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STRUCTURAL CALCULATIONS FOR AMORPHOUS SYSTEMS USING STRUCTURAL DIFFUSION MODEL

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We present the results of calculations of the structure factor S(k) and the pair distribution function g(r) for amorphous Iron, Cobalt and Nickel using Structural Diffusion Model (SDM). With the choice of local lattice structure made in this work, the agreement between the calculated and experimental S(k) and g(r) is reasonably good. We suggest that the most promising procedure to choose the local lattice for Structural Diffusion Model calculation of the amorphous systems studied in this work is to start with the fcc crystallographic unit cell.

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1. Introduction

This work aimed forwards the studies of the static structure of the amorphous Iron, Cobalt and Nickel using the Structural Diffusion Model (SDM). The most commonly employed description of the structure in amorphous systems is the pair distribution function g(r), which can be deduced by the Fourier inversion of the experimental static structure factor S(k) [1-2]. g(r) is one-dimensional real-space pair distribution function, from which the regeneration of the underlying three-dimensional structure can never be unique.

This work is concerned with a specific model, the Structural Diffusion Model (SDM). It was originally proposed by Baer [3], and has been used to describe the structure of liquids and amorphous solids [4, 5, 6, 7]. At its simplest the SDM characterises the local spatial arrangement of atoms in disordered systems by a lattice L, and viewing the disorder as due to a spatial decay of coherence between local structures, the spatial diffusion process. In its most recent form [8], used in this work, we associate the local structure with a *virtual* lattice L which may include vacancies. The spatial diffusion process is characterised by a statistical parameter, the *structural diffusion* coefficient D. The local lattice is determined by ($3n$+1) parameters - where n is of the order of the number of relevant neighbours- and on a couple of statistical parameters. The latter are determined by an optimisation process, simulated annealing [9], to the local configuration. The expression for the structure factor $S(k)$, or the pair distribution $g(r)$, is related to a spatial, radically evolving, Fokker-Planck equation in reciprocal space. Each of these properties, namely $S(k)$ and $g(r)$, can be evaluated independently, thus avoiding the truncation errors arising from Fourier transforming one into the other. This is precisely what we do in the calculations presented below.

With an increase in complexity of L, namely when the number n approaches $N \approx$ O (10^3), the SDM recovers a single configuration, say $\{\mathbf{r}^N\} \equiv \{\mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_N\}$, produced by the Reverse Monte Carlo Simulation (RMC), originally developed by McGreevy and Pusztai [10]. For O (10^3) a single "typical" RMC configuration is expected to give full information on the structure of the system, as far as low order ($n << N$) correlations are concerned. Yet, there is some redundancy in the information contained in $\{\mathbf{r}^N\}$. For instance, for two atoms far apart, the atomic positions in the neighbourhood of one atom relative to the other atom become unimportant. Whence if the relevant information sought is on the average configuration, this can be achieved by a distribution law that drastically reduces the number of parameters required. Moreover, while it is hoped that the RMC will eventually "converge" to an optimised structure, both in principle and in practice, this is not always possible. The difficulties of principle, which also apply to the SDM, have been discussed by Evans [11], and by van der Lugt and Winnink [12]. The practical difficulties have been overcome, sometimes, in the RMC method by the introduction of constraints to help with the optimisation procedure. In the end both the RMC and SDM seek to describe the experimental structure factor $S(k)$, or the deduced pair distribution function g(r). Both these properties are one-dimensional constructs either in reciprocal or real space from which the regeneration of the underlying three-dimensional structure can never be unique.

In this work we have taken the view that the proper choice of local for the description of the pair distribution function of an amorphous system, within the SDM, must be related to the crystallographic structure with which it completes. We specifically propose that a distorted fcc unit cell is proper choice of local lattice structure for amorphous systems whose parent crystallographic structure is fcc.

We show in Section 3 that, in fact, the SDM reproduces the structural of amorphous Fe, Co and Ni. The calculations are carried out by using concise analytical expressions for both $S(k)$ and g(r); these are presented, together with a brief outline of the SDM, in Section 2. This is followed, in Section 3, by the presentation and discussion of our results. Finally, in Section 4, we sum up and briefly comment on the results of our work.

2. Theory

The SDM assumes that the local configuration, i.e., the relative positions of a small group of neighbouring atoms, can always be approximated by a suitable domain in an ordered structure specified by a lattice, L. Further, the spatial disorder is introduced as a random relative displacement of the locally observed lattice structures at different points in space.

The resulting expression for the pair distribution function $g(r)$, has the form of a theta-type infinite series,

$$\rho g(r) \equiv G(r) = \sum_{\nu} G_{\nu}(r) = \sum_{\nu} \rho C_{\nu} \exp\left(-W b_{\nu}\right)\frac{\sin b_{\nu} r}{b_{\nu} r} \tag{1}$$

Here the sum extends over all points (shells) of the reciprocal lattice $L^{*}=\{b_{\nu}\}$, ρ is the density and C_{ν} is a *unit cell structure factor* given by $C_{\nu} = C(b_{\nu})$, where

$$C(k) = \left|\frac{1}{n}\sum \exp\left(i\mathrm{k}\cdot\mathrm{a}_{\sigma}\right)\right|^{2} \tag{2}$$

with the sum extending over the n points in the unit cell. $W = W(r) > 0$ serves as a *width function* which is a measure of the decay of coherence between local structures at two localities separated by a distance r. $W(r) \approx Dr$ when $r \to \infty$,. Moreover, $W(r)$ decays faster than r when r goes to zero, i.e.

For reasons of convenient analytic evaluation, we make use of the following specific form of $W(r)$,

$$\frac{\mathrm{d}W(r)}{\mathrm{d}r} \to 0 \quad as \quad r \to 0.$$

previously introduced by Egelstaff and Schofield [13], namely,

$$W(r) = D\left[\sqrt{r^{2} + r_{0}^{2}} - r_{0}\right] + W_{0} \tag{3}$$

where r_0 is the average exclusion parameter.

For disordered systems such as amorphous solids and liquids, an optimal L is not strictly unique because of an element of randomness present in the local arrangement of atoms. Consequently, it is possible to choose for L increasingly complex lattices possessing larger unit cells, together with coefficients D, giving increasingly accurate modelling for given $S(k)$ data. Indeed, in the limit of a very large cell having the size of the typical volume used in computer simulations with periodic boundary conditions, by putting $D = 0$ we can choose any representative configuration of the atoms as defining the unit cell of L. We denote any such macroscopically complex lattice by L_{∞}. In practice, the usefulness of the SDM lies in finding a relatively small local structure which reproduces with sufficient accuracy the $g(r)$ data. The details of the structure and its statics are then hidden in the spatial random process, exhibited by $D > 0$.

The expression for $g(r)$ used here is a generalisation of (1) following from the consideration of an additional spatial random process taking into account the effect of vacancies of the local structure. In its simplest version it leads to the consistency requirement

$$g(r)-1=\left(\frac{\rho_L}{\rho}\right)^2\left[g_L(r)-1\right] \quad (g(r)>0) \tag{4}$$

where $g_L(r)$ is the SDM expression (1) with the correct density ρ_L for L and ρ is the experimental density. We carried out the optimization results with respect to the local structure L and the statistical parameters D and r_0 using (4).

With the above choice we fit directly to the $S(k)$ experimental data and use the fact that the Fourier transform of $g(r)$ can be evaluated analytically, which is particularly important in the low k range [14]. We have

$$S(k)=\sum_{v} S_v(k)=\sum_{v}\int G_v(r)\exp(i\mathrm{k}\cdot\mathrm{r})d\mathrm{r} \tag{5}$$

Moreover, choosing (3) we have

$$S_v(k)=2\pi r_0^2 D C_v b_v \exp\left[\left(D r_0-W_0\right)b_v^2\right]\frac{1}{k}\left\{\frac{K_1(X_{v-})}{X_{v-}}-\frac{K_1(X_{v+})}{X_{v+}}\right\} \tag{6}$$

where $K_1(X)$ is the modified Bessel function of the second kind and

$$X_{v\pm}=X_v(\pm k)=r_0\sqrt{(Db_v^2)^2+(b_v\pm k)^2} \tag{7}$$

The optimization was carried out with respect to [13],

$$\chi^2=\sum_i y_i^2\left[(X(y_i))-X_{\exp}(y_i)\right]^2/\sigma^2 \tag{8}$$

where σ is related to the variance at each step of the minimization process.

In Eq (8) $X_{\exp}(y_i)$ denotes either the experimental or simulated structure factor or pair distribution function, y stands for either r or k, and $X(y_i,\mathrm{p})$ the $S(k)$ or $g(r)$ obtained from the SDM with the set of parameters **p**.

3. Results and discussion

All the systems considered in this work have, in their crystalline state, a fcc crystallographic structure that we take as our initial local lattice. a_i (i = 1, 2, 3) denote the elementary vectors, and α_i (i = 1, 2, 3) denote the internal angles. We also specify the initial position vectors s_k (k = 1, ...,n) of the 8 atoms inside the unit cell. $a_{\min}$ denotes the minimum value allowed for nearest neighbour distances during the iteration cycle; any lattice with smaller distances, produced in the iteration cycle, is rejected.

In the simulation annealing process the ($3n$+1) parameters of L_n , plus the two parameters D and r_0 defining $W(r)$ (we keep W_0 fixed) are varied in random steps, and χ^2 calculated by using Eq (8). The change in the parameters is then accepted or rejected according to the probability law which, say, for move m reads

$$P=\begin{cases}1 & \chi_m^2<\chi_{m-1}^2\\ \exp\left[-\beta\left(\chi_m^2-\chi_{m-1}^2\right)/\chi_{m-1}^2\right] & \chi_m^2>\chi_{m-1}^2\end{cases} \tag{9}$$

Convergence to the present accuracy is normally achieved in about 60 moves.

We only compare directly in Figures 1-3 our results with the experimental data of $S(k)$ and with the $g(r)$ deduced from the same experimental data by Fourier transform.

3.1. Amorphous Iron (a-Fe)

The structure factor of a-Fe has been measured by Lauriat [15]. The latter were measured using both polarized x-ray and polarized neutron scattering on a sample of ex-carbonyl amorphous iron obtained from $Fe(CO)_5$ molecular gas decomposed by continuous electrical discharges in neon at low temperature. Both S(k) are shown in figure(1-a). We note that the differences between the experimental S(k) in a-Fe not very large, bearing in mind the different techniques used in either sample preparation and types of radiation used. In figure (1-b) we also compare with the x-ray scattering data of Ichikawa [16].

In our calculations we have used fixed bond length the value 2.55 A^{o}, the average exclusion parameter 0.74 A^{o} and diffusion constant 0.0102. Also our choice of number density is 0.08486 Å^{-3} [17] and the value of angles is 60 ^{0}.

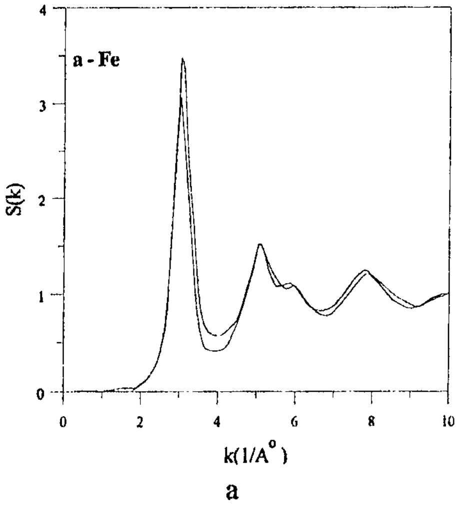


Fig. 1a. Static structure factor for a-Fe using the Polarized X-ray scattering data and Polarized neutron scattering data in Ref. [15].

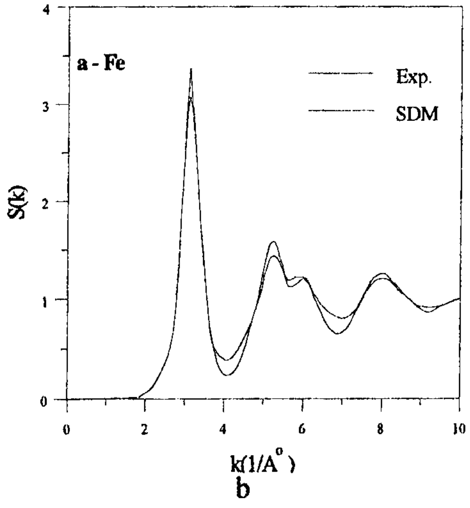


Fig . 1b. Static structure factor for a-Fe using the X-ray scattering data in Ref. [16].

The results for S(k) using the SDM are reasonably good. The general shape and positions of the peaks are well reproduced in all the system studied here. However the calculated main peak heights are, in most cases, lower than the experimental ones also our SDM calculation do not reproduce in a completely satisfactory manner the full details of the split second peak. Even though the correct trends are always present, it is possible, within the SDM to improve the quality of the calculated S(k)'s by using a more sophisticated dispersion law for W(r) as suggested in a previous work [18].

We have also calculated the corresponding pair distribution function , g(r)'s are obtained by the Fourier inversion of our S(k) results. Our g(r) result is shown in figure(1-c) for a-Fe.

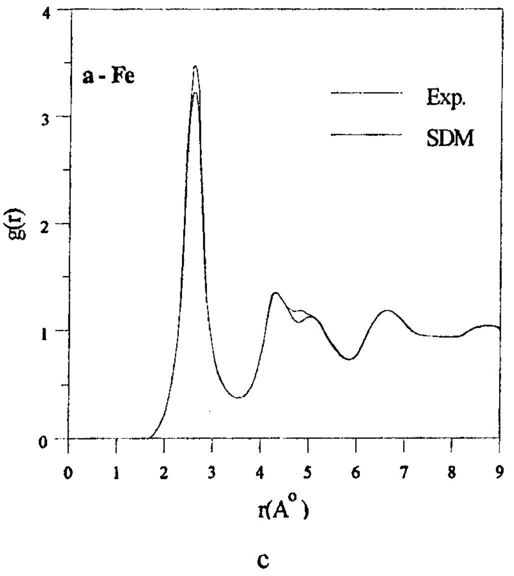
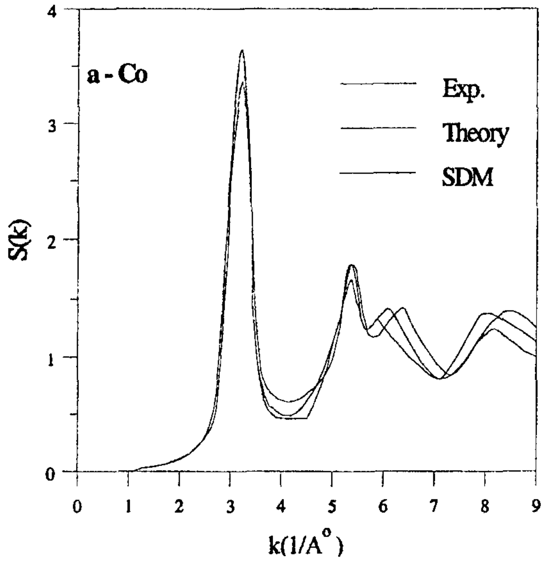


Fig. 1c. Pair distribution function for a-Fe using the X-ray scattering data in Ref. [16].

It is compared with the corresponding g(r) deduced from experimental data. It was obtained from the diffraction pattern of a thin film of amorphous material prepared by law-temperature condensation in high vacuum [16]. Our g(r)'s calculations reproduce well the shape, position and height of the peak of g(r) and account for the small irregularity in the third minimum.

3.2. Amorphous Cobalt (a-Co)

We present, in figure (2-a), the results of our SDM calculation for a-Co. The figures compare our result with the electron diffraction data of Leung and Wright [19]. We have also included, for comparison, the theoretical S(k) obtained by Sadchev and Nelson [20] using a Ginzburg-Landau theory based on the symmetries of a perfect icosahedral solid in a four-dimensional curved space. SDM result shows a lower S(k)-maximum with experimental results. For a-Co, we have used fixed bond length the value 2.45 A^o, the average exclusion parameter 0.72 A^o and diffusion constant 0.0098. Also our choice of number density is 0.09094 $Å^{-3}$ [17] and the value of angles is 60 ^{0}.



a

Fig. 2a. Static structure factor for a-Co using the Electron diffraction data in Ref.[19] and Theoretical calculations in Ref.[20].

We used the SDM result of S(k) to calculate the pair distribution function for a-Co. It is shown in figure (2-b). The results for Co were obtained by scattering electron diffraction of a thin film prepared by ultra-high vacuum at 4 °K [19]. The experimental results for amorphous systems at law temperatures reveal that the width of the first peak of g(r) is more narrow relative to the liquid phase as a result of more restricted particle displacement. For the same reason the short range order extends to large distances than for liquids. Some authors refer to third behaviour as intermediate short range order [21]. Moreover the second peak splits in to two sub peaks. This feature of g(r) has sometimes been taken to be as a sign of the true glassy state [22]. Another common feature of the g(r)'s of amorphous systems is an irregularity is also obtained in the third minimum. This behaviour is also obtained in results of computer simulation. The second peak splits gradually in to two subpeaks as the as the liquid is cooled down to temperatures below freezing [23,24].

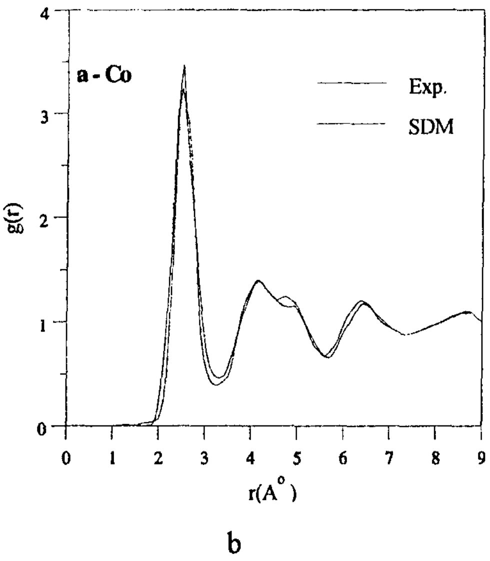


Fig. 2b. Pair distribution function for a-Co using the Electron diffraction data in Ref. [19].

3.3. Amorphous Nickel (a-Ni)

Our SDM fitting of the a-Ni structure factor , figure (3-a) , is in excellent agreement with the experimental data of Ichikawa [16] , except both second peak and minimum the height of the second peak is lower than experiment and also the minima is below experiment; otherwise our fitting follows closely the experimental data. We have used fixed bond length the value 2.48 A^o, the average exclusion parameter 0.69 A^o and diffusion constant 0.0099. Also our choice of number density is 0.09141Å^{-3} [17] and the value of angles is 60 ^{0} for amorphous a-Ni.

Our result for g(r), is shown in figure (3-b) along with the X-ray scattering data [16]. It is very good and it shows a marked shoulder on the high-r side of the second peak. The observed properties for a-Ni are similar to a-Fe and a-Co.

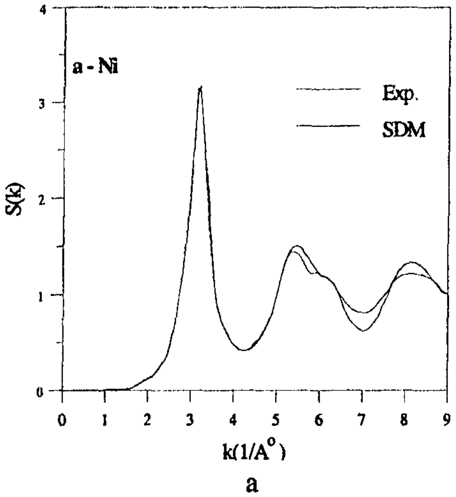


Fig. 3a. Static structure factor for a-Ni using the X-ray scattering data in Ref. [16].

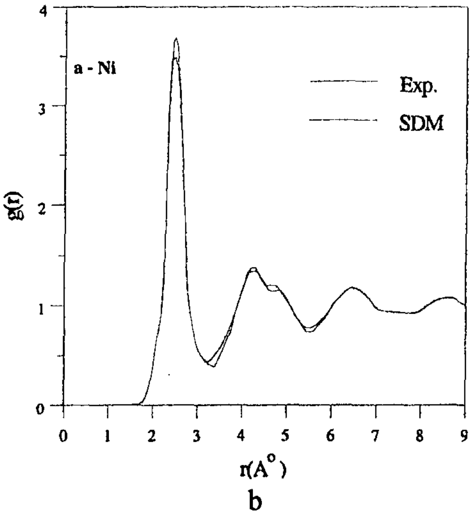


Fig. 3b. Pair distribution function for a-Ni using the X-ray scattering data in Ref. [16].

4. Conclusions

We have analysed the structure of a-Fe, a-Co and a-Ni using the Structural Diffusion Model (SDM) which, while based on a similar philosophy, is computationally simpler. We have also described satisfactorily the typical short and intermediate-range order observed in a-Fe, a-Co and a-Ni. Moreover we put forward the proposition that the local lattice structure used in this work is the proper choice of local lattice for a SDM description of the atomic arrangements of all the amorphous solids whose parent crystallographic structure is fcc. It is also likely that a similar choice of local lattice is capable to describe the correct g(r) of amorphous systems whose crystallographic structure is hcp. As a result of our calculations we suggest that the small peak, or shoulder, following the second peak of $g(r)$ is a real feature that reflects, weakly, the third-neighbour peak in the crystalline phase of the tetrahedrally bonded amorphous systems. Within the SDM description of g(r) it is not possible to assert whether the system is in the amorphous phase or, indeed, how it has reached that phase. For the latter we would need information on the kinetic processes involved in the transition, which no static model or theory of the structure provides.

Finally, the following comments are in order. The structural disorder in an amorphous solid implies a non-zero configurational (structural) entropy, $S > 0$. The SDM offers the possibility of obtaining compact expressions for the structural entropy [25], a property that is difficult to study using standard statistical theories or computer simulations.

The SDM provides a modelling by analytic functions which are computationally convenient and can produce result for both the static structure factor and pair distribution function as well their spectral representations. We propose that the SDM is a convenient, simple model to describe the structure of amorphous systems.

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