ATOMIC STRUCTURE
THE OBSERVATION OF CHEMICAL SHORT RANGE ORDER IN LIQUID AND AMORPHOUS METALLIC SYSTEMS BY DIFFRACTION METHODS

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The model of random dense packed hard spheres (RDPHS) has been shown to be of fundamental importance for the description of simple monatomic liquids [1] and it has also been successfully applied to binary systems [2,3]. Hafner demonstrated [3] that physico-chemical properties of binary melts may correctly be calculated by the intermediate of a RDPHS system, provided the chemical interactions between the 1 and 2 types of atoms were influencing only the hard sphere diameters \( q_i \) which became therefore composition dependent. However, the method fails if any ordering takes place between the 1 and 2 particles. As deduced from thermodynamics, such an ordering is far from exceptional in liquid alloys [4,5], and is likely to occur in the glass phases prepared from them. Moreover in the diffraction patterns of some liquid alloys similar effects have been observed as for disordered polycrystalline substitutional alloys, with tendency for heterocoordination (short-range order) or self-coordination (cluster formation) respectively, both effects being described with the same formalism and under the same head-line "short-range order" by Warren, in his book on X-Ray Diffraction [6]. We will adopt here the same nomenclature with a slight modification since we use the word chemical short-range order (CSRO) in order to distinguish these ordering effects from the topological short-range order of the global atomic arrangement which is responsible for the non-crystalline structure.

Formalism

As a simple starting point, the 1 and 2 particles of a binary alloy are more or less randomly distributed over the identical sites of a structure, which we call the "global structure", yielding what is called a substitutional alloy and for which the mean global surroundings of the 1 and 2 particles are identical. Of course, this approach fails in the case of particles of different sizes. It has been shown however, for crystalline solid solutions that a substitutional alloy model is a very powerful starting point, as long as the size difference is not too large. For binary melts and metallic glasses, one should therefore try to start with the same model, the global structure being here not a crystalline structure anymore (like fcc in the case of solid Cu Au) but a RDPHS by example. Such an approach was already proposed by Keating in 1963 [7]. The question for CSRO would then be to gather information on the distribution of the 1 and 2 particles over the sites of the global structure. From the different partial structure factors which have been proposed to describe binary phases, the most directly affected by CSRO is the \( S_{CC} \) partial structure factor which has been introduced by Bhatia and Thornton (BT) [8]. If we call \( b \) the coherent scattering amplitude and \( f_1^C(q) \) the coherent scattering intensity per atom, we define the total structure factor \( S(q) \) or \( S_2(q) \) of a binary alloy as:

\[
S(q) = f_1^C(q) / \langle b^2 \rangle + f_2^C(q) / \langle b^2 \rangle = x_1 b_1^2 + x_2 b_2^2,
\]

\( x_i \) are the atomic fractions, and \( q \) is the absolute value of the scattering vector. According to BT, \( S(q) \) may be subdivided into

(1) \( S(q) = S_{NN}(q) + S_{NC}(q) + (1-a) S_{CC}(q) / x_1 x_2 \)

where

(2) \( a = \langle b^2 / \langle b^2 \rangle \rangle \)

(1-a) = \( x_1 x_2 \Delta b^2 / \langle b^2 \rangle \)

\( \Delta b = b_1 - b_2 \)

and \( \langle b \rangle = x_1 b_1 + x_2 b_2 \)

\( S_{NN}(q) \) oscillates around 1. It is equal to \( S(q) \) for \( b_1 = b_2 \). Its Fourier Transform (FT) is related to the global structure of the alloy [9]. \( S_{NC}(q) \) oscillates around 0. It is identical to zero for identical global surroundings of the 1 and 2 particles.
$S_{CC}(q)$ oscillates around $x_1 x_2$. It is identical to $x_1 x_2$ if there are no distance correlated concentration fluctuations, i.e., in the case of random substitutional alloys without size effect and identical thermal vibrations of the two particles. The FT of $S_{CC}/x_1 x_2$ yields $\rho_{CC}(r)$:

$$\left(2\pi^2 \right)^{-1} \int_q (S_{CC}/x_1 x_2 - 1) \sin(qr) dq = r \cdot \rho_{CC}(r)$$

which is given in terms of the Faber Ziman partial pair correlation functions $\rho_{kk}(r)$, $(k, \ell = 1, 2)$, by:

$$\rho_{CC}(r) = x_2 (\rho_{11}(r) + \rho_{12}(r) + \rho_{22}(r)) + x_1 (\rho_{11}(r) - \rho_{21}(r)/x_1)$$

$4\pi^2 \rho_{CC}(r)$ was called by Ruppersberg and Egger [9], the "radial concentration-correlation function" (RCF). The RCF is zero for distances where no atomic pairs exist (all $\rho_{kk}(r)$ terms vanish). The RCF is also identical to zero if for each $k, \ell$ pair, $\rho_{kk}(r) = x_k N/V$, i.e., for a statistical distribution at the distance $r$. Finally, the RCF is positive for distances with preferred self-coordination and vice versa.

In the case of polycrystalline disordered substitutional alloys where the BT formalism applies also, one generally does not discuss the full RCF curve, but simply introduce [9] the Warren-Cowley short-range order parameters $\alpha_p$:

$$\alpha_p = 2^{-1} \int_{r_p-\epsilon}^{r_p+\epsilon} 4\pi^2 \rho_{CC}(r) \ dr,$$

$r_p$ is the mean distance from an atom to its $p$th coordination shell of thickness $2\epsilon$, $z_p$ is the total number of atoms in the $p$th shell. If $z_p$ is the mean number of atoms 2 in the $p$th shell of an atom 1, we have

$$\alpha_p = 1 - 2^{-11} (z_2 x_2) = 1 - 2^{-21} (z_2 x_2)$$

and as a consequence $\alpha_p > x_p/z_p$, where $p$ refers to the more concentrated species. Zero, positive or negative values of the $\alpha_p$ parameter indicate a statistical distribution or a preferred self or heterocoordination in the $p$th shell. One has observed that the RCF curves of some liquids are very similar to those obtained for the polycrystalline disordered substitutional alloys. Reiter et al. [10] showed that melting left the CSRO of the solid Ag-Li $\alpha$-solution practically unchanged. Thus it seems logical to keep the same formalism for the liquid phase. However, there are then no well defined coordination shells and eq.(5) and (6) apply only if used with an appropriate model of the global structure. The $\alpha_1$ parameter obtained in that way is therefore a useful criterion of CSRO in non crystalline phases as long as the systems are close to the substitutional type. A different approach must however be used if the alloys are far from substitutional or if rather complex ions are formed as we shall see later on in this paper. Finally, without measuring the whole $S_{CC}(q)$, one may already obtain some important information about the composition fluctuations in liquid alloys from the value of $S_{CC}(0)$. It has been shown by BT [8], that this value is proportional to the mean-squared composition fluctuation $\langle \delta x^2 \rangle$ which is, on the other hand, related to the curvature of the free energy $G$ in the $O-x$ diagram:

$$\partial G/\partial x = \partial S_{CC}(0)/\partial x = \partial E_{CC}/\partial x$$

$E_{CC}$ is the "excess stability function" introduced by Darken [12]; $\gamma$ is the activity coefficient; $R$ is the molar gas constant and $T$ the temperature. According to Thompson [13], whenever $E_{CC}$ is different from zero, CSRO occurs.

**Determination of $S_{CC}(q)$**

The complete set of three partial structure factors may, in principle, be obtained from three independent scattering experiments with different scattering coefficients [14]. Important information may also be obtained from two or one scattering experiments, by comparison with models [11,15] or by discussion of CSRO effects like a prepeak. If the alloy is of the substitutional type it may be assumed that $S_{NC} = 0$ or is hard sphere like. There is however a severe restriction to the application of these methods since the contrast for the $S_{CC}$ partial is often poor due to a small value of $(1-a)$ in eq.(1). One notices that the contrast $(1-a)$ is composition dependent and is optimal at $x_1^0$ where it depends only on the ratio of the scattering lengths. $x_1^0$ is given by

$$x_1^0 = (1 + b_1/b_2)/(1 - (b_1/b_2)^2)$$

where $|b_1| > |b_2|$. We display on Figure 1 the optimum composition $x_1^0$ and the corresponding contrast as a function of $b_2/b_1$.
We see on figure 1 that unless $b_2/b_1$ is smaller than 0.5, the contrast is less than 10%. This is for example the case for CuSn, CuZr, AuCu and MgAl. X Ray scattering gives an excellent contrast for dilute solutions of an heavy solute in a light solvent. A contrast value of 1 at the optimal composition, is obtained if $b_1$ and $b_2$ have different signs as it is possible in neutron scattering for which the following series of isotopes or elements have negative scattering lengths (relative phase shift of $\pi$ of the scattered wave): $^{1}$H, $^{7}$Li, $^{nat}$Mn, $^{62}$Ni, $^{nat}$Ti, $^{152}$Sm, $^{162}$Dy and $^{190}$W. In this case, at the optimal composition $x_1^0$, which is called the "zero alloy" composition, the sum of three partials, eqn. (1), reduces to a single partial, $S_{CC}(q)$ which is unambiguously obtained in a single experiment. Of course, this is a very powerful method for studying CSRO effects.

Results
We will now present some examples of CSRO as obtained for metallic A) segregating systems, B) almost ideal alloys, C) compound forming systems, and D) systems with metal to non-metal transition or with complex ion formation.

A) The NaLi phase diagram is dominated by a region of two miscible liquids. The consolute point at $T_c = 557 \pm 2$ K and $x_{Li} = 0.64 \pm 0.02$ is close to the zero-alloy composition $x_{Li}^0 = 0.61$. $S(q) = S_{CC}(q)/x_1^0 x_2^0$, which was measured by Ruppersberg and Knoll [17] at $T = 13$ K is shown in Fig. 2. This curve is very different from a RDFHS curve but similar to zero alloy curves obtained with solid Ni-Cu alloys [16]. It is dominated by a strong small-angle scattering (SAS) produced by concentration fluctuations. Critical amplitudes and exponents for $S_{CC}(0)$ and for the correlation length $\xi$ of the fluctuations could be calculated from Ornstein-Zernike plots of SAS patterns yielding $S(0) = 80$ at $T = T_c + 13$ K in Fig. 2. RCF curves are shown in Fig. 3 for $T_c + 13$ and $T_c + 150$ K, respectively.

![Fig. 2: RCF for liquid Li$_{0.61}$Na$_{0.39}$](image)

The dotted curves come from the critical SAS and have maximum amplitude at $r = \xi$. The RCFs are positive over large distances, indicating fluctuations with preferred self-coordination. The small peaks at 3 and 4 Å are related to preferred Li-Li and Na-Na distances. With the assumption that each atom is surrounded by 10 neighbours, $\alpha_i$ values of 0.5 and 0.3 were obtained for the two temperatures from Eq. (5), which means that a Li atom has 8 and 7 Li neighbours instead of 6 for a random distribution. On approaching $T_c$ from 590 K, the RCF will remain almost invariant at small distances, however, the $r$-range of positive $\rho_{CC}(r)$ will diverge at $T_c$.

There are numerous systems where SAS, i.e. segregating tendency has been observed. SAS was detected close to the eutectic composition of liquid Ag/Ge [24] and was related to an hypothetical miscibility gap in the undercooled liquid. A reminiscence of a critical transformation which occurs far below the melting point has indeed been observed by Weber et al. [25] for the magnetic neutron scattering from spin fluctuations in liquid Fe, Co and Ni. SAS has been observed in Na/Cs [26] and, with a very small amplitude also in Na/K [27]. Steeb and coworkers detected more or less pronounced SAS in Al/Sn, In [28], [29], Cd/Ga [30] and Cu/Bi, Sb [31], [32] melts. For the last mentioned Cu/Sb system, isotopic substitution experiments were performed, and though the best $S_{CC}$-contrast was only 10 %,
the authors could calculate $S_{CC}(q)$, $S_{CC}(o)/x_1x_2$ came out to be 2.5, and the RCF was different from the LiNa curves shown in Fig. 3 and looked more or less like the upside down RCF of compound forming system shown in Fig. 7. SAS observed in the $S(q)$ of amorphous samples seems not related to composition fluctuations but to effects such as voids, dislocations etc.. This is shown, for example, by Steeb et al. for Fe$_{80}$B$_{20}$ [34].

Let us add a comment on the detection of SAS in segregating systems. If the partial molar volumes $V_i$ of the 1 and 2 species are different, the concentration fluctuations become correlated with density fluctuations and are then visible also in the small angle parts of $S_{NC}(q)$ and $S_{NC}(o)$ as it is shown for CuPb alloys by Fabre-Bonté et al. [33]. The (1-a) contrast introduced to indicate the strength of the $S_{CC}(q)$ partial is then not adequate anymore to describe the possibility of SAS detection in $S(q)$. As a matter of fact the appropriate contrast $C$ for SAS in $S(q)$ is proportional to the difference between the scattering amplitudes per unit volume of the two components [42].

$$C = \left| \frac{\bar{V}_1 - \bar{V}_2}{\sqrt{V_1 V_2}} \right| \left( x_1^2 + x_2^2 \right)^{1/2}.$$

One notices that this contrast is composition dependent through the partial molar volumes and is also affected by isotopic substitution in neutron scattering experiments [43, 44]. In the zero alloy case C simply equals $1/x_1x_2$.

B) For the liquid zero alloy Li$_{0.68}$Ca$_{0.32}$, $S_{CC}(o)$ has been found by Ruppersberg [18] to be almost ideal, i.e. equal to $x_1x_2$ (see Eqn. (7)). The strong oscillations of $S_{CC}(q)$ as displayed on figure 4 are due to the large size difference ($a_L/a_{Ca}=0.78$) between the two species and are therefore very similar to the RDPHS curve calculated in the PY approximation.

$$S(q) = S_{CC}(q)/x_1x_2$$ of the Li-Ca zero alloy

The raising part of the RCF of fig. 5, between 2 and 2.7 Å is similar to the radial distribution function of pure Lithium the later having however its maximum at 3 Å, where the RCF already decreases due to the negative peak of the Li-Ca pairs. The 4 Å peak belongs to the Ca-Ca pairs.

$$\frac{\alpha}{\frac{1}{2}} \frac{\beta}{\frac{1}{2}}$$

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C) A tendency towards compound formation has been detected in the diffraction pattern of numerous alloys including the important Fe-C melts [37]. However the partial $S_{CC}(q)$ curves are known in a few cases only. The one obtained from Lithium zero alloys is certainly too small (0.2% for Mg$_{30}$Ca$_{70}$ [35] and Mg$_{50}$Zn$_{30}$ [36] to allow the observation of CSRO.

$$S_{CC}(q) = \frac{x_1x_2}{S(q)}$$ for compound forming Lithium zero alloys (temperature near melting point)
For Li$_{0.5}$Ag$_{0.5}$ a superlattice peak observed in the low temperature solid, transforms on heating into a broad peak typical of CSRO in the solid disordered solution. Practically unaltered by melting this becomes the main $S_{CC}$ peak of the liquid [10], located at $q_c$, as displayed on the figure.

The first peak of the $S_{NN}$ partial, at $q_H$, which generally dominates the total scattering pattern of binary alloys is located at higher $q$ values. A simple sticky hard sphere model gives a peak position ratio $= 0.61$ [11]. The main peak of the $S_{CC}$ partial is therefore observed, depending on the strength of the CSRO and on the contrast, as a more or less intense "prepeak". Such a prepeak has first been detected by Steeb and Hezel [38] in the X Ray diffraction pattern of AgMg alloys. In the case of Li$_{0.8}$Pb$_{0.2}$ the $S_{CC}$ peak is very strong, see fig. 6, and is even higher than the $S(q)$ peak of pure metals near the melting point. It is much weaker for Li$_{0.7}$Mg$_{0.3}$. A strong CSRO effect like in the first case would be detected in $S(q)$ even with a contrast of only 2%; a contrast of 20% would be required in the second case.

The RCF curves are shown on figure 7.

In all three cases there is a negative peak at the nearest neighbor distance indicating a preferred hetero-coordination. There are good reasons to believe that the alloys are of the substitutional type with $S_{NN}(q)$ not too far from a RDFHS curve [9]. If we assume therefore a mean value of ten nearest neighbors, the short-range order parameter $\alpha_{1}$ turns out to be $-0.25$ for Li$_{0.8}$Pb$_{0.2}$ (preliminary result only, [18]), $-0.15$ for the LiAg and $-0.04$ for the LiMg alloy. Thus, referring to Eqn.6, we have maximum ordering in Li$_{4}$Pb near the melting point. From these results, it seems that the highest excess-stability function, i.e., the smallest $S_{CC}(0)$ might be correlated with the highest $S_{CC}$ peak and the most negative $\alpha_{1}$ value.

This is not necessarily the case however since one might imagine a segregation tendency between a pure element and an hetero-coordinated cluster, which will give at the same time a prepeak and SAS. On the other hand the heights of the main $S_{CC}$ and RCF peaks are not directly connected either. The figure 8 displays RCF curves calculated from the complete $S_{CC}(q)$ curves of Li$_{4}$Pb and from only the positive part of the first peak of $q(S_{CC} - x_{1}x_{2})$. We see that the strength of the $S_{CC}$ peak is in that case characteristic of the range of CSRO effects in real space, its width yielding a correlation length which for extended CSRO will probably be strongly affected by temperature. The $\alpha_{1}$ parameter itself depends on the whole $S_{CC}$ partial and one must be cautious at interpreting total $S(q)$ curves. These two parameters, $\alpha_{1}$ and correlation length, might be sufficient to characterize the CSRO of the system. An interesting additional information is revealed by the RCF's: the compound formation tendency seems to be correlated with a relative contraction of the 1-2 nearest neighbor distance as compared to the mean 1-1 and 2-2 distances [10].

![Fig. 7: RCF curves for compound forming lithium zero alloys](image1)

![Fig. 8:](image2)
composition and temperature variation of RCF curves. Very little, if nothing is known from diffraction experiments about CSRO in non substitutional type of alloys.

D) Diffraction experiments might help to elucidate the nature of bonding in more complicated disordered metallic systems. Let us first take the solutions of alkali metals in their molten salts, a well known case of transition from metallic to ionic behavior[45]. The partial structure factors of the molten salts have been considerably investigated both on the theoretical and on the experimental side [46]. The figure 9 displays the characteristic features of the total structure factors $S(q)$ obtained for different chlorine isotopes and the $S_{NN}, S_{CC}$ partials of a typical purely ionic alkali halide salt. (One reminds that in this case, $x_1 = x_2 = 0.5$ and the $S_{CC}$ partial becomes effectively a charge fluctuation partial $S_{CC} = \frac{1}{2}(S_{++}+S_{--}-2S_{+-})$). In alkali halide systems $S_{NN}(q)$ is found equal to zero which yields $S_{NN}(q) = S_{--}(q)$. The system is totally described with two partials, $S_{NN}, S_{CC}$. One notices on the figure 9 that the first maximum of the total structure factor corresponds to the main peak of $S_{CC}$ whose position $q_c$ is related to the periodicity of the charge oscillation. The second maximum in $S(q)$ corresponds to the main peak of $S_{NN}$ at $q_N$ and is related to the nearest neighbor distance $r_+$. The relative position of these two peaks is very accurately defined in the alkali halide series, $q_c/q_N = 0.67$, which is different from the value 0.61 observed in compound forming alloys. This produces the typical alternance of $S_{qq}$ and $S_{NN}$ peaks in the total structure factor.

If one mixes a molten salt with an alkali metal one observes the set of patterns displayed on the figure 10 [44]. The addition of salt produces a broad peak culminating at the $q_M$ value of the pure molten salt ($q_M = 2.33 \text{ Å}^{-1}$). This effect is even more visible on the Fourier transforms of figure 11 where one detects the characteristic $r_+$ distance of the salt, $d_+$, at a concentration of only 5% KCl in K.

It would of course be quite interesting to obtain detailed partial structure factors for this system and this is the object of further investigation [44]. Since it turns out that the main potassium metal peak just occurs at the $q_c$ position of the salt $S_{CC}$ peak we have even no qualitative proof of charge oscillations.

![Fig. 9: Total and partial structure factors of KCl](image1)

![Fig. 10: $S(q)$ for K-KCl](image2)

![Fig. 11: and the pair correlation functions](image3)

We just may state from the appearance of a peak at $q_M$ that a local order similar to the salt is already present in the strong metallic region [44] of this system (the electrical conductivity is still $10^3 \text{ Ù cm}^{-1}$ at a concentration of 50% K+ in KCl for $T \sim 800^\circ$C). A simple way to understand this fact is the tendency for separation into a salt like and a metal like phase as is known from thermodynamics and is consistent with the observed significant SAS. (A crude estimate of the correlation length for the fluctuations measured by SAS is 3 Å).
A very similar behavior is observed for the Au-Cs system studied by Steeb et al. [47] where the 50% Au-Cs alloy is ionic like. One notices on the figure 12 all the trends of the K-KCl system, including the significant SAS.

Fig. 12: $S(q)$ and \(g(r)\) for Au-Cs [47]

Here again the first $S(q)$ peak of the pure metal is located at about the $q_c$ position of the salt and prevents any estimate on charge oscillations for the metal-rich alloys. Close to the pure salt concentration the $q_c$ peak becomes however detectable at about 1.2 Å⁻¹, and it is interesting to note that $q_c/q_{Na}=0.60$ which is between the value of 0.57 observed for CuCl and the value of compound forming alloys, but distinctly different from the value of the alkali halides.

We shall now consider a class of metallic systems where large structural units, complexes or clusters with rather strong interatomic bonding, exist in the liquid state, such as the alkali metal suboxides of Rb or Cs which display unusual structures in the solid [48]. The figure 13 shows a typical stable atomic arrangement or cluster in which two oxygen atoms are surrounded by two face sharing octaeada of Rb atoms. This cluster is found in the metallic solid compounds Rb₆O₂ and Rb₆O displayed on the same figure. The interatomic distances within the cluster are characteristic of the Rb⁺ and O²⁻ ionic radii (the Rb-O distances are 2.70 and 2.80 Å). The intercluster Rb-Rb distances are longer than intra-cluster distances and comparable to interatomic distances in the pure metal. This is why these systems have been referred as "complex" metals, in the sense that the simple ions of the metal were replaced by complex ionic clusters. The question is to know if these structures are conserved in the melt. The figure 14 displays the $S(q)$ of the Rb₆O liquid at a temperature of 47°C as compared to the $S(q)$ of the pure metal at the same temperature, both obtained from neutron scattering measurements. Since these systems do not offer the possibility of isotopic substitution it will be quite difficult to obtain partial structure factors. Another approach should be investigated. The Fourier transform (see fig. 14) of the total structure factor displays well defined short interatomic distances of 2.8 and 4.0 Å attributed by comparison with the solid to intracluster bonds. An appropriate analysis is therefore as in the molecular systems, to test several solid state cluster geometries by fitting the corresponding molecular form factor on the medium and high q part of $S(q)$. In this framework the prepeak of the structure factor should correspond to the average intercluster distance. The height of this peak is not as strong as what one would expect for a pure molecular system which indicates some looseness in the packing or weakness in the cluster stability.

Fig. 13: S(q) and g(r) of liquid Rb₆O as compared to pure Rb(——) from [48]

Fig. 14: S(q) and g(r) of liquid Rb₆O as compared to pure Rb(——) from [48]
As seen from the strength of the Rb\textsubscript{0} main peak which corresponds to the Rb metal peak a significant amount of excess free Rb atoms is still present in liquid Rb\textsubscript{0} as might be expected (cf. fig. 13). Obviously these comments await for a more quantitative data evaluation. It is interesting to note that the prepeak to main peak position ratio equals 0.68/1.58 = 0.43, which as compared to the q\textsubscript{p}/q\textsubscript{m} ratio obtained previously is quite small. This confirms the idea of rather complex clusters as opposed to simple CSRO effects between the two atomic species.

The solutions of alkali metals in liquid ammonia [49] present some analogy with the alkali metal suboxides since, roughly speaking, in the highly concentrated region the ions of the metal are replaced by "solvated" ions. This is especially the case for the Li-Ammonia system, Lithium being the only alkali which forms a compound, Li\textsubscript{4}NH\textsubscript{3} with the solvent. The figure 15 displays the diffusion pattern of the pure deuterated solvent at 20\degree C and of the Li-4ND\textsubscript{3} solution at -65\degree C [50]. The prepeak one observes is not due, as in aqueous solutions of Li\textsubscript{4}Cl\textsubscript{2}, for example, [51] to the metal-metal correlations alone because |b\textsubscript{1.1}| is too small to produce such an effect. The prepeak to main peak position ratio has again a very low value, it corresponds to the concentration should certainly be investigated in more detail. This series of examples shows clearly to what wide extent on the experimental as well as on theoretical and computer simulation side the field is open to further investigation.

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