STRUCTURAL MODELLING OF A MOLTEN SALT 
BY SIMULATED ANNEALING

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ABSTRACT

A new method for limiting structural models during modelling procedures on disordered compounds is described. Instead of using the well known periodic boundary, the data derived from neutron diffraction experiments are modified to take into account a spherical limitation of the model. Compared to cubic periodic modelling, this method reduces the computation time and improves model reliability since it introduces no artificial anisotropy. The method has been successfully tested in the structural modelling of molten NaCl.

INTRODUCTION

Until now, the structure of molten salts has been considered to be difficult to obtain. Indeed, as for liquids and amorphous solids, the models are built from experimental data which are mainly derived from diffraction experiments. These experiments use either electromagnetic radiations (X rays) or particles (neutrons). They only provide statistical data about the time and space averaged structure of such disordered objects. Moreover, attempts to obtain the 3D structure has often been considered as useless because most of the physical properties only reflect the average structure. Therefore a statistical description seemed to be sufficient.

Such a description, which is adequate to understand the macroscopic behavior of disordered compounds, is not adapted to the study of chemical reactions in molten salts. In that case it is the short and medium range organization of the molten salt which is of primary importance by strongly influencing the molecules in solution. Therefore, any attempt to model the physicochemical behavior of chemical species in solution has to take into account the structure of the solvent, which has to be known as well as possible. It is the reason why it seemed important to undertake this work in order to obtain a realistic 3D structural model in agreement with the available experimental data.
The structural modelling of disordered compounds is commonly performed by using various techniques based on thermodynamic criteria (Molecular Dynamics or Monte Carlo methods) or on the fit between the model and experimental data. Regardless of the technique, the same method is used for limiting the size of the model: the model is considered to be periodic. However, this limitation induces an artificial anisotropy which degrades the quality of the structural models and increases computation time. We suggest in this paper a new way for bounding the models which improves the quality of the modellings and shortens the calculation time. This new method has been tested in the static modelling of molten NaCl using neutron diffraction data as the experimental basis.

PREPROCESSING OF EXPERIMENTAL DATA

The experimental data which are used in modellings of disordered compounds are derived from the diffracted intensity by standard Fourier Transform processing (1)(2). They are the partial pair distribution functions $g_{++}(r)$, $g_{--}(r)$, $g_{+-}(r)$. The average number of ions located between $r$ and $r+dr$ from a given ion ($N_{exp}(r)$) has been chosen as the experimental basis during the optimization process and have been calculated from the experimental partial pair distribution functions. However, these values correspond to unlimited models. Yet, building a structural model that is too large is meaningless since the propagation of order does not exceed 15Å. Therefore, the model has to be limited. Moreover a spatial limitation of the model facilitates modelling operations since it shortens the calculation time. To overcome this problem, periodic boundary conditions have been commonly used to limit the model (3). This choice gives rise to a certain number of problems. The intrinsic anisotropy induced by this type of limitation may influence the geometry of voids in the structural model, thus reducing the quality of the information available from the model. Therefore, we have chosen to limit the model by using the most isotropic limitation: a sphere. Consequently the $N_{exp}$ had to be corrected with a factor $Q$ which is the self convolution of a 3D slit function with a radius equal to $R$ (4). This correction is isotropic and can be expressed as a function of $r/R$ ($R$: radius of the model). It is presented in figure 1 and has the following form with $x = r/R$:

$$Q(x) = 1 - \frac{3x}{4} + \frac{x^3}{16}$$  \[1\]

MODELLING METHOD

In order to obtain a structural model in agreement with the experimental data, we have chosen simulated annealing as the modelling method. This method belongs to the family of the Monte Carlo methods which are commonly used for optimization, and which have already been used for structural studies on alloys (3), solids (5), surfaces (6) and liquids (7). The main originality of this method is its aptitude not to converge systematically towards the closest local mimima. By this way it is different from classical full deterministic minimization procedures for which the probability of evolution of the modelled system towards states with lower cost function is 1. In the case of simulated annealing this probability depends on a pseudo-temperature with a Boltzmann type relation. This method allows jumps over local minima which are less favorable for the minimization. Therefore it gives deeper minima than purely deterministic methods which only provide the local minimum closest to the starting state.
RESULTS

A model with 396 ions has been built with a good fit with experimental data (98%) (Figure 2). It is limited by a sphere with a radius of 14.4Å which corresponds to the experimental density of molten NaCl (1.55g/cm³). $10^7$ steps have been necessary to obtain a constant value for the cost function. Figure 3 presents a comparison between:

a) the experimental partial pair distribution functions (2),
b) the partial pair distribution functions derived from the present model,
c) the partial pair distribution functions derived from a model generated from a theoretical interionic potential (8). Therefore, this method produces a better fit with experimental data than a theoretical interionic potential for which R=86% up to 10Å. The realism of the correction factor we have used here to take into account the limitation of the model has been checked by determining the local density of a model with 200 ions. Figures 4 clearly show that the local density is relatively constant with the distance to the center of the model and thus is consistent with thermodynamics. If no correction is performed, this density is no longer constant: most of the ions are located near the boundaries of the model since the $N(r)$'s corresponding to a high value of $r$ are amplified by the parabolic law:

$$N_{exp+}(r) = 4\pi D_{-} g+-(r) r^2 \Delta r$$

[2]

$N_{exp+}$: Average number of cations located at a distance between $r$ and $r+\Delta r$ from an anion.

D. : Average number of anions per volume unit.

$g+-(r)$ : Partial pair distribution function.

COMPARISON WITH MODELLING USING PERIODIC BOUNDARIES

This method has also been compared with classical methodology using periodic boundaries. As it does not require any artificial repetitions of the model, it takes into account less ions and is therefore less time consuming as it can be seen in figure 5. Moreover, the isotropy of models obtained using spherical or periodic boundaries have been compared. For this purpose, the $g(r)$ have been calculated for each model in two 3Å thick cylindrical slices. For the cubic periodic model, the directions of the slices were 100 and 110. For the spherical model, the slices were perpendicular. As can be seen in figure 6, the spherical models are rather isotropic (the $g(r)$ of the two sections almost coincide), while on the contrary, the cubic models are very anisotropic (the $g(r)$ do not coincide) which is not coherent with the structure of a liquid. These observations give evidence that spherical structural models are much more realistic than periodic models: they do not introduce any artificial anisotropy, which is important even in large cubic models. Therefore, the validity of the structural models previously obtained with a periodic limitation is questionable especially if the geometry of the voids in the models are taken into account for physico-chemical studies.
DISCUSSION

Two very important points have to be emphasized:
1- a model obtained by this method is not unique. Modellings carried out from different initial configurations lead to different models, i.e. models that cannot be superimposed. Notwithstanding, all of these models have common structural features which reflect the common experimental data (6). Therefore, a single model is sufficient for visualizing the main features of molten salt organization.

2- such a model is static even though the experimental data are obtained from moving ions. The diffraction measurements perform a time averaging simultaneously with the space averaging generated by the size of the real sample. If a static model is large enough to simultaneously contain all the main local configurations which appear during the time dependant evolution of the liquid i.e. allowing a good fit with experimental data, then this model is significant.

The main originality of the method we describe here is the way the model is limited. Compared to the periodic limitation of the models, this method produces, with less computation time, more realistic isotropic models of liquids.

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Figure 1: Correction function for a limited spherical model.

Figure 2: 5Å thick slice of a model with 396 ions.
Figures 3(a)(b)(c): Comparison of the partial pair correlation functions derived from the experiment and from models built by a theoretical interionic potential and by the present method. The reliability factor obtained with the present method is 96% which is better than what was obtained with a theoretical potential (86%).
Figure 4: Local density of a model with 200 ions with and without a correction of the N(ri). The model obtained with a correction has a local density which is approximately constant unlike the one obtained without any correction.

Figure 5: Comparison between spherical and periodic modelling. Computational effort for models of increasing size on a Silicon Graphics Indigo R4000 workstation.
Figures 6: Comparison between a spherical and a cubic periodic model. Each of these figures presents the comparison between the g(r) of two different slices of a model. The slices are perpendicular for the spherical model and they coincide with the 100 and 110 directions for the cubic model. The models contain 400 ions and the slices 68 ions.