^2$, when the number $n$ of point charges increases. Numerical simulations were performed for $n = 2, 3, 4$ while the convergence to Gaussian distributions was proven when $n$ goes to infinity. Actually, the five distributions converge rapidly to Gaussians which are excellent approximations for $n$ larger than 4–5. The EFG distribution is then the one predicted by the Czjzek model. As required by the statistical invariance by rotation of the previous point charge problem (section 2.1 and [26]), the distribution of $U_1$ is found to be asymmetric while the distributions of the $U_{k,k>1}$ are identical and symmetric.

Figure 7 gives the distributions of the $U_i$ components ($U_1$ and $U_{k,k>1}$) for the $^{17}$O sites (BO and NBO) encountered in our NaPO$_3$ glass model. These distributions are compared to the discrete charge model described above. Using reduced units ($q_n = r_n = 1$), a unique scaling factor is needed to match the two distributions. The $^{17}$O sites are analysed with one or two charges, in order to mimic either the single covalent bond of NBO or the two covalent bonds of BO.

The distribution obtained from a single charge accounts accurately for the distributions of the five $U_i$ of NBO. A
first conclusion is that these distributions are fully consistent with statistical isotropy of the EFG tensor as described in section 2.1. Second, these distributions are not very sensitive to a distribution of the scaling factor mentioned above. Indeed, Gaussian or uniform distributions of this factor do not change the central parts of the $P(U_k)$ distributions (figure 7 top, see further section B.2 and figure B.2). Further, $P(U_1)$ presents a sharp peak on the left side as suggested by the distribution obtained from the MD–DFT calculations (figure 7). It is important to note that even if the marginal distributions $P(U_k)$ are correctly described by the previous model, the distribution of $\eta_Q$ due to the effect of a single charge is a delta peak at $\eta_Q = 0$ in contradiction with the calculated one (figure 6). Indeed, the axial symmetry of the single point charge yields an asymmetry parameter equal to zero. Therefore, it is necessary to add a background to the EFG of this charge. Choosing a Czjzek EFG tensor to account for this background and expressing the total EFG tensor in the frame of reference of the EFG due to the single charge yields the ECM (equation (5)). It is still an ECM in the presence of fluctuating scaling factors (see appendix B). Moreover, the Czjzek background leaves essentially unchanged the $U_i$ distributions. The latter have a rather limited discriminating power and are less suited than the distribution of $\eta_Q$ to evidence fine effects. Slight changes of the EFG vector may have a weak incidence on the $U$ distributions while they may produce significant changes of $\eta_Q$ which is a ratio formed from them. This explains the higher sensitivity of the $\eta_Q$ distribution. To summarize, the distributions of the $U_1$ and $U_{k,k>1}$ of the NBO are largely defined by local structural parameters (i.e., the number of covalent bonds shared with the phosphorus) whereas the distribution of the asymmetry parameter $\eta_Q$ is influenced by second or more remote coordination spheres.

For BO sites, the distributions of the $U_i$s can be reproduced by a two-charge model, where both charges mimic the anisotropy in the electronic structure produced by two covalent bonds. The resulting distributions are strongly dependent on the angle between the two charges and the centre of the sphere (i.e. angle POP). This strong dependence of the EFG distribution on the POP angle is consistent with a previous work of Clark et al [38], revisited recently in a MD + DFT–GIPAW approach [19], who established a correlation between the quadrupolar parameters and the $\text{Si–O–Si}$ angle of $^{17}\text{O}$ BO, in silicate glasses. For the present two-charge model, only three parameters are needed to define the EFG tensor (five in the general case), correlating the principal components of the tensor ($V_{zz}$ and $\eta_Q$). The observed
EFG distributions can then be reduced to the distribution of two point charges with an effective angle. The distribution of the BO $U_1$ and $U_{k,k-1}$ are well accounted for by the EFG due to two charges with an angle deduced from the MD and DFT calculations. As above, the distributions $P(U_k)$ are fully consistent with the requirements of statistical isotropy (section 2.1). Distributions $P(U_{k,k-1})$ due to the effect of two charges making an angle $2\theta$ differ just a little from those obtained from uniform distributions of the angle in domains $[2\theta_1, 2\theta_2]$ centred on $2\theta$ with a width as large as $16^\circ$. These angle distributions leave essentially unchanged the distribution $P(U_1)$ (figure 7 bottom, see in addition section B.1 and figure B.1) except for the sharp peak which becomes rounded off. The ability of the $P(U_k)$ distributions to evidence fine effects is again less than it is for the $\eta_Q$ distribution.

Finally, the analysis of the ECM distribution for the calculated $^{17}\text{O}$ EFG parameters shows some limitations to perfectly reproduce the $\eta_Q$ distribution. This is partially due to the simplified way of modelling the local contribution to the full EFG tensor by a single fixed tensor (equation (5)). Indeed, by simply considering a narrow Gaussian distribution of $\eta_Q(0)$, it is possible to reproduce the observed $\eta_Q$ distribution (left top dash line figure 6). This additional distribution of the anisotropic contribution could be interpreted as a small structural distribution of the local geometrical parameters (distances and angles).

In summary, the $P(U_k)$ are fully consistent with the statistical isotropy of the model glass. The modelling of the EFG tensors in terms of the contribution of one or of two charges with an additional Czjzek contribution from the background corresponds to the ECM (equation (5)) provided that the local frame of reference is chosen to be the one associated with the single charge or the doublet of charges. However, the previous ECM distributions deduced from the MD + DFT calculated EFG parameters of $^{17}\text{O}$ atoms do not account perfectly for their $\eta_Q$ distributions. This is partially due to a simplified modelling of the local contribution to the total ECM (section 2.3.1). As emphasized by Le Caër et al in the conclusion of [35], a first step to make the ECM more realistic is to distribute the local contribution on a physical basis sound. Here, a narrow Gaussian distribution of $\eta_Q(0)$ is indeed shown to suffice for account for fine details of the $\eta_Q$ distribution calculated from the glass model as shown in figure 6 (dashed line, top left subfigure).

5.2. The case of sodium ($^{23}\text{Na}$)

The ECM analysis of $^{23}\text{Na}$ sites reveals a trend of the EFG tensor of these nuclei to be distributed according to a Czjzek model. This observation was expected when considering the properties of a distributed point charge model as presented previously. Indeed, a structural analysis of the MD model reveals that sodium atoms have a distributed coordination number which ranges between 4 and 8, with more than 80% of them being 5- and 6-folded. For such coordinations, all the EFG components of the discrete charge model are normally distributed. Moreover, figure 8 presents the distribution of $\eta_Q$ for two sodium coordination numbers, $N = 5$ and 6, from our MD configurations. Both $\eta_Q$ distributions show the general features of the GIM. Other coordination numbers ($N = 4$ and 7) also show the same trend despite the small sample size (ca. 50 sites for each coordination). More generally, these results confirm the statement that the GIM is valid when the coordination number is at least equal to 4 [24, 26].

6. Towards ECM analysis of the CSA tensor

Both the Czjzek model and the extended Czjzek model, which are based on quite general assumptions, are not restricted solely to the analysis of EFG tensors. Physical properties of statistically isotropic disordered solids which are represented in 3D space by symmetric second-rank tensors can be analysed in a way similar to the one performed in the present paper provided that the tensor elements are sums of various contributions to which the central limit theorem may apply. These physical properties may be measured or/and calculated from structural models. This is for instance the case of the deviatoric part of the atomic level stress tensor (ALS) in metallic glasses [69, 70] which was analysed with a GIM in [71]. The trace of the stress tensor is the local pressure whose distribution is approximately Gaussian [69]. Similarly, the extended Czjzek model was applied to demagnetizing tensors to account for superparamagnetic resonance spectra of ferromagnetic particles in a diamagnetic matrix [72]. The chemical shielding anisotropy (CSA) tensor is worth being analysed with the previous methods. In contrast to the EFG tensor, the CSA tensor has an isotropic part (non-zero trace) and is then completely determined by three parameters instead of two ($V_{zz}$ and $\eta_Q$) for the EFG tensor. Within the Haebellren convention [73], we define the isotropic chemical shielding ($\sigma_{\text{iso}}$), the reduced anisotropy ($\Delta_{\text{CS}}$) and the asymmetry parameter $\eta_{\text{CS}}$ from the three principal components of the CSA tensor ($\sigma_i$, $i = 1, 2, 3$).

$$\sigma_{\text{iso}} = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33})$$

$\Delta_{\text{CS}} = \sigma_{33} - \sigma_{\text{iso}}$

Figure 8. Distributions of $\eta_Q$ of $^{23}\text{Na}$ in MD configurations for two different coordination numbers ($N = 5, 6$). These distributions are similar in shape to the Czjzek $\eta_Q$ distribution (solid line). A similar trend is found for the other coordination numbers ($N = 4$ and 7) despite the limited number of atoms used to calculate them (~50 sites).
The CSA tensor is completely characterized by six components. Five of them are defined by the five real $U_i$ components given by equation (2), substituting $v_{\alpha\beta}$ by $\sigma_{\alpha\beta}$. The additional component, denoted as $U_0$, corresponding to the isotropic parameter of the CSA interaction, is expressed by the following relation:

$$U_0 = -\frac{1}{\sqrt{3}}(\sigma_{11} + \sigma_{22} + \sigma_{33}).$$

(13)

However, to preserve the conditions imposed by statistical isotropy, the $U_1$ component should be now defined by

$$U_1 = (1/2)[\sigma_{33} - \sigma_{\text{iso}}].$$

(14)

To illustrate the similarity between the CSA and EFG distributions, we analysed the distribution of $U_i$ for the CSA tensor of oxygen sites. The data were obtained from the DFT–GIPAW calculation of the NaPO$_3$ configurations generated by MD. First, as expected, the distribution of $U_0$ is well described by a Gaussian, centred around the chemical shielding experimentally observed for both NBO and BO (not shown). Figure 9 shows the $U_i$ distributions for the two oxygen environments, namely BO and NBO. The distributions of $U_1$, for both oxygens, are asymmetric, as those observed for the EFG. The distributions of the remaining components have a symmetric shape which differs from a Gaussian. The distributions of figure 9 show clear similarities with those of figure 7. These results lead to the conclusion that the $^{17}$O CSA distributions need more than the GIM to be described properly. Therefore, the ECM analysis can be used to characterize the CSA distribution, revealing at the same time, the local structural information that is encoded into the anisotropic part of this interaction.

Figure 10 presents the distributions of $\eta_{\text{CS}}$ and $\Delta_{\text{CS}}$ parameters for sodium nuclei in our MD structural model. A Czjzek-like feature is easily identified for the $\eta_{\text{CS}}$ distribution, while the $\Delta_{\text{CS}}$ parameter presents an almost symmetrical distribution about zero, and is close to the shape of the $C_{zz}$ distribution in the Czjzek model. Both results indicate clearly that the distribution of the CSA tensor obeys the two general assumptions which lead to the GIM.

7. Conclusion

We applied a general multi-approach whose aim is to analyse and to model the NMR tensor distribution in disordered systems. This approach makes use of MD simulations and DFT calculations of NMR properties (i.e.
electric field gradient (EFG) and chemical shift anisotropy (CSA)) to provide both structural and NMR information. More importantly, this combined approach yields the full distributions of the considered tensors which cannot be measured experimentally in general. The distributions of the NMR interaction tensors are analysed through two different models: the Gaussian isotropic model (GIM) also known as the Czjzek model and an extension of it, the extended Czjzek model (ECM). We propose in particular a simple procedure to extract the main parameters of these models from a given tensor distribution.

We applied this procedure to a simple binary glass: the sodium metaphosphate (NaPO3). Using the strong sensitivity of NMR to the structural atomic arrangement, we validated the structural models generated by MD comparing the theoretical NMR response to high-resolved solid-state NMR experiments. The ECM was used to calculate the distributions of the EFG of the two quadrupolar nuclei present in this system (i.e. 23Na and 17O). The ECM analysis reveals the validity of the GIM in case of sodium, showing its broad applicability. As discussed in previous studies, the universal nature of such distributions (central limit theorem) makes the extraction of structural information very difficult. In the case of oxygen, the tensor distributions are shown to be dominated by a large local contribution. A simple additional analysis based on discrete charge distributions showed indeed that simple structural information might be extracted from the distribution of the components $U_i$ of the investigated tensors.

Finally, from the simple observations made about the CSA tensor distributions of 17O and 23Na nuclei, it is clear that CSA and EFG tensors can be analysed with similar tools. In other words, both GIM and ECM analyses might be useful and relevant to discuss experimental and theoretical observations of CSA distributions.

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Appendix A. Additional remarks on the ECM

All the ECM tensors $V(\epsilon)$ are expressed in a local frame of reference which is chosen, without loss of generality, as the one in which $V_0$ is diagonal and changes from atom to atom. By contrast, the distribution of the EFG tensor $V(\epsilon)$ (presented in appendix B) of all ‘sites’ belonging to the same family is calculated in a fixed global frame of reference identical for all atoms. It differs thus from the distribution of the tensor $V(\epsilon)$ (equation (5)). The spatial extent of a cluster around the considered atomic probe is expected to depend on the investigated solid and on the physical origins of the EFG (ex: close neighbourhood for covalent glasses). The statistical isotropy of this family would mean that the previous clusters have an overall random orientation in the considered solid. This general property holds for any geometrical characteristics of these clusters. The only general a priori knowledge about the distribution of $V(\epsilon)$ at the cluster centres is that it depends on the invariants of the EFG tensor when statistical isotropy holds (see equations (7), (8) and (10) of [25]). In addition, the associated distributions $P(U')$ of $V(\epsilon)$ the vector associated with $V(\epsilon)$ (equation (2)), cannot be derived directly from equation (5).

Appendix B. Rotation of the ECM tensor

Consider a particular tensor $V(\epsilon)$ obtained by choosing at random some $V_{\text{GIM}}$ tensor in equation (5), $V(\epsilon) = V_0 + \rho(\epsilon)V_{\text{GIM}}$, where $V_0$ is diagonal. The considered symmetric second-rank tensor is transformed into a diagonal tensor $V(D(\epsilon))$ by some rotation whose associated $(3 \times 3)$ matrix is $H_0$, in matrix notation:

$$V_D(\epsilon) = H_0 V(\epsilon) H_0^\top$$

and thus, $V_D(\epsilon) = H_0^\top V(\epsilon) H_0$, where $H_0^\top$ is the transpose of $H_0$ ($H_0 H_0^\top = H_0^\top H_0 = I$). The tensor $V(\epsilon)$ is transformed by a rotation $H_1$ into a tensor $V'(\epsilon)$:

$$V'(\epsilon) = H_1 V(\epsilon) H_1^\top = H_1 H_0^\top V_D(\epsilon) H_0 H_1^\top$$

or equivalently:

$$V'(\epsilon) = H_2 V_D(\epsilon) H_2^\top$$

where $H_2 = H_1 H_0^\top$ is a rotation matrix. The distribution of $H_1$ must be taken as uniform over the special orthogonal group $SO(3)$ to obtain a global statistical isotropy of the EFG tensor $V'(\epsilon)$. The standard definition of uniformity requires the distribution of $H_1$ to remain unchanged when composed with any arbitrary rotation (Haar measure). Therefore, the distribution of $H_2$ is uniform too and the principal values of the tensors $V'(\epsilon)$ and $V(\epsilon)$ coincide with the diagonal elements of $V_D(\epsilon)$. This line of reasoning can be applied to any tensor formed as above from equation (5). Thus, by construction, the global distribution of the EFG tensor $V'(\epsilon)$ is statistically isotropic and its principal value distribution is...
identical with that of $V(\epsilon)$. Therefore, the knowledge of the \textit{a priori} complicated distribution of $V(\epsilon)$ is useless when only principal values matter. Equation (5) suffices to provide the required information about the $\eta_Q$ and $V_{zz}$ distributions of the associated statistically isotropic EFG tensor $\mathbf{V}'(\epsilon)$. However, by this choice, the distribution $P(U(\epsilon))$ cannot be derived without additional calculations based on equation (B.3). Simplified examples are given below to illustrate the need of more than a single family of sites to account for the EFG distribution of some disordered solids described by the ECM.

### B.1. Uniform rotation

We consider the fixed diagonal part $V_0$ of the ECM model (equation (5)) which is expressed in its system of principal axes. The associated vector $U_0$ has therefore only two non-zero components, namely $U_1(0) = V_{zz}(0)/2$ and $U_3(0) = \eta_Q(0)V_{zz}(0)/2\sqrt{3}$. When the principal axis system is rotated uniformly in all directions, the tensor $V_0$ is transformed into a tensor $V'_0$ whose elements are consequently distributed. By construction, the distribution of $V'_0$ is then statistically isotropic and the components of the associated vector $U'_0$ have marginal distributions which fulfil the conditions described in section 2.1. The distributions $P(U'_1(0))$ can be obtained either in closed form for $k = 1$ and for any $k$ for $\eta_Q(0) = 0$ or by numerical simulations for any $k > 1$ as soon as $V_{zz}(0)$ and $\eta_Q(0)$ are known. These two parameters are obtained in the examples discussed below from simple physical models.

This appendix aims to present the distribution of the first component $U'_1(0)$ of $U'_0$.

After a rotation of the previous frame of reference by the Euler angles $\alpha, \beta, \gamma$, with $0 \leq \alpha, \gamma < 2\pi, 0 \leq \beta < \pi$, $U'_1(0)$ is directly calculated from the expressions given in appendix B of [26] to be:

$$U'_1(0) = \frac{\beta_0}{2}(3\cos^2(\beta) - 1 + \eta_Q(0)\sin^2(\beta)\cos(2\alpha))$$

(B.4)

with

$$-\rho_0 < U'_1(0) < \rho_0$$

(B.5)

where $\rho_0$ is some positive scale factor and $\rho_0 = \beta_0(1 + \eta_Q(0))/2$. To derive the sought-after distribution, it suffices therefore to consider a random rotation $(0 \leq \alpha < \pi/2, 0 \leq \beta < \pi/2)$ with a weight $(2/\pi)\sin\beta\ d\alpha\ d\beta$. Focusing on the
angular part of equation (B.4) we obtain two integrals which depends on \(\cos(2\alpha)\). The first integral is obtained when \(U'_1(0) < \beta_0(\eta_Q(0) - 1)/2\) and the second when \(U'_1(0) > \beta_0(\eta_Q(0) - 1)/2\). The final distribution reads \((z = U'_1(0))\)

\[
P(z) = 2F_1\left(1; \frac{1}{2}; 1; A\right) \left(4\beta_0 \eta_Q(0)(\beta_0 - z)\right)^{-1/2}
- \rho_0 < z < \rho_0 - \beta_0
\]

\[
P(z) = 2F_1\left(1; \frac{1}{2}; 1; \frac{1}{A}\right) \left(2\beta_0(3 - \eta_Q(0))(\rho_0 + z)\right)^{-1/2}
\rho_0 - \beta_0 < z < \beta_0
\]

\[
P(U'_1(0)) = \frac{2F_1\left(1; \frac{1}{2}; 1; \frac{\beta_0 - U'_1(0)}{\beta_0 + |U'_1(0)|}\right)}{2|\beta_0(\beta_0 + |U'_1(0)|)|}
\]

\[
- \beta_0 < U'_1(0) < \beta_0 \quad \text{as} \quad \rho_0 = \beta_0.
\]

The latter distribution is similar to the distribution \(P(U'_1)\) calculated for a single charge. Using the statistical invariance by rotation, the variance of \(U'_1(0)\) is readily obtained to be:

\[
\langle U'_1(0)^2 \rangle = \frac{\beta_0^2}{5} \left(1 + \frac{\eta_Q(0)^2}{3}\right).
\]

### B.2. The case of a single charge

As a second example, we consider the EFG at the nuclei of a given isotope which is determined by a single neighbouring point charge and by more remote atomic shells whose total contribution is described by a Czjzek tensor. The \(V_0\) contribution to equation (5) is then due to this single charge. If the charge does not fluctuate in value and in distance from the considered atom, the total EFG is described by a single ECM (equation (5)) with \(\eta_Q(0) = 0\). If the charge fluctuates in value or (and) in distance, then the EFG must be described by a distribution of ECM, all with \(\eta_Q(0) = 0\). We focus below on the distribution of the sole local part. The effect of the addition of a small Czjzek noise is just a smoothing of the distributions shown in figure B.2.

The marginal distributions of the components of \((U'_1 = (U'_{1x}, U'_{1y}, U'_{1z}))\), are obtained from equation (9) with \(n = 1\) for a random distribution of \(\theta\) and \(\phi\) (with \(P(\theta, \phi) = \frac{1}{2\pi}\ sin(\theta) d\theta d\phi\)). The distribution of \(P(U'_1)\) is asymmetrical as expected from the conditions given at the end of section 2.1 and has a simple closed form:

\[
P(U'_1) = (3\beta_0^2 + 6\beta_0 U'_1)^{-1/2} \left(-\frac{\beta_0}{2} < U'_1 < \beta_0\right)
\]

where the proportionality constant \(\beta_0\) is chosen here to be positive and is related to the characteristic parameters (i.e. charge and distance) of the problem. By contrast, the distributions \(P(U'_{k,k>1})\) are all identical and symmetric:

\[
P(U'_k) = \frac{2F_1\left(1; \frac{1}{2}; 1; \frac{\alpha - |U'_k|}{\alpha + |U'_k|}\right)}{2\sqrt{\alpha(\alpha + |U'_k|)}} \quad -\alpha < U'_k < \alpha
\]

where \(\alpha = \beta_0\sqrt{3}/2\) and \(2F_1(\ldots)\) is a hypergeometric function. In figure B.2, we represent two examples of distributions obtained from equations (B.12) and (B.13): with and without a uniform distribution of \(\beta_0\) where \(\beta_0\) is chosen to reproduce the characteristic distribution observed in our structural model (see the binned distribution, figure 7 top right, solid line).

### B.3. A perturbed diamond lattice

A third example deals with a diamond lattice whose atomic positions are very slightly shifted with random displacements derived from an isotropic Gaussian distribution. For simplicity, we assume that the EFG is due to point charges located at the lattice sites. In addition, the EFG at any site of this perturbed diamond lattice is assumed to be essentially due to its four first neighbours while more remote shells contribute to a Czjzek background. We focus on the distribution of \(\eta_Q\) obtained from \(V(\varepsilon)\) (equation (5)). Indeed, although the principal values of \(V(\varepsilon)\) have very small magnitudes, they suffice to change significantly \(\eta_Q\) as it is a ratio. An expansion of the EFG tensor in terms of the Gaussian atomic displacements gives a zero-order tensor \(V_0\) which comes from the tetrahedral coordination of a site and a first-order EFG tensor whose elements are centred Gaussians. This expansion yields equation (5) as the first-order tensor is a Czjzek tensor by itself. When added to the background tensor, the sum is still
a Czjzek tensor because the sum of two independent Czjzek tensors with parameters $\sigma_1$ and $\sigma_2$ is a Czjzek tensor whose parameter is $\sigma = \sqrt{\sigma_1^2 + \sigma_2^2}$. If all atoms are identical, $V_0 = 0$ and the EFG distribution is then a Czjzek distribution. If two different atomic species A and B, with different charges $q_A$ and $q_B$ ($\Delta q = |q_A - q_B|$), are distributed at random on the lattice sites with a composition $A_{1}B_{1-x}$, without any change of the atomic positions, then the distribution of $\eta_0$ at the A nuclei is a mixture of three distributions:

(i) a Czjzek distribution which comes from A atoms, denoted $[A_2]$ and $[A_3]$, which are surrounded respectively by four A atoms and by four B atoms, with a weight $(x^4 + (1 - x)^4)$ ($V_{zz}(0) = 0$).

(ii) an ECM distribution which originates from $[A_3B]$ and $[A_2B_2]$ atoms, with a weight $(4x^3(1 - x) + 4x(1 - x)^3)$ and $\eta_0(0) = 0$ ($V_{zz}(0) \propto \Delta q$).

(iii) an ECM distribution which arises from $[A_2B_2]$ atoms, with a weight $6x^2(1 - x)^2$ and $\eta_0(0) = 1$, ($V_{zz}(0) \propto \Delta q$).

In (ii) and (iii), the tensor $V_0$ and the values of $\eta_0(0)$ reflect the symmetries of the underlying tetrahedral shell. The previous example, although oversimplified, sketches however situations which are encountered in real semiconductors. Indeed, a recent $^{75}$As and $^{69}$Ga solid-state NMR study of Al$_2$Ga$_{1-x}$As thin films combines on the one hand experimental results and on the other structural modelling of disorder in the Ga and Al positions together with first-principles DFT calculations to obtain, among others, the EFG distributions at the tetrahedrally coordinated As sites [32]. Knijn et al found that the EFG distributions at $[As]$, $[AsGa]$ sites are accurately described by the Czjzek distribution. In addition, they showed that the EFG distributions at the As sites $[AsGa]$ and $[AsGa]$ are accurately described by extended Czjzek distributions whose $\eta_0(0)$ are respectively 0, 0, 1 as above for symmetry reasons (figure 13 of [32]).

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