Atomic-scale structures of liquid Sn, Ge and Si by reverse Monte Carlo simulations

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Abstract. The atomic-scale structures of liquid Si, Ge and Sn have been modelled by the reverse Monte Carlo method. A geometrical analysis of the model atomic configurations has been carried out in terms of bond angle distributions and spherical harmonics invariants. Similar geometrical features, including signatures of local tetrahedral order, have been found in the first coordination shells of all the liquid metals studied. A relation between the local atomic ordering in liquid Si, Ge and Sn, and that of the corresponding solids with the tetrahedral white-tin-type structure has been established. The influence of the local and medium-range atomic orderings in liquid Se, Ge and Sn on the shape of the respective structure factors has been discussed.

1. Introduction

It is well known that liquid tin (l-Sn), liquid germanium (l-Ge) and liquid silicon (l-Si) exhibit specific structural features which cannot be accounted for in the framework of the random hard-spheres-packing type of model usually employed to describe the atomic ordering in the liquid monatomic metals [1, 2]. The features are as follows.

(i) The first coordination numbers of l-Si and l-Ge are approximately 6 which is lower than the number of 10–11 nearest neighbours found in most liquid metals.

(ii) The atomic pair distribution function $g(r)$ for l-Si and l-Ge do not have the usual minimum between the first and the second main peaks; a flat maximum is located in this region.

(iii) The first peak of the static structure factor $S(q)$ for l-Sn, l-Ge and l-Si has a shoulder on the higher side of the wavevector q.

These structural peculiarities are attributed to a fraction with the nature of the solid crystalline state of Si, Ge, and Sn preserved in their liquid state [3, 4]. In a recent study we considered the possible relation between the atomic arrangements of solid Ge and l-Ge and found that the essential structural features of l-Ge are likely to be described by an atomic arrangement of tetrahedral type encountered in the high-pressure form of solid Ge with minor modification [5]. In the present work we verify this model picture for l-Ge and extend it to l-Si and l-Sn by constructing and carefully analysing three-dimensional structure models that completely reproduce their important structural features. The reverse Monte Carlo (RMC) method has been employed to generate the models.

2. Reverse Monte Carlo simulations

In brief, the RMC method 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 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 statistically representative model of the disordered material under study. From the configuration, local structural characteristics such as bond angles and spherical harmonics invariants are determined by geometrical analysis of the atomic coordinates [6–8].

To simulate the atomic-scale structures of l-Si, l-Ge and l-Sn, 3200, 3100 and 3800 atoms were placed in cubic boxes of appropriate edge lengths, resulting in the experimental atomic number densities ρ_0 of 0.0553 atoms Å^{-3}, 0.0465 atoms Å^{-3} and 0.0353 atoms Å^{-3}, respectively. In each of the cases, simulations were carried out starting from different initial configurations. The final results (structure-sensitive functions, atomic configurations and their local geometrical characteristics) were found not to depend on the different starting conditions as it should be. During the simulations the random atomic moves were limited by 'cut-off' distances which prevented the atoms from approaching each other to an unrealistically close distance. The following 'cut-off' distances of 2.1 Å, 2.3 Å and 2.6 Å were used for the Si–Si, Ge–Ge and Sn–Sn atomic pairs, respectively. The amplitude of random atomic moves was a maximum of 0.5 Å initially and it was gradually reduced to a value of 0.01 Å in the final stages of modelling. No other definitive constraints on the atomic moves were imposed. The probability of accepting an atomic move was determined by comparing the model calculated with the corresponding experimental data which for l-Si and l-Sn were taken from literature sources [3] and for l-Ge recently measured by one of us [5]. All data have been obtained by x-ray diffraction experiments. Unfortunately, the experimental structure factor available for l-Si appeared to contain some systematic errors, a fact already noticed by Howe *et al* [9]. Since the effect of certain systematic experimental errors can be avoided in real space and, in addition, the modelling proceeds more rapidly in real that in reciprocal space, the pair distribution function $g(r) = \rho(r)/\rho_0$, where $\rho(r)$ is the local atomic density, was chosen as a structural quantity to govern the simulation process. Comparisons between the model and experimental data in reciprocal space, i.e. between the model and experimental structure factors, were also made at certain stages of the simulations. They were terminated after at least 5×10^6 trial atomic moves when the experimental data in both real and reciprocal space were almost perfectly fitted. The values of the goodness-of-fit indicator achieved in real space are 4%, 3% and 2% for l-Si, l-Ge and l-Sn, respectively.

3. Results

A comparison between the experimental and model-derived $g(r)$-values is shown in figure 1. The agreement is almost perfect. The model and experimental structure factors are compared in figure 2. Again an excellent correspondence is found for l-Ge and l-Sn. The structure factor of l-Si is also reproduced by the RMC model structure except for the height of the first peak. To clarify the reason for this discrepancy we transformed the experimental $S(q)$ for l-Si to a $g(r)$ which turned out to contain considerable unphysical oscillations at low r-values. If these oscillations are included in the model $g(r)$ for l-Si and this compound function back Fourier transformed, the resulting structure factor fits the original $S(q)$ even in

the region of its first peak. This observation shows that the discrepancy between the model and experimental $S(q)$ for l-Si is presumably due to the presence of some errors in the experimental data. Thus one can state that the results of all RMC simulations carried out are, within the limits of the experimental accuracy, consistent with the available experimental information. Therefore, the characteristics of the local atomic ordering in l-Si, l-Ge and l-Sn can be assessed from the three-dimensional atomic configurations constructed.
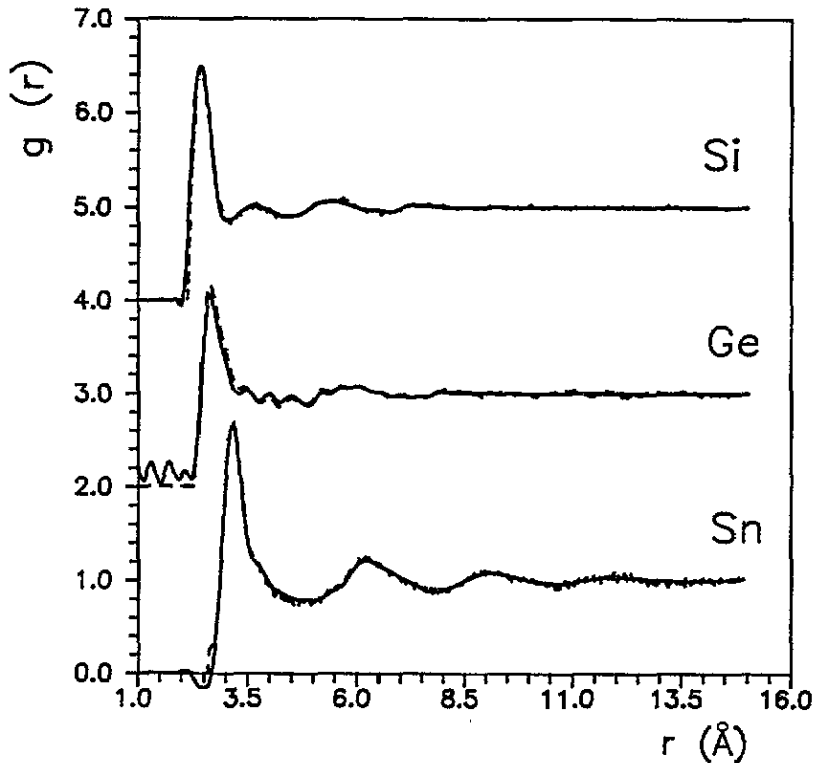

Figure 1. Pair distribution functions for l-Si. l-Ge and l-Sn: ———, experimental data; – – –, RMC fits.

The orientational three-particle correlations in the liquid metals under study have been estimated by calculating the so-named '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. 'Bond-angle' distributions for l-Si, l-Ge and l-Sn obtained by considering coordination shells of six atoms on average, with boundaries at 3.01 Å, 3.21 Å and 3.48 Å, respectively, are shown in figure 3. With this choice of the coordination shell all atoms under the first peak of $g(r)$ for l-Si and l-Ge, and a fraction of the atoms in the first peak of $g(r)$ for l-Sn are counted as nearest neighbours. The inspection of figure 3 shows that all 'bond-angle' distributions exhibit a distinct peak at $\theta \simeq 60°$ which is most prominent with l-Si. Less pronounced but still detectable angular correlations are seen at $\theta = 90–110°$. It is worth noting that the 'bond-angle' distribution for l-Si obtained by the present RMC study is quite similar to that derived from a structure model constructed by *ab-initio* molecular dynamics simulations (see figure 2 in [10]). This means that the RMC method, based solely on the experimental data for l-Si, and the molecular dynamics method, which relies on
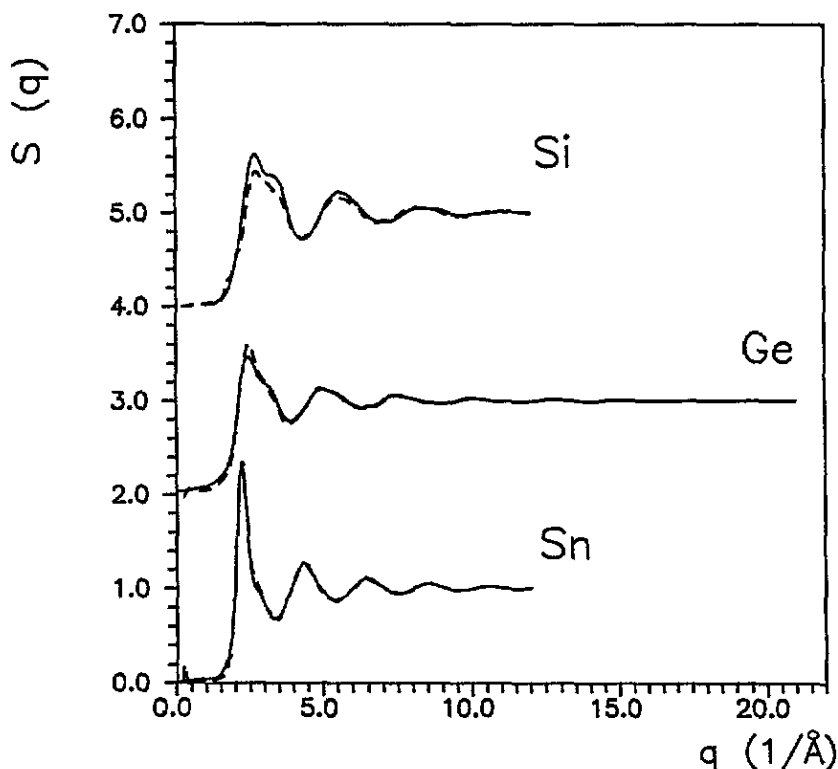
Figure 2. Structure factors for l-Si, l-Ge and l-Sn: ——, experimental data; – – –, RMC results.

realistic interatomic potentials, have produced virtually identical models for a non-simple structure such as that of l-Si! This result provides strong evidence for the physical relevance of the structure models produced by the RMC method. In particular, it shows that all details of the 'bond-angle' distribution for l-Si given in figure 3 are physically sensible and are not artefacts of the RMC simulation technique.

It was demonstrated recently that the orientational correlations in disordered structures are best represented by the distribution of the cosine of the 'bond angles' [11]. For this reason the 'bond angle' distributions for l-Si, l-Ge and l-Sn of figure 3 were recast in terms of cosine 'bond-angle' distributions. The result is shown in figure 4. As can be seen, the orientational correlations between the position of the nearest six atomic neighbours in l-Si, l-Ge and l-Sn are quite similar. These are characterized with a dominant peak at $\theta \simeq 60°$ ($\cos \theta \simeq 0.5$), a less defined peak at $\theta \simeq 160°$ ($\cos \theta \simeq -0.95$) and a broad distribution in the interval from $\theta \simeq 95°$ to $\theta \simeq 110°$ ($\cos \theta \simeq -0.1$ to $\cos \theta \simeq -0.35$) which includes the tetrahedral angle of $\theta \simeq 109°$ ($\cos \theta \simeq 0.325$). It is worth noting that the atomic correlations for l-Si are more distinct, i.e. stronger, than those for l-Ge and l-Sn. This is to be expected since for Si the strength of atomic bonding, measured by the melting point, is much higher than for Ge and Sn.

'Bond-angle' distributions for coordination shells including on average ten Si atoms, ten Ge atoms and ten Sn atoms have also been calculated. The boundaries of the corresponding coordination shells are at 3.67 Å, 3.76 Å and 4.01 Å, respectively. They fall in the region between the first and the second main peaks of the $g(r)$-values for l-Si and l-Ge, and just at the position of the first minimum of $g(r)$ for l-Sn. The 'bond-angle' distribution for
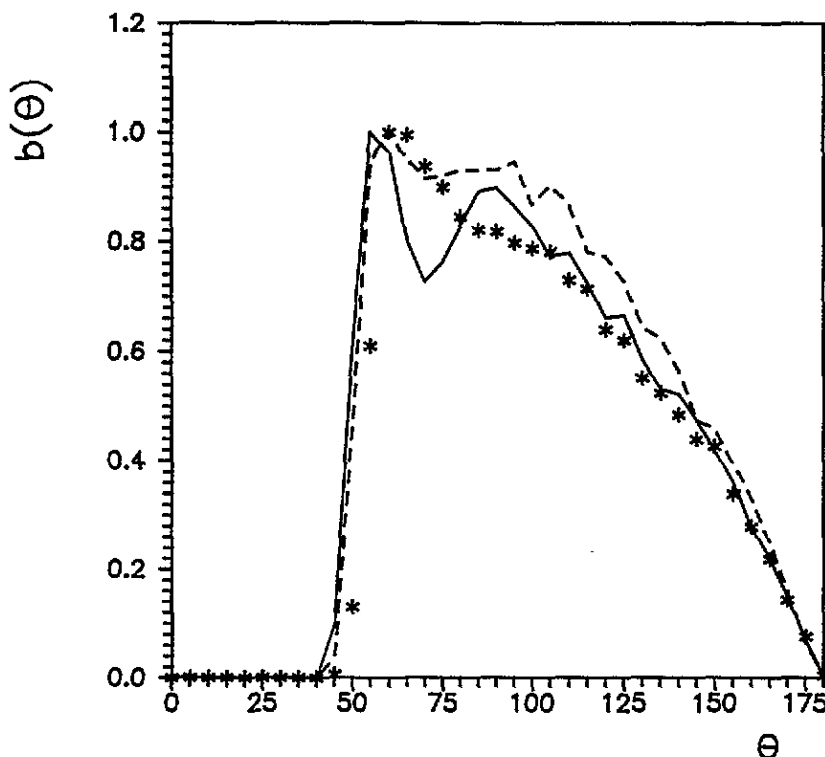
Figure 3. Bond-angle distributions for l-Si (———), l-Ge (– – –) and l-Sn (*). The number of atomic neighbours considered is six on average.

coordination shells of ten atoms, shown in figure 5, are quite alike, which reflects the similar spatial arrangement of the first ten neighbours in l-Si, l-Ge and l-Sn. They are, however, not so informative as those for six neighbours. The reason is that the relatively weak orientational correlations in the liquid metals under study are too averaged and smoothed out when ten atoms are counted as nearest neighbours.

Table 1. Spherical harmonics invariants for perfect and disordered white-tin-type (β-Sn) crystalline lattices (the root mean square deviation of the atoms of disordered white-tin-type lattice from their positions in the perfect white-tin-type lattice is approximately 30%), l-Si, l-Ge and l-Sn. The number of atomic neighbours considered is six on average. For the meaning of the quantity Q_l ($l = 2, 4, 6, 8$ and 10) see the original papers [12, 13].

	l-Si	l-Ge	l-Sn	β-Sn (disordered)	β-Sn (perfect)
Q_2	0.70	0.68	0.66	0.62	0.19
Q_4	1.06	1.08	1.11	1.15	1.52
Q_6	1.16	1.15	1.14	1.10	0.93
Q_8	1.07	1.05	1.02	1.04	1.00
Q_{10}	1.02	1.04	1.06	1.07	1.35

The analysis of the spherical harmonics invariants is also known to be quite useful in characterizing the local ordering in computer-generated models of dense liquids and glasses [12, 13]. It provides a set of parameters (usually the first five even-l-order invariants Q_l)
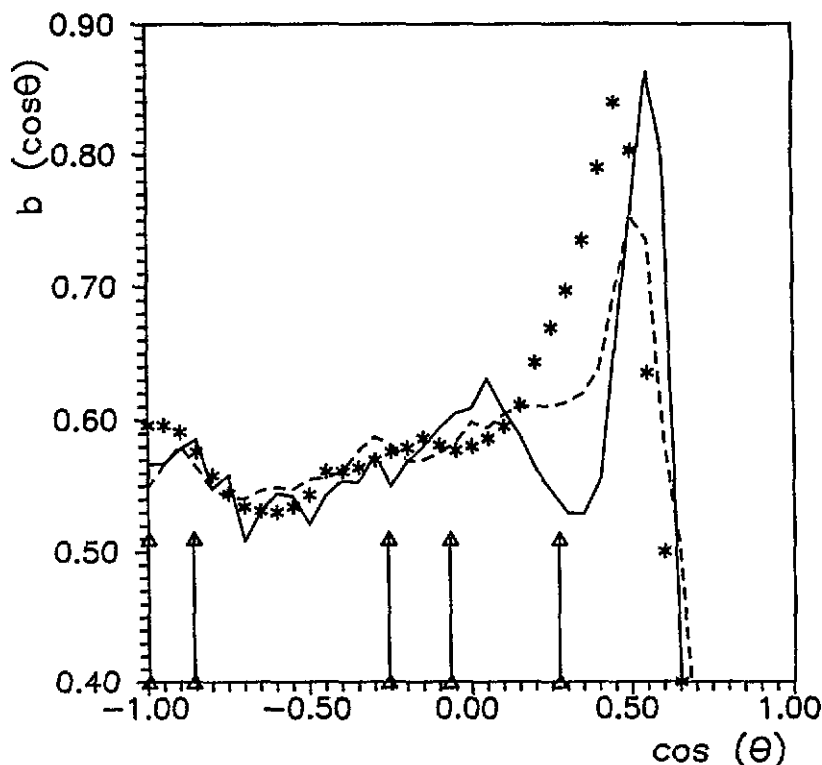
Figure 4. Distribution of the cosine of the bond angles for l-Si (——), l-Ge (– – –) and l-Sn (*). The number of atomic neighbours considered is six on average. The distribution of the cosine of the bond angles between the first six neighbours of the white-tin-type crystalline lattice is given in the lower part of the figure by bars capped with triangles.

which can be used to differentiate between geometrical alternatives of coordination spheres and to detect traces of long-range crystalline structures. A spherical harmonics invariant analysis of the RMC models for l-Si, l-Ge and l-Sn has also been carried out. The results are presented in tables 1 and 2. The invariants for both coordination shells considered are close to but not equal to unity, which corresponds to complete disorder; so it is worth examining this.

4. Discussion

A survey of tables 1 and 2 reveals that all sets of invariants Q_l for l-Si, l-Ge and l-Sn obey the following trend: the Q_l are of minimal values for $l = 2$, of maximal values for $l = 6$, and close to unity for $l = 10$. Also, the absolute values of the corresponding invariants for a given coordination shell are very close to each other, which shows that the model atomic configurations have similar local symmetries. These findings are in line with the results of the 'bond-angle' distribution analysis from the previous paragraph, all indicating that the local atomic orderings of l-Si, l-Ge and l-Sn are quite similar.

To identify the type of this ordering, the structural characteristics of l-Si, l-Ge and l-Sn, derived from their RMC models, have been compared with the corresponding characteristics for well defined crystalline atomic configurations. We concentrate on the white-tin-type
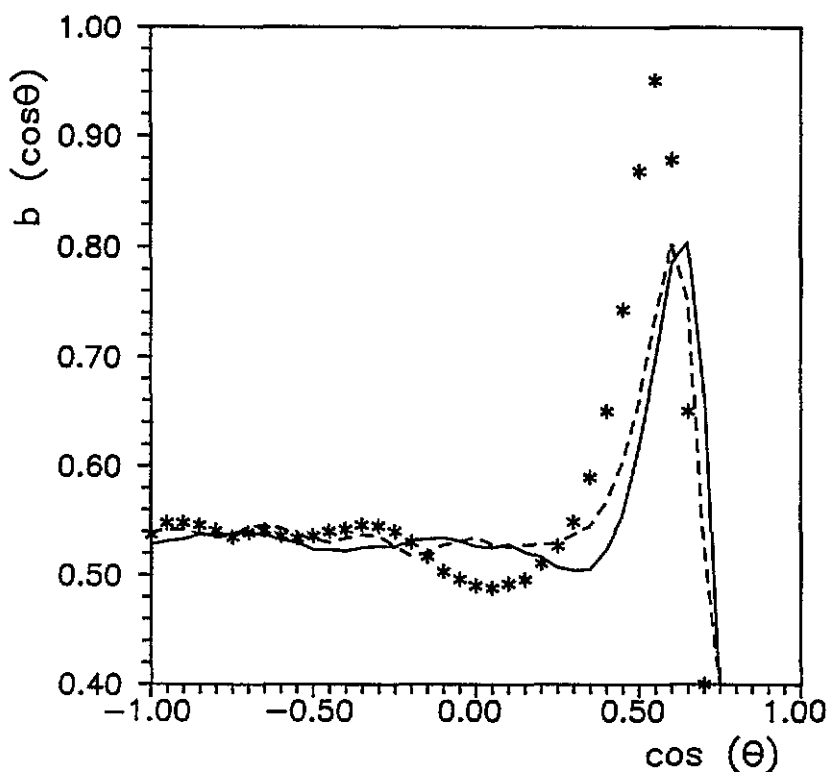
Figure 5. Distribution of the cosine of the bond angles for l-Si (——), l-Ge (– – –) and l-Sn (*). The number of atomic neighbours considered is ten on average.

Table 2. Spherical harmonics invariants for perfect and disordered white-tin-type (β-Sn) crystalline lattices, l-Si, l-Ge and l-Sn. The number of atomic neighbours considered is ten on average.

	l-Si	l-Ge	l-Sn	β-Sn (disordered)	β-Sn (perfect)
Q_2	0.61	0.56	0.47	0.42	0.24
Q_4	0.88	0.90	0.92	1.07	1.39
Q_6	1.22	1.27	1.37	1.35	1.17
Q_8	1.21	1.21	1.19	1.21	1.19
Q_{10}	1.08	1.07	1.05	0.96	1.01

crystalline lattice, which occurs with the normal form of solid Sn and with the high-pressure metallic forms of solid Ge and Si, since it has been found very useful in explaining the essential structural features of l-Ge [5].

As can be seen in figure 4, the bond angles of the white-tin-type arrangement are grouped in three regions: near to $\theta = 180°$, $\theta = 100°$ and $\theta = 70°$. These regions closely match the peaks in the 'bond-angle' distributions for l-Si, l-Ge and l-Sn. The spherical harmonics invariants for the perfect white-tin-type arrangement are not quite close to those for the heavily disordered model configurations but the agreement is highly improved upon respective randomization of the crystalline arrangement. Critical comparisons with other sets of invariants for a variety of crystalline symmetries given in [13] have also been made but the best agreement found is that shown in tables 1 and 2. Summarizing, one can conclude

that the specific local atomic ordering of l-Si, l-Ge and l-Sn may well be described as a disordered variant of the white-tin-type crystalline arrangement.

With the white-tin-type structure, each atom has four immediate neighbours which reside on the vertices of a slightly deformed tetrahedral unit [14]. It is thus to be expected that the immediate four atomic neighbours in l-Si, l-Ge and l-Sn will also show a tendency to form tetrahedra. Distributions of the cosine of 'bond-angles' for coordination shells including up to four atoms have been calculated to check this expectation. The boundaries of the corresponding coordination shells are at 3.26 Å for l-Si, at 2.94 Å for l-Ge and at 2.73 Å for l-Sn. The resulting 'bond-angle' distributions are shown in figure 6. As can be seen, the distributions for l-Sn and l-Ge are peaked around the tetrahedral angle $\theta \simeq 109°$, indicating a dominantly tetrahedral arrangement of the immediate four atomic neighbours. The same holds for l-Si where, in addition, some triangular configurations of atoms, responsible for the sharp peak at $\theta \simeq 60°$, are present. The tendency observed correlates well with the results of recent structural studies on l-Ge [15] and l-Si [10] which have identified a persistence of covalent bonding and corresponding local tetrahedral ordering in these liquid metals.
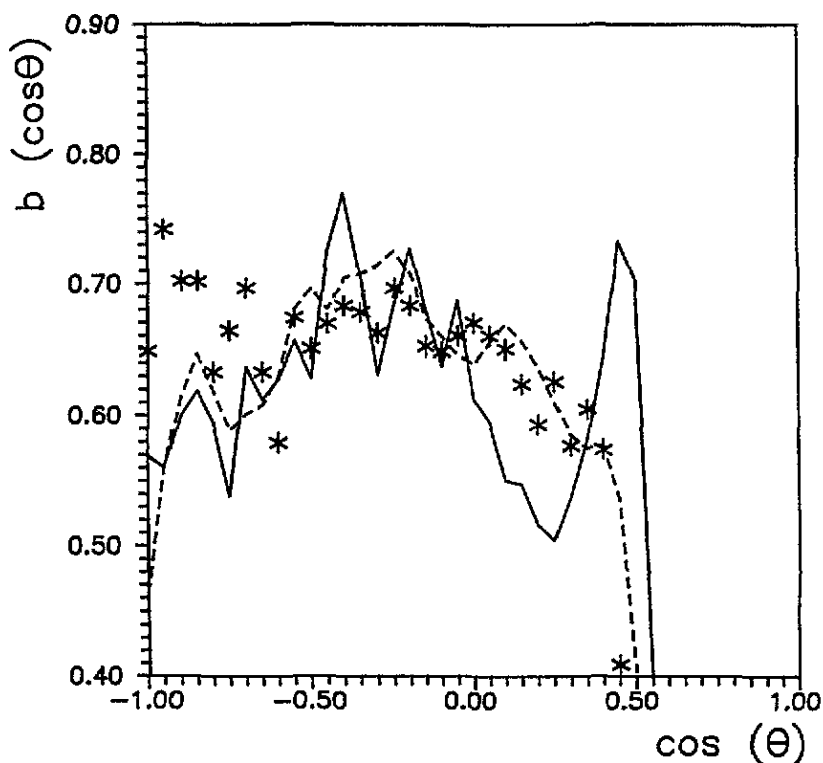

Figure 6. Distribution of the cosine of the bond angles for l-Si (——), l-Ge (– – –) and l-Sn (*). The number of atomic neighbours considered is four on average.

The following coherent picture of the local atomic ordering in l-Si, l-Ge and l-Sn emerges from the results of our structural study. Upon melting, the tetrahedral diamond-type atomic ordering of solid Si and Ge [14] collapses towards the more densely packed tetrahedral white-tin-type ordering. The process should be accompanied by increases in the densities of Si and Ge, which is an experimental fact [16]. A similar structural transformation takes

place when solid Si and Ge are pressurized. Therefore, Si and Ge appear to be an example illustrating the empirical suggestion of Stishov [17], namely that for non-close-packed substances the structure of the molten state may resemble that of the high-pressure solid state. Upon crystallization, a continuous perfect tetrahedral network of Si and Ge atoms is reconstructed from melts showing signatures of tetrahedral ordering. The process, however, should involve a modification of the tetrahedral ordering from a white-tin-type to the more open diamond type which may be responsible for the very pronounced pre-crystallization anomalies of the structure-sensitive properties of Si and Ge [16]. Upon melting, the three-dimensional lattice of solid Sn is destroyed but its tetrahedral features, although smeared, survive in the melt. Upon crystallization, the regular white-tin-type arrangement of Sn atoms evolves from melt with similar local atomic ordering. No drastic change in the type of local atomic ordering accompanies the solid–liquid phase transition with Sn, which may explain the lack for pre-crystallization anomalies in its structure-sensitive properties [16].

An important point which should also be addressed by our study is why l-Si, l-Ge and l-Sn, which have rather similar local atomic arrangements, show some differences in their structure factors, especially in the region of the first peak. To answer this question we calculated the separate contributions of the local atomic ordering including the nearest ten atomic neighbours and of the more distant medium-range atomic ordering involving all next-nearest atomic neighbours, with separations from the boundary of the first coordination shell of ten atoms up to the limits of our models (approximately 18 Å), to the respective structure factors. The results of our calculations are presented in figure 7. It should be noted that the combined contributions of the local and medium-range atomic orderings in l-Si, l-Ge and l-Sn to the respective structure factors have already been calculated and found to reproduce the experimental data well (see figure 2). As can be seen in figure 7 the local atomic ordering in l-Si, l-Ge and l-Sn determines the global behaviours of their structure factors. These behaviours are quite similar for all liquid metals studied as it should be according to our model pictures showing similarities in their local structure. Inspection of figure 7 also shows that the medium-range atomic ordering in l-Si, l-Ge and l-Sn is the mainly contributor to the peculiar fine features in their structure factors. There are many similarities in the contributions of that ordering to the respective structure factors, the most striking of which is the broad oscillation at 3.0–3.5 Å^{-1}, resulting in the characteristic shoulder of the first peak in all structure factors. This observation indicates that not only the local but also the medium-range atomic orderings in l-Si, l-Ge and l-Sn exhibit similar features. Some significant differences are, however, also seen. For l-Sn a sharp oscillation at approximately 2 Å^{-1} is present; it is hardly seen for l-Ge and is not observed at all for l-Si. The result is that the first peak in the structure factor of l-Sn is sharper and higher than in the structure factors of l-Ge and l-Si. Furthermore, for l-Sn the contribution from the medium-range atomic ordering to the structure factor oscillates out of phase with that from the local atomic ordering in the interval from 3.0 to 3.5 Å^{-1}. For l-Ge and l-Si both contributions to the structure factor oscillate almost in phase in that region. The result is that for l-Si and l-Ge the characteristic shoulder in the first peak of the total structure factors is much more pronounced than that for l-Sn. The observed small but significant differences in the contributions of the medium-range atomic orderings in l-Si, l-Ge and l-Sn to their structure factors may come only from some differences in the details of these orderings. In fact, a careful inspection of the regions above the first peak in the atomic distribution functions of figure 1 shows that the latter differences are really present. Thus, according to our model calculations, the specific superposition of the contributions from the rather similar local and slightly different medium-range atomic orderings in l-Si, l-Ge and l-Sn to the structure factors are responsible for the specific shape of their first peaks.
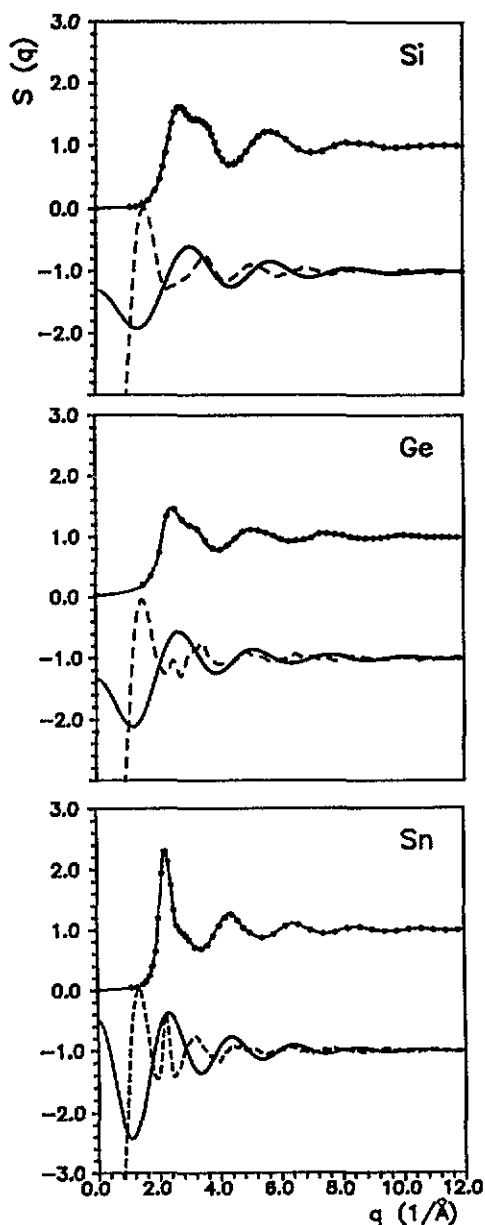
Figure 7. Contributions of the local (——) and medium-range (– – –) atomic orderings in l-Si, l-Ge and l-Sn to their structure factors (—●—).

5. Conclusion

We have carried out a RMC modelling of the structures of l-Si, l-Ge and l-Sn. The *models constructed are fully consistent with the available experimental structure-sensitive* information. They are in excellent agreement with the results of *ab-initio* molecular dynamics simulations as well. This is one more piece of strong evidence that the RMC method, which does not use interatomic potentials, produces physically sensible results.

Similar local atomic orderings of tetrahedral type have been found in the first coordination shells of l-Si, l-Ge and l-Sn by comparing the geometrical characteristics of the three-dimensional atomic configurations resulting from the simulations. It has also been found, quite in accordance with the results of our independent studies on l-Ge [5], that this ordering is related to the white-tin-type structure occurring in solid Si, Ge and Sn. It has been demonstrated that for l-Si, l-Ge and l-Sn the similar local atomic ordering determines the similar global and the slightly different medium-range atomic orderings the slightly different fine features in the experimental structure factors.

Acknowledgments

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