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Atomic ordering in liquid Se by unconstrained reverse Monte Carlo simulations

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Abstract. A three-dimensional model of the atomic arrangement in liquid Se has been constructed by the reverse Monte Carlo method without applying structural constraints. The model has been analysed in terms of ring size statistics, and near-atomic-neighbour and bond-angle distributions. It has been found that, on an atomic scale, liquid Se may well be described as a branched network of short chains which also involves many rings. The relationship between the structural features of liquid Se, revealed by the present reverse Monte Carlo simulations, and those of solid crystalline and amorphous Se, previously well established, has also been discussed.

1. Introduction

There have been a number of structural studies on liquid Se (l-Se) in the past few decades. It has been firmly established, mainly by x-ray and neutron diffraction experiments, that with l-Se the first coordination sphere is well defined, the number of nearest atomic neighbours is approximately 2 and the first- and second-nearest atomic distances are 2.33 Å and 3.72 Å, respectively [1–5]. On the basis of these experimental findings and taking into account the fact that with all normal-pressure crystalline modifications of Se the constituent Se atoms are twofold coordinated and the first- and the second-atomic-neighbour distances are 2.3 Å and 3.5–3.6 Å [6], respectively, it has been concluded that l-Se and solid Se share some similar structural characteristics [7]. Two basic types of crystalline modification of Se are known to exist under normal pressure and temperature conditions. These are trigonal and monoclinic Se. Trigonal Se contains parallel helical chains of Se atoms. Monoclinic Se can be considered as a build-up of eight-member (Se_8) rings of Se atoms [6]. By analogy with the chain structure of trigonal Se it has been suggested that l-Se consists of freely rotating chains of Se atoms [3, 7] where the number of atoms per chain is approximately 10^4 – 10^5 at the melting point of Se [8–10]. It has also been suggested that a very small number of Se_8 rings is present in l-Se [11].

A number of computer simulations have been carried out in order to check the validity of the freely rotating chain model picture for l-Se. The simulations *a priori* assuming the existence of a chain-like atomic arrangement in l-Se did provide some evidence in support of this [3, 12]. However, the more comprehensive first-principles molecular dynamics simulations of Hohl and Jones [13] as well as the recent quantum Monte Carlo simulations of Bichara *et al* [14], which do not rely on any *a priori* structural assumption, have suggested that the atomic arrangement in l-Se is ‘more complex than a simple assembly of randomly

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oriented long chains'. In particular, it has been suggested that the chains are not long but involve only a few Se atoms and, furthermore, they form some kind of a branched network. Since this peculiar microscopic picture of the l-Se structure may have been influenced by the particular interatomic potentials employed, it makes sense to verify this by an independent modelling not relying on such potentials. Also, it is interesting to investigate the presence of rings in the suggested network structure of l-Se. Such an investigation has not been carried out in the previous molecular dynamics and quantum Monte Carlo simulations [13, 14] because of the small size of the atomic configurations (a few hundred atoms only) constructed. The relatively newly emerged reverse Monte Carlo (RMC) modelling technique offers an opportunity to tackle these tasks since it does not rely on any interatomic potentials and can treat model atomic configurations of a few thousand atoms [15–17]. To some extent this opportunity has been exploited by Maruyama *et al* [18] who modelled the structure of l-Se by reverse Monte Carlo simulations but, since the size of the atomic configuration constructed in this study is also small (540 atoms) and, because of that, the possible atomic configurations of longer spatial extent, such as, rings may not have been well revealed, a new, more extensive RMC modelling is worthwhile. In the present paper, the results of such a RMC modelling on a configuration of 4056 atoms are presented. The outcomes of a comparison of the structural characteristics of l-Se suggested by the model constructed and those of solid crystalline and amorphous Se are also reported.

2. Reverse Monte Carlo simulations on liquid Se

In brief, the RMC method for modelling disordered structures involves random movements of atoms placed in a simulation box with periodic boundary conditions. Moves are accepted if the difference between the model calculated and the experimentally derived structure-sensitive data, usually given in terms of structure factors and radial distribution functions, is reduced. The process is repeated until an almost perfect fit to the experimental data is achieved. The resulting three-dimensional atomic configuration is considered to be a possible model of the disordered material under study. From the configuration, important structural characteristics such as near-atomic-neighbour and bond angle distributions and ring statistics are determined by geometrical analysis of the atomic coordinates. The great potential of the method in studying liquids and melts has already been demonstrated in a number of papers [19–21].

To simulate the atomic scale structure of l-Se, 4056 atoms were placed in a cubic box with an edge length of 51.5 Å, yielding the experimental number density of 0.029 atoms Å⁻³. Simulations were carried out starting from several structurally different initial atomic configurations including one with the helical chain structure of trigonal Se, another with the ring structure of monoclinic Se and one with a random structure. However, since to our knowledge no strong experimental or theoretical evidence that unambiguously indicates the presence of a particular structural motif in l-Se exists, no attempt has been made to preserve the features of the starting atomic configurations in the model being constructed. As a consequence, the final structural characteristics of the models resulting from the different runs (structure-sensitive functions, atomic configurations and their local geometrical characteristics) were found not to depend considerably on the different starting conditions as expected. During the simulations the random atomic moves were only limited by a 'cut-off' distance of 2.0 Å which prevented the atoms from approaching each other to an unrealistically close distance. The amplitude of atomic moves had a maximum of 0.65 Å initially and it was gradually reduced to a value of 0.01 Å in the final stages of the modelling. No other definitive constraints on the atomic moves were imposed in the present

simulations in order to obtain a model not biased towards a structure with specific features. The probability of accepting an atomic move was determined by comparing the model calculated with high-quality x-ray diffraction data for l-Se taken from literature sources [5]. Their uncertainty is estimated to be not higher than 1.5% [22]. The experimental data have been obtained at 523 K, i.e. quite close to the melting point of Se. Initially, the experimental pair distribution function $g(r) = \rho(r)/\rho_0$, where $\rho(r)$ and ρ_0 are the local and average atomic densities, respectively, was chosen as a structural quantity to govern the simulation process. Then the simulations were carried out with the requirement that the model reproduced well not only $g(r)$ but also the structure factor $S(q)$, where q is the magnitude of the scattering vector, for l-Se. This simulation approach turned out to save a considerable amount of computational time and at the same time ensured that not only the atomic distribution function $g(r)$ but also the structure factor $S(q)$, which is the directly measurable quantity, were reproduced in every detail. The simulation process was terminated when approximately 10^6 accepted moves were completed and the experimental data in both real and reciprocal space were well fitted. The value of the goodness-of-fit indicator achieved in real space is 1.5%.

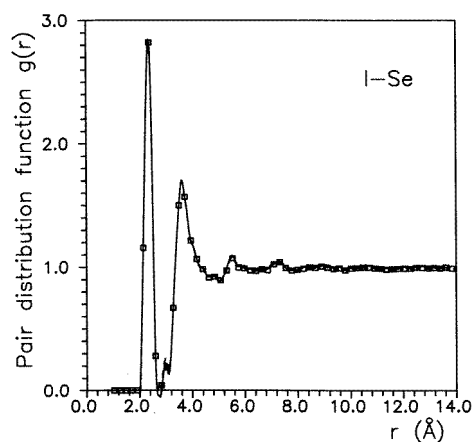


Figure 1. Pair distribution function $g(r)$ for l-Se: —, experimental data; —□—, RMC fit.

3. Results

A comparison between the experimental and model derived pair distribution functions for l-Se is shown in figure 1. As one can see in the figure the present model perfectly reproduces all details of the experimental $g(r)$ including its well defined first peak at 2.33 Å and the deep minimum between the first and the second peaks. Such perfect agreement with the experimental data has not been achieved with the previous molecular dynamics and quantum Monte Carlo simulations which, in particular, fail to reproduce well the shape and the height of the first peak in the experimental $g(r)$ (see figure 2 in [13] and figure 1 in [14]). The average coordination number of the Se atoms from the model atomic configuration has been estimated by integrating the area under the first peak of the model $g(r)$ and it has been found to be 2.0 ± 0.1 . The value obtained is quite close to the experimentally derived value which indicates that our model well represents the short-range atomic order in l-Se.

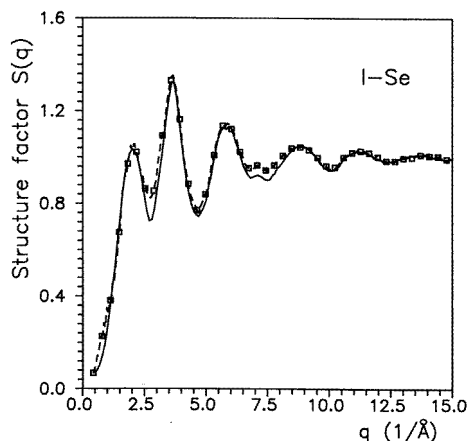


Figure 2. Structure factor $S(q)$ for l-Se: —, experimental data; —□—, RMC results.

The present model and the experimental structure factors $S(q)$ are compared in figure 2. The correspondence is again quite good. It is to be noted that the close correspondence between the model and experimental data in the vicinity of the first peak in $S(q)$ at 1.87 \AA^{-1} , which reflects the correlations beyond the first-neighbour atoms in l-Se, shows that the present model represents well not only the short-range order but also the medium-range order in l-Se. Given the good consistency of our simulations with the experimental data in both real and reciprocal space, one may conjecture that the characteristics of the atomic ordering in l-Se are likely to be well assessed from the three-dimensional atomic configuration constructed.

Table 1. Distribution of the first atomic neighbours in l-Se according to the present RMC model.

Number of first neighbours	1	2	3	4
Frequency (%)	12	65	22	1

An important structural characteristic of l-Se is the distribution of the first atomic neighbours. It was obtained by counting all atomic pairs contributing to the first peak in the pair distribution function. The boundary of the first coordination shell considered coincides with the first minimum in $g(r)$ at 2.92 \AA . The resulting data for the first-atomic-neighbour distribution are presented in table 1. The analysis of the data suggests that the majority of the atoms of l-Se are twofold coordinated as they are in the normal-pressure crystalline Se. In accordance with the previous results [13, 14, 18], however, we have also found a considerable number of Se atoms with one or three first neighbours. A small amount of fourfold-coordinated Se atoms has also been encountered. The portion of the atoms lacking exact twofold coordination that we have found (35%) is quite close to that (25–30%) suggested by the previous modelling studies on l-Se [13, 14, 18]. This rather good agreement between the predictions of our and the previous independent computer models [13, 14, 18] we consider as a clear indication that a considerable amount (approximately $30 \pm 5\%$) of under-coordinated (one) and over-coordinated (threefold- or fourfold-coordinated) atoms is really present in l-Se.

Another important structural characteristic of l-Se which we derived from the RMC

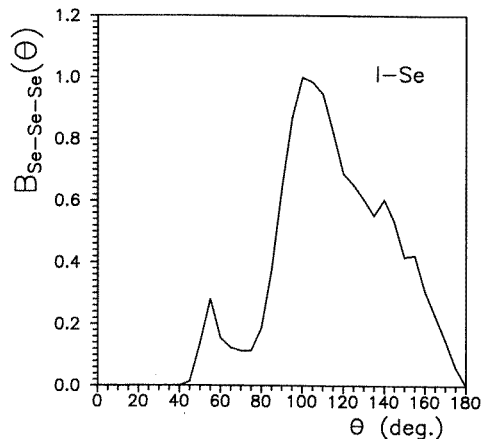


Figure 3. Bond-angle distribution in l-Se according to the present RMC model.

model atomic configuration is the so-called ‘bond-angle’ distribution defined as the number of angles θ between the two vectors joining a central atom with any two neighbours of its coordination shell. The distribution obtained when this coordination shell is considered to be extended to the first deep minimum in the atomic distribution function at 2.92 Å is shown in figure 3. As one can see in the figure the ‘bond angles’ in l-Se most frequently occur around 103°, which is the exact value of the characteristic ‘bond angle’ in trigonal crystalline Se. A small peak in the ‘bond-angle’ distribution at 60°, indicating the presence of well defined, nearly equilateral triangular configurations of Se atoms, is also seen. It may be noted that a similar, although weaker, indication for the presence of triangular atomic configurations in l-Se is also seen as a bump in the ‘bond-angle’ distribution derived from the quantum Monte Carlo model of Bichara *et al* [14, figure 4]. In general, the shape of the present ‘bond-angle’ distribution agrees well with that of the distributions obtained in the previous molecular dynamics and quantum Monte Carlo modelling studies [13, 14]. One may only notice that the present ‘bond-angle’ distribution spreads over an interval of angles (50–170°) slightly wider than those (55–150°) covered by the distributions previously obtained [13, 14]. We attribute this feature to the slightly larger number of under-coordinated and over-coordinated Se atoms found in our RMC model. We would like also to add that the ‘bond-angle’ distribution resulting from the present RMC simulations and that one derived from the RMC model of Maruyama *et al* [18, figure 6] show some considerable differences when compared with each other. In particular, the ‘bond-angle’ distribution obtained by Maruyama *et al* exhibits a rather strong peak at 60° and a not so sharp peak around 103° which is contrary to our findings as well to the findings of the molecular dynamics and quantum Monte Carlo simulations [13, 14]. It may be the relatively small size of the atomic configuration constructed by Maruyama *et al* which prevented it from completely relaxing to the state reached by our more extensive RMC model.

The finding that the majority of the atoms from our model atomic configuration are twofold coordinated prompted us to investigate the possible chain structure of l-Se as well. To do this, we calculated the number and the length of the chains involving Se atoms separated by less than 2.92 Å, which is the maximum first coordination distance in l-Se. We considered as a chain any series of twofold-coordinated Se atoms (Se²) terminated at both ends by fourfold-coordinated (Se⁴), threefold-coordinated (Se³) or onefold-coordinated

(Se¹) atoms. The results of our calculations are presented in figure 4. A statistical analysis of the connectivity of the chains found is given in table 2.

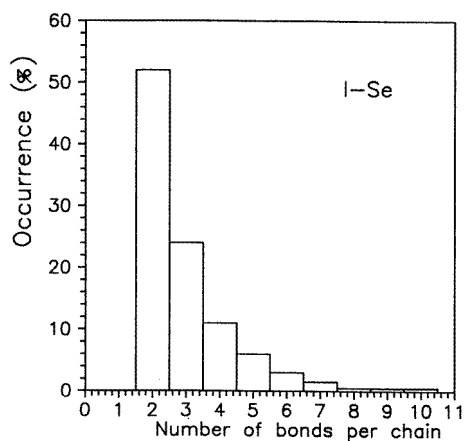


Figure 4. Distribution of chain lengths in l-Se according to the present RMC model.

Table 2. Types of chain encountered in the present RMC model of l-Se.

Chain type	Occurrence (%)	Connectivity
Se ¹ -(Se ²) _n -Se ¹	6	Free
Se ¹ -(Se ²) _n -Se ³	17	Free on the one end only
Se ¹ -(Se ²) _n -Se ⁴	3	
Se ³ -(Se ²) _n -Se ³	55	Connected
Se ³ -(Se ²) _n -Se ⁴	15	
Se ⁴ -(Se ²) _n -Se ⁴	4	

4. Discussion

The analysis of the data presented in figure 4 suggests that the constituent atoms of l-Se do form chains. We would like to emphasize that nothing in our simulations has promoted the formation or preservation of chains of Se atoms and they naturally evolve in our model as they do also in the unbiased models of Jones and Hohl [13] and Bichara *et al* [14]. This corroborates the generally accepted belief that the presence of chains is an intrinsic feature of the l-Se structure. Contrary to the earlier studies, which predict that close to the melting point of Se the chains should involve of the order of 10⁴ atoms [8–10], and quite in accord with the recent studies of Hohl and Jones [13] and Bichara *et al* [14], which conclude that the chains have to be quite short, we found an average value of 3.5 bonds per chain in our model of the l-Se structure. Since the chains are rather short, it is not surprising that we found no particular dihedral angle to be preferred over the others. A random distribution of the dihedral angles in l-Se has been suggested by other studies as well [3, 4, 14]. The absence of a preference for a dihedral angle of 102°, which is the characteristic dihedral angle of

the helical chains in trigonal Se, the rather short length of the chains as well as the fact that only 6% of the chains in our model atomic configuration are free (see table 2) are findings of our study which do not support the previous suggestions that l-Se may be considered as an assembly of long helical and/or more or less freely rotating chains [3,4]. Our findings coupled to the observation that the greatest majority of the chains (94%) are linked to each other (see table 2) rather suggest that l-Se may well be described as an irregular, nominally connected network of relatively short Se chains with the angles between the neighbouring segments of the constituent chains (Se–Se–Se ‘bond angles’) are most frequently close to 103°.

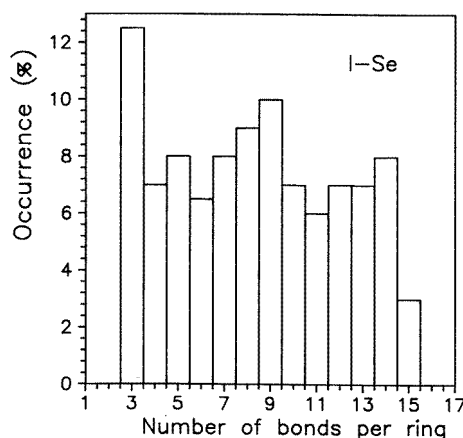


Figure 5. Ring statistics for l-Se according to the present RMC model.

Having in mind the relatively high interconnectivity of the chains in the l-Se network, which is demonstrated by the fact that the most frequently occurring chains have been found to be of the type $\text{Se}^3-(\text{Se}^2)_n-\text{Se}^3$ and $\text{Se}^3-(\text{Se}^2)_n-\text{Se}^4$ (see table 2), we investigated the presence of rings in the model structure as well. According to the definition introduced in [23] we considered as a ring any shortest closed path of bonds connecting a given Se atom with its neighbours. Because of the relatively large size of our simulation box, approximately 50 Å, we were able to check for the existence of rings constituted of up to 15 Se atoms. Our analyses showed that approximately 60% of the atoms of the l-Se network participate in rings of various sizes the distribution of which is shown in figure 5. No rings isolated from the network have been found. Since our results show that the rings involve by far not all atoms of the model atomic configuration, one may state that no complete description of the l-Se structure can be made on the basis of ring structural units alone and, therefore, chains rather than rings are the primary constituents of l-Se. Nevertheless, according to our model picture, the rings involve a sufficiently large portion of Se atoms that the analysis of the ring size distribution could provide some valuable information about the longer-range ordering in the underlying network. As one can see in figure 5, apart from the trivial three-member rings, the eight- and nine-member rings most frequently occur in l-Se. The observed slight preference for eight- and nine-member rings, indicated by the small but clearly discernible peak in the ring size distribution centred at eight-member rings, suggests that the branched-chain network of l-Se exhibits some medium-range order regularities and that there is some similarity between the atomic orderings in l-Se and solid monoclinic Se the building units of which are Se_8 rings. Thus, according to our study, signatures of

the atomic arrangements of both crystalline modifications of solid Se, chain-built trigonal and ring-built monoclinic Se, are present in the l-Se structure. The presence already of chain-like and ring-like structural motifs in l-Se, which we have established and which is well illustrated in figure 6, is in line with the fact that, upon crystallization, Se easily forms a large number of allotropes with chain or ring-type structures. It is to be expected that the unique features of the branched-chain network structure of l-Se with the variety of rings involved and approximately 30% of the constituent atoms lacking exact twofold coordination, if really present, will be preserved to a great extent in the structure of solid amorphous Se resulted from rapid quenching of the liquid. Since data from infrared and Raman spectroscopy measurements have been interpreted as indicating that amorphous Se consists of a mixture of eight member rings and branched polymer chains [24, 25] and the important photoconductivity properties of amorphous Se have been linked to the presence of a considerable amount of atoms lacking twofold coordination as well as to the presence of ring-like molecules [26–28], we maintain the point of view that the model picture of the l-Se structure suggested by our RMC simulations reflects well the physical reality.

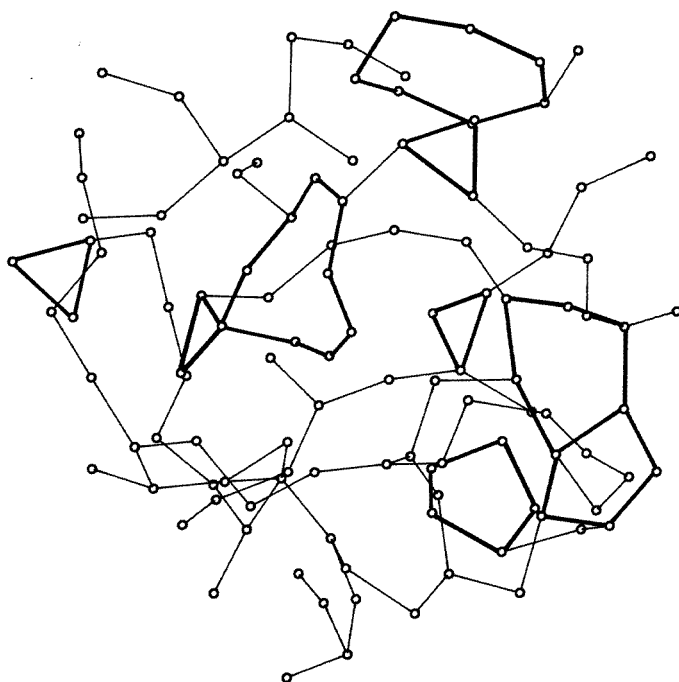


Figure 6. Representative configuration from the present three-dimensional RMC model of l-Se exhibiting the features of an irregular network of short Se chains (—) involving rings of various sizes (—).

5. Conclusion

We have carried out extensive RMC simulations on the l-Se structure by fitting the experimental structure functions of l-Se only. The model constructed is fully consistent with the high-quality experimental data previously obtained. It suggests that, near the

melting point, l-Se may be viewed as an irregular nominally connected network of short branches each constituted of four to five atoms on average. This result is quite in line with the outcomes of previous independent molecular dynamics and quantum Monte Carlo simulations which show that the network model picture is not an artefact of a particular simulation study but a firmly supported and, therefore, reasonable representation of the real structure of l-Se. Our model also suggests that approximately two thirds of the atoms of the l-Se network participate in rings of various sizes where rings of eight and nine atoms are slightly preferred over the others. Thus the widely accepted belief about the presence of a close relationship between the atomic arrangements in l-Se and those in solid crystalline and amorphous Se has been considerably clarified. The scopes of this relationship can be outlined as follows.

(i) The bond lengths, the 'bond angles' (Se–Se–Se) and the presumably twofold atomic coordination in l-Se are similar to those encountered in both trigonal and monoclinic crystalline modifications of Se.

(ii) The primary constituents of l-Se are chains which, although not long and helical, resemble in their nature the basic chain structural units of trigonal Se.

(iii) With l-Se, as with monoclinic Se, a preference for the formation of eight-member rings is observed. However, with l-Se this preference is slight only whereas with monoclinic Se it is dominant.

(iv) The mixed chain-ring structure encountered in solid amorphous Se may be simply considered as a hard copy of the branched-chain, ring-involving network structure of l-Se.

Acknowledgments

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