

Interionic pair potentials and partial structure factors of compound-forming quaternary NaSn liquid alloy: First principle approach

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Abstract. In this paper formulae for partial structure factors have been used to study partial structure factors of compound-forming quaternary liquid alloys by considering Hoshino's m -component hard-sphere mixture, which is based on Percus-Yevic equation of Hiroike. Formulae are applied to NaSn (Na, Sn, NaSn, Na₃Sn) which is considered as a quaternary liquid mixture with the formation of two compounds simultaneously. We have compared the total structure factors for ternary and quaternary alloys with experimental total structure factors which are found to be in good agreement. This suggests that, for suitable stoichiometric composition, two compounds are formed simultaneously. The hard-sphere diameters needed have been calculated using Troullier and Martins *ab-initio* pseudopotentials.

Keywords. Liquid; alloys; compound; quaternary; *ab-initio*; hard spheres.

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1. Introduction

The outstanding properties of binary liquid alloys with strong non-ideal mixing behavior have been of longstanding interest in the past decade and are useful in many diversified fields. The study of liquid metals and alloys are of immense importance for not only physicists but also chemists and engineers. This study is important for metallurgical chemistry and geology which involve the study of core of earth and astrophysics which involves the study of interior of planets (the core of the earth and interior of the planet are made up in part of a liquid mixture). Alloys with miscibility gap in the liquid state are especially interesting for advanced bearing materials.

The compound-forming liquid alloys have been extensively studied both theoretically and experimentally and are recognized as compound-forming solutions or regular solutions. These compound-forming liquid alloys exhibit anomalous

properties in some specific composition called stoichiometric composition indicating pronounced deviation from ideal mixing.

A model has been developed by Bhatia and Singh [1] to determine concentration dependence of thermodynamic quantities like free energy of mixing G_M . Bhatia and Hargrove [2,3], Tamaki and Cusack [4], Hoshino [5] and Singh [6] have made considerable progress in understanding the anomalous behavior of thermodynamics of compound-forming liquid alloys.

However, structural properties have been studied by a few. Neutron diffraction investigation of liquid Li-Pb alloy has been done by Ruppertsberg [7] and Ruppertsberg and Reiter [8]. Neutron diffraction study of liquid Na-Sn alloy by Alblas *et al* [9] indicate appreciable ordering in alloy. Huijben *et al* [10] measured structure factors of Na-Cs alloy. In the hard-sphere reference system, Ashcroft and Langreth [11,12] derived expression for partial structure factors and total structure factors of liquid binary alloys. These calculations are based on the exact solution of Percus-Yevic equation by Lebowitz [13]. This equation has been extensively used for calculating partial structure factors of various binary liquid alloys.

As regard the structural properties of liquid alloys beyond binary not much work has been done. Exact solution of Percus-Yevic equation had already been studied by Hiroke [16]. Hoshino and Young [14] proposed a theory of mixing of compound-forming liquid alloys where three types of hard spheres co-exist and applied it to Li-Pb alloy. But nothing was done regarding structural properties. Hoshino [15] explained entropy of mixing of liquid Na-Sn alloy obtained experimentally by Tamaki *et al*. They assumed two types of compounds. The exact solution of Percus-Yevic equation by Lebowitz has been utilized for one-component hard-sphere system by Ashcroft and Leneker to calculate partial structure factors. Lately, Hoshino [17] has derived expression for m-component hard-sphere mixture and applied it successfully to Li-Pb alloy which is considered as a ternary mixture of Li, Pb and Li_4Pb .

The above considerations motivated us to explore the Hoshino [17] approach further to quaternary liquid alloys. In the present work we have extended the m-component formalism for quaternary NaSn (Na, Sn, NaSn, Na_3Sn) liquid alloy system. In §2 we have discussed the formulae used for calculating interionic pair potentials and method of determining *ab-initio* pseudopotentials for calculating pseudopotentials. In §3 we have derived the formulae for partial structure factors and determinant of the matrix $|1 - \partial(k)|^{-1}$. In §4 application model to quaternary NaSn and LiPb has been discussed. The model has been applied to quaternary liquid alloy near stoichiometric compositions. In §5 we have discussed the features of partial structure factors implied from the figures. Finally, in §6 we have written the conclusion drawn from the discussion in §5.

2. Interionic pair potential and hard-sphere diameters

To calculate hard-sphere diameters, interionic pair potential can be used by generalizing Harrison's [18] approach of pair-wise potential between the metallic ions.

The pair potential has the familiar form of the screened Coulomb potential

$$V_{ij} = \frac{Z_i^* Z_j^*}{R} \left[1 - \frac{2}{\pi} \int_0^\infty F_{ij}^N(q) \frac{\sin(qR)}{q} dq \right], \quad (1)$$

where Z_i^* , Z_j^* [19–21] are the effective valencies and $F_{ij}^N(q)$ is the normalized energy wave number-dependent characteristic that contains total band-structure effects in the alloy using the self-consistent electron screening. In many cases, especially for non-local pseudopotentials, valence Z is replaced by effective valence Z^* . We note that when a non-local pseudopotential is used, the calculation of $F^N(q)$ and Z^* requires the self-consistent solution of a system of coupled non-linear equations [22]. The effective valence charges Z_i^* and Z_j^* are given in the form $Z_i^*Z_j^* = Z_iZ_j - \bar{Z}_i\bar{Z}_j$, where Z is the true valence and \bar{Z} is the depletion hole charge that originates from orthogonality condition between valence and core electron wave functions. $F_{ij}^N(q)$ is given by

$$F_{ij}^N(q) = -\left(\frac{q^2\Omega}{2\pi Z_i Z_j}\right)F_{ij}(q), \quad (2)$$

where, in the general case $F_{ij}(q)$ is given by

$$F_{ij}(q) = -\left(\frac{q^2\Omega}{8\pi}\right)\left[w_i(q)w_j(q)\frac{\epsilon^*(q)-1}{\epsilon^*(q)}\frac{1}{1-G(q)}\right]. \quad (3)$$

Here the quantities $w_i(q)$, $w_j(q)$ are Fourier transforms of self-consistent bare ion (unscreened) atomic pseudopotentials. For metallic component of alloy have been obtained by using generalized first principle pseudopotential theory for which Troullier and Martins (TM) unscreened pseudopotentials have been used. In the present work, semi-local form of pseudopotentials have been used to calculate pair potentials. $G(q)$ is the exchange-correlation functional by Vashishta and Singwi [23]. $\epsilon^*(q)$ is the modified Hartree dielectric function. Here $\Omega = \Omega_{\text{ideal}} = (1-c_2)\Omega_1 + c_2\Omega_2$ where c_2 is the concentration of the second component in the alloy and Ω_1 and Ω_2 are the atomic volumes of pure elements. In the present work, volume of alloy for NaSn alloy volume used has been obtained by using ideal volumes.

2.1 Construction of *ab-initio* pseudopotentials

For the calculation of *ab-initio* screened pseudopotentials, Troullier and Martins (TM) method [24] has been used, because this method produces computationally efficient pseudopotentials with a plane-wave basis set. The problem of transferability as compared to traditionally used model pseudopotentials also does not exist. TM pseudopotentials have proved their applicability with the calculations of systems of a larger number of elements in the periodic table in contrast to other *ab-initio* pseudopotentials like that of Bachelet *et al* [25]. In the present work, fhi98PP [26] code has been used to generate TM *ab-initio* pseudopotentials. The first *ab-initio* pseudopotentials are constructed by all-electron calculation of free atom in a reference configuration and then the method of Troullier and Martins is used to construct the screened pseudopotentials.

2.2 Pseudopotential generation, in general

The pseudopotential generation is mainly a three-step process. First, density functional theory (DFT) atomic levels and wave functions are generated. From this one

then generates the pseudopotentials. Finally it is checked whether what has been done is useful or not, and if it is not, then it is tried again in a different way. It is invariably done by assuming a spherically symmetric self-consistent Hamiltonian, so that all elementary quantum mechanics results for the atom apply. Then atomic state is defined by the electronic configuration and one-electron states are obtained by solving a self-consistent radial Schrödinger-like (Kohn–Sham [27,28]) equation. We have implemented it by using TM method. It has the advantage of producing simple pseudopotentials and uses Kleinman–Bylander [29] projection to generate the pseudopotentials in numerical form.

Choosing a valence and core states is a trivial step. Often valence states are those states that contribute to bonding, and core states are those that do not contribute. We can calculate pseudopotential for as high angular momentum l as one want but the general rule is that if atom has states up to $l = l_c$ in the core, we need a pseudopotential with angular momentum up to $l = l_c + 1$. Angular momentum $l > l_c + 1$ will feel the same potential as $l = l_c + 1$, because for all of them there is no orthogonalization to core sates. Sometimes we may generate a good pseudopotential but ghost states may appear and our result for a particular physical system may not be matching with the experimental results. Then in either case we have to start with different reference configuration or matching radii.

2.3 Troullier–Martins pseudopotentials

The first *ab-initio* pseudopotentials are constructed by all-electron calculations of free atom in a reference configuration. Having obtained all-electron potential and valence states, we use the method of Troullier and Martins to construct the screened pseudopotentials. Here it is assumed that a pseudowave function R^{ps} has the following form:

$$\begin{aligned} R^{ps}(r) &= r^{l+1} e^{p(r)} r \leq r_c, \\ R^{ps}(r) &= R(r) r \geq r_c, \end{aligned} \quad (4)$$

where

$$p(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}. \quad (5)$$

These seven coefficients are solved using conditions of norm conservation of charge and continuity of the pseudowave function and its first four derivatives. On the wave function given by eq. (8) are imposed norm conservation condition:

$$\int_{r < r_c} (R^{ps}(r))^2 dr = \int_{r < r_c} (R(r))^2 dr. \quad (6)$$

The continuity conditions are also imposed on the wave function and its derivatives up to fourth order at the matching points which are given by

$$\frac{d^n R^{ps}(r_c)}{dr^n} = \frac{d^n R(r_c)}{dr^n}, \quad n = 0, 1, 2, 3, 4,$$

$$R^{ps}(r_c) = r_c^{l+1} e^{p(r_c)} = R(r_c), \quad (7)$$

where

$$p(r_c) = \log \frac{R(r_c)}{r_c^{l+1}}.$$

Continuity of the first derivative of wave function is given by

$$p'(r_c) = \frac{dR(r_c)}{dr} \frac{1}{R^{ps}(r_c)} - \frac{l+1}{r_c}. \quad (8)$$

Continuity of second derivative of wave function using radial Schrödinger equation is given by

$$p''(r_c) = \frac{2m}{\hbar^2} (V(r_c) - \epsilon) - 2 \frac{l+1}{r_c} p'(r_c) - [p'(r_c)]^2. \quad (9)$$

If the third and fourth derivatives of $p(r)$ are continuous, then continuity of third and fourth derivatives of wave functions are

$$p'''(r_c) = \frac{2m}{\hbar^2} V'(r_c) + 2 \frac{l+1}{r_c^2} p'(r_c) - 2 \frac{l+1}{r_c} p''(r_c) - 2p'(r_c)p''(r_c) \quad (10)$$

and

$$p''''(r_c) = \frac{2m}{\hbar^2} V''(r_c) - 4 \frac{l+1}{r_c^3} p'(r_c) + 4 \frac{l+1}{r_c^2} p''(r_c) - 2 \frac{l+1}{r_c} p'''(r_c) - 2[p''(r_c)p'''(r_c)]^2 - 2p'(r_c)p''''(r_c). \quad (11)$$

By imposing additional condition $V'''(0) = 0$ the screened pseudopotential is given by

$$V(r) = \frac{\hbar^2}{2m} (2c_2(2l+3) + ((2l+5)c_4 + c_2^2)r^2) + \epsilon, \quad (12)$$

where additional constraint $(2l+5)(c_4 + c_2^2)r^2 = 0$ gives smooth pseudopotentials.

To check correctness of pseudopotentials and to get a feeling of transferability, results of pseudopotential (PP) and all-electron (AE) atomic calculations on atomic configurations are checked. The error in total energy differences between PP and AE results gives a feeling of how good the pseudopotential was. Moreover, pseudowave functions and atomic wave functions can also be compared by plotting them. For a good *ab-initio* pseudopotential there should be a matching of two types of pseudopotentials.

3. Partial structure factors for quaternary hard-sphere liquid alloys

3.1 Formalism

The partial structure factor $S_{ij}(k)$ is the inverse matrix $|1 - \partial(k)|^{-1}$ and is given by $S_{ij}(k) = \frac{|1 - \partial(k)|_{ij}}{|1 - \partial(k)|}$. Here $|1 - \partial(k)|$ is the determinant of matrix $1 - \partial(k)$ and $|1 - \partial(k)|_{ij}$ is the cofactor of the determinant. There are $\frac{4(4+1)}{2} = 10$ partial structure factors due to symmetric matrix, i.e., $S_{ij}(k) = S_{ji}(k)$.

3.2 Hard-sphere model

For the m-component hard-sphere mixture model, diameters are taken as $\sigma_1 < \sigma_2 < \sigma_3 < \sigma_4, \dots, < \sigma_m$ and hard-sphere ratio is given by $\gamma_{ij} = \sigma_i/\sigma_j$. The $(2m - 1)$ parameters which describe the hard-sphere system involve $X_i = n_i/n$ where $n = N/V$, $n_i = N_i/V$ and $\sum_{i=1}^m x_i = 1$ and packing fraction $\eta_i = (\pi/6)\eta_i\sigma_i^3$ satisfying $\eta = \sum_{i=1}^m \eta_i$.

3.3 Partial structure factors for quaternary alloy

To calculate the partial structure factors for quaternary alloy we first write four-component hard-sphere mixture alloy given by $|1 - \partial(k)|^{-1}$ as follows:

$$S(k) = \begin{vmatrix} S_{11}(k) & S_{12}(k) & S_{13}(k) & S_{14}(k) \\ S_{21}(k) & S_{22}(k) & S_{23}(k) & S_{24}(k) \\ S_{31}(k) & S_{32}(k) & S_{33}(k) & S_{34}(k) \\ S_{41}(k) & S_{42}(k) & S_{43}(k) & S_{44}(k) \end{vmatrix} \quad (13)$$

$$= \begin{vmatrix} 1 - n_1c_{11}(k) & -\sqrt{n_1n_2}c_{12}(k) & -\sqrt{n_1n_3}c_{13}(k) & -\sqrt{n_1n_4}c_{14}(k) \\ -\sqrt{n_2n_1}c_{21}(k) & 1 - n_2c_{22}(k) & -\sqrt{n_2n_3}c_{23}(k) & -\sqrt{n_2n_4}c_{24}(k) \\ -\sqrt{n_3n_1}c_{31}(k) & -\sqrt{n_3n_2}c_{32}(k) & 1 - n_3c_{33}(k) & -\sqrt{n_3n_4}c_{34}(k) \\ -\sqrt{n_4n_1}c_{41}(k) & -\sqrt{n_4n_2}c_{42}(k) & -\sqrt{n_4n_3}c_{43}(k) & 1 - n_4c_{44}(k) \end{vmatrix}^{-1} \quad (14)$$

Symmetrical nature of partial structure factors and correlation functions contribute only ten independent partial structure factors given in Appendix.

4. Application to quaternary hard-sphere mixture

Hard-sphere diameters used for ternary NaSn are: $\sigma_1(\text{Na}) = 2.82 \text{ \AA}$, $\sigma_2(\text{Sn}) = 3.04 \text{ \AA}$, $\sigma_3(\text{Na}_3\text{Sn}) = 4.1 \text{ \AA}$.

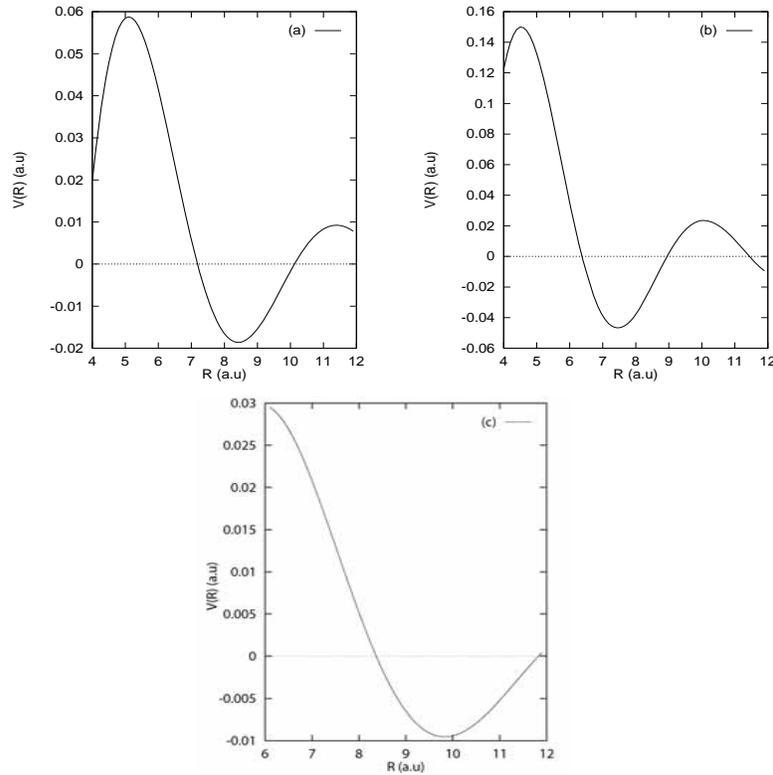


Figure 1. Interionic pair potential for binary liquid alloy. (a) $V_{\text{Na-Na}}$ in pure liquid Na, (b) $V_{\text{Sn-Sn}}$ in pure liquid Sn, (c) $V_{\text{Na-Sn}}$ in NaSn alloy.

In the case of quaternary NaSn, hard-sphere diameters are: $\sigma_1(\text{Na}) = 2.84 \text{ \AA}$, $\sigma_2(\text{Sn}) = 3.02 \text{ \AA}$, $\sigma_3(\text{Na}_3\text{Sn}) = 7.34 \text{ \AA}$, $\sigma_4(\text{NaSn}) = 8.72 \text{ \AA}$. σ_3 for Na_3Sn compound has been determined by the relation $(4\pi/3)\sigma_3^3 = (4\pi/3)(3\sigma_1^3 + \sigma_2^3)$.

σ_4 for NaSn compound has been determined by $(4\pi/3)\sigma_4^3 = (4\pi/3)(\sigma_1^3 + \sigma_2^3)$. In the case of ternary NaSn, stoichiometric alloy is $\text{Na}_{0.75}\text{Sn}_{0.25}$. For quaternary alloys, stoichiometric alloys at respective compositions are: $\text{Na}_{0.75}\text{Sn}_{0.25}$ and $\text{Na}_{0.5}\text{Sn}_{0.5}$. The concentrations x_3 and x_4 have been considered as disposable parameters on the line of Hoshino [17].

5. Discussion

The hard-sphere diameters are determined using the relation $V_{ij}(\sigma_i) = V_{\min} + \frac{3}{2}K_{\text{B}}T$ at temperature $T = 773 \text{ K}$ for NaSn alloy. Here V_{\min} is the first minimum in the interionic pair potential. Pair potentials are calculated through eq. (3) using *ab-initio* pseudopotentials. Figure 1 shows the calculated pair potentials for NaSn alloy. Figure 1c shows the interionic pair potentials for $\text{Na}_{0.8}\text{Sn}_{0.2}$. Graphs show that the depths of potentials are decreasing for Na in the alloy state, which indicates

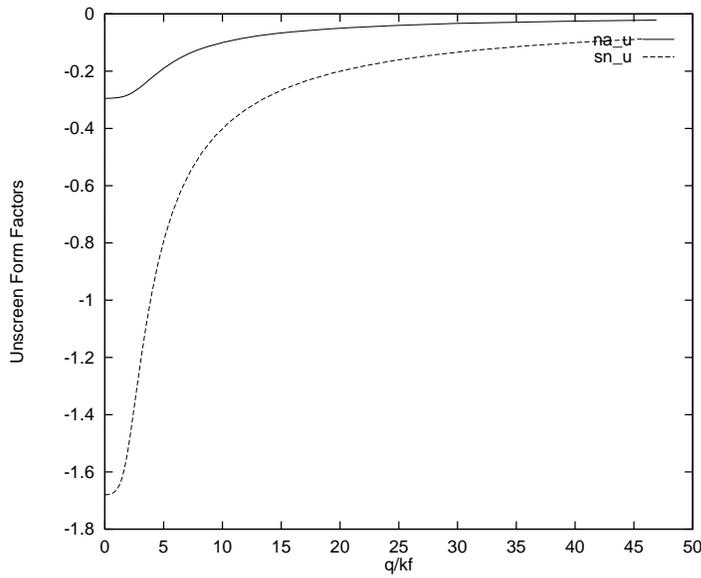


Figure 2. Form factors for pure Na and pure Sn.

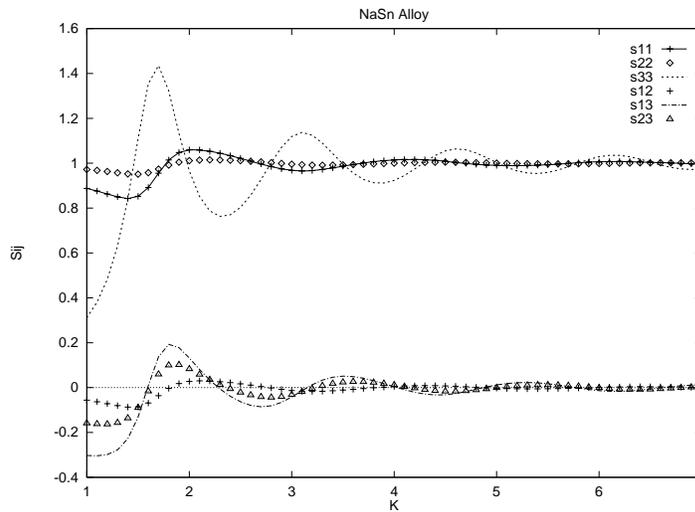


Figure 3. Partial structure factors for ternary (NaSn) alloy at $x_1 = 0.24, x_2 = 0.08, x_3 = 0.68$.

that effective interaction between alkali-alkali atoms decreases on alloying and this is consistent with other work [10]. Figure 2 shows bare ion form factors for pure Na and Sn for calculation of pair potentials.

Partial structure factors for ternary NaSn are shown in figure 3 and quaternary partial structure factors are shown in figures 4 and 5 respectively. In figure 3 ternary partial structure factors are shown at stoichiometric composition where $x_1/x_2 = 3$

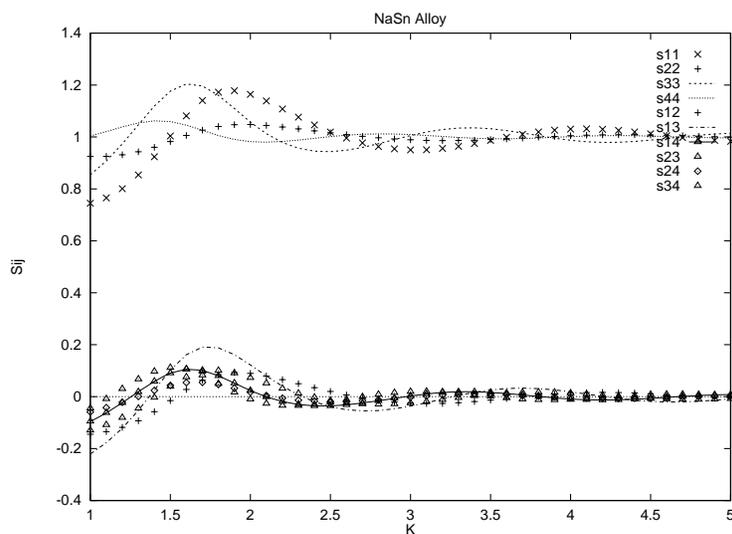


Figure 4. Partial structure factors for quaternary (NaSn) alloy at $x_1 = 0.48, x_2 = 0.16, x_3 = 0.30, x_4 = 0.06$

for parameters $x_1 = 0.24, x_2 = 0.08, x_3 = 0.68$. In figures 4 and 5 quaternary structure factors are shown at stoichiometric compositions where $x_1/x_2 = 3$ for Na_3Sn and $x_1/x_2 = 1$ for NaSn compound for two pairs of parameters ($x_1 = 0.48, x_2 = 0.16, x_3 = 0.30, x_4 = 0.06$) and ($x_1 = 0.15, x_2 = 0.15, x_3 = 0.67, x_4 = 0.03$) respectively. In figure 3, $S_{33}(k)$ has sharp high peaks whereas $S_{11}(k)$ and $S_{22}(k)$ oscillate around unity irrespective of the value of k , whereas $S_{12}(k)$, $S_{13}(k)$ and $S_{23}(k)$ oscillate around zero. This feature implies that Na and Sn ions behave like free ions whereas Na_3Sn has strong short-range order to form compound.

In figure 4, $S_{33}(k)$ peaks are dominant whereas in figure 5, $S_{44}(k)$ peaks are also appreciable with other peaks. In figure 6, ternary and quaternary total partial structure factors are shown for NaSn alloy. Computed values of total partial structure factors predict the position and magnitude of peak values in excellent agreement but found to shift very little towards a longer wavelength side of experimental values. Agreement of structure factors for the first two peaks is important. For smaller values of q , neutron diffraction experiments can be done effectively. Therefore, experimental results are more accurate in the region of smaller values of q only. Moreover, first two prominent peaks in the region of small q values is indicative of the presence of chemical short-range order which is characteristic of liquids.

Partial structure factors of unlike species S_{12} , S_{13} , S_{14} , S_{23} , S_{24} and S_{34} are oscillating about zero in both ternary and quaternary NaSn alloy, whereas partial structure factors for like species S_{11} , S_{22} , S_{33} and S_{44} are oscillating around one. This behavior shows similarity between ternary and quaternary liquid alloys. Peak values of S_{12} have been found in both ternary and quaternary alloys to be more shifted towards the longer wavelength side of S_{13} and S_{23} but their magnitudes have been found much less than that of S_{13} . Peak values of S_{33} have been found

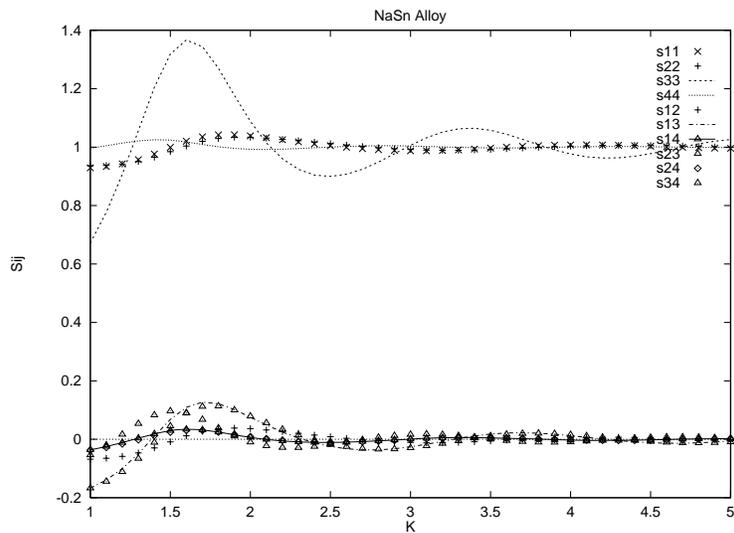


Figure 5. Partial structure factors for quaternary (NaSn) alloy at $x_1 = 0.15, x_2 = 0.15, x_3 = 0.67, x_4 = 0.03$

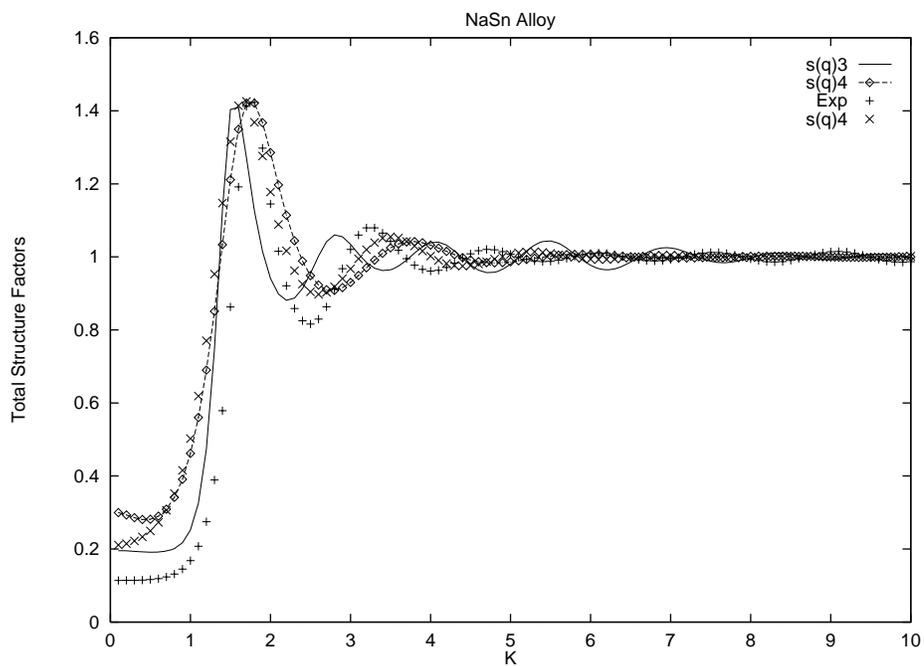


Figure 6. Total structure factors $S(q)$ for NaSn alloy. $S(q)3$ – ternary NaSn alloy at $x_1 = 0.45, x_2 = 0.15, x_3 = 0.40$, $S(q)4$ – quaternary NaSn alloy at $x_1 = 0.48, x_2 = 0.16, x_3 = 0.30, x_4 = 0.06$, $S(q)4$ – quaternary NaSn alloy at $x_1 = 0.15, x_2 = 0.15, x_3 = 0.67, x_4 = 0.03$, Exp – experimental results due to Alblas *et al* [9].

Table 1. Electronic configuration and pseudocore radii for constructing *ab-initio* pseudopotentials.

Metal	Electronic configuration	Core radii (a.u.)
Na	$3s^{1.0}3p^{0.25}43d^{0.25}$	$r_c(s, p, d)=(2.2, 2.2, 2.5)$
Sn	$5s^{2.0}5p^{2.0}5d^{0.0}4f^{0.0}$	$r_c(s, p, d, f)=(2.3, 2.3, 2.3)$

in all cases to be much higher than that of S_{11} . In quaternary NaSn, S_{34} peaks are appreciable whereas S_{44} peaks are weak.

Electronic configuration and pseudising core radii used to generate *ab-initio* pseudopotentials for Na and Sn are given in table 1. In most cases atomic ground states work very well for the occupied atomic orbitals. But a specific way for the configuration to resemble the solid state can be used if it does not change the result much. For example, we have used the configuration of Na. Calculated bare ion form factors which have been used in the present work are shown in figure 2.

6. Conclusion

Structural properties of quaternary alloys have been explained. Formulae obtained have been applied for quaternary partial structure factors to liquid alloys NaSn which is considered as quaternary mixture of Na, Sn, NaSn and Na_3Sn . Figures 3–5 show the characteristic features of partial structure factors similar to that explained by Hoshino [15]. In figure 6, total structure factors for ternary and quaternary NaSn are in excellent agreement with experimental total structure factors as obtained by Alblas *et al* [9]. Both these show the simultaneous formation of two compounds.

Therefore, it is implied that like ternary alloys which can better explain binary experimental total structure factors [8,9], quaternary alloy model of hard spheres can also help in describing the thermodynamic and structural properties on the basis of compound-forming model, which can further be useful to explain transport properties like resistivity of alloys in a better way.

Acknowledgement

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Appendix: Partial structure factors for quaternary binary alloy

$$\begin{aligned}
 S_{11}(k) = & [(1 - n_2c_{22}(k))(1 - n_3c_{33}(k))(1 - n_4c_{44}(k)) \\
 & - n_2n_3(1 - n_4c_{44}(k))c_{23}^2(k) - n_2n_4(1 - n_3c_{33}(k))c_{24}^2(k) \\
 & - n_3n_4(1 - n_2c_{22}(k))c_{34}^2(k) - 2n_2n_3n_4c_{23}(k)c_{24}(k)c_{34}(k)]/D(k), \quad (15)
 \end{aligned}$$

$$S_{22}(k) = [(1 - n_1 c_{11}(k))(1 - n_3 c_{33}(k))(1 - n_4 c_{44}(k)) - n_1 n_3 (1 - n_4 c_{44}(k)) c_{13}^2(k) - n_1 n_4 (1 - n_3 c_{33}(k)) c_{14}^2(k) - n_3 n_4 (1 - n_1 c_{11}(k)) c_{34}^2(k) - 2 n_1 n_3 n_4 c_{13}(k) c_{34}(k) c_{14}(k)] / D(k), \quad (16)$$

$$S_{33}(k) = [(1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k))(1 - n_4 c_{44}(k)) - n_1 n_2 (1 - n_4 c_{44}(k)) c_{12}^2(k) - n_1 n_4 (1 - n_2 c_{22}(k)) c_{14}^2(k) - n_2 n_4 (1 - n_1 c_{11}(k)) c_{24}^2(k) - 2 n_1 n_2 n_4 c_{12}(k) c_{24}(k) c_{14}(k)] / D(k), \quad (17)$$

$$S_{44}(k) = [(1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k))(1 - n_3 c_{33}(k)) - n_1 n_2 (1 - n_3 c_{33}(k)) c_{12}^2(k) - n_1 n_3 (1 - n_2 c_{22}(k)) c_{13}^2(k) - n_2 n_3 (1 - n_1 c_{11}(k)) c_{23}^2(k) - 2 n_1 n_2 n_3 c_{12}(k) c_{23}(k) c_{13}(k)] / D(k), \quad (18)$$

$$S_{12}(k) = [((1 - n_3 c_{33}(k))(1 - n_4 c_{44}(k)) c_{12}(k) + n_3 (1 - n_4 c_{44}(k)) c_{13}(k) c_{23}(k) + n_3 n_4 c_{14}(k) c_{34}(k) c_{23}(k) + n_3 n_4 c_{13}(k) c_{24}(k) c_{34}(k) + n_4 (1 - n_3 c_{33}(k)) c_{14}(k) c_{24}(k) - n_3 n_4 c_{12}(k) c_{34}^2(k) \sqrt{n_1 n_2})] / D(k), \quad (19)$$

$$S_{13}(k) = [((1 - n_2 c_{22}(k))(1 - n_4 c_{44}(k)) c_{13}(k) + n_4 (1 - n_2 c_{22}(k)) c_{14}(k) c_{34}(k) + n_2 n_4 c_{12}(k) c_{24}(k) c_{34}(k) + n_2 n_4 c_{14}(k) c_{24}(k) c_{23}(k) + n_2 (1 - n_4 c_{44}(k)) c_{12}(k) c_{23}(k) - n_2 n_4 c_{13}(k) c_{24}^2(k) \sqrt{n_1 n_3})] / D(k), \quad (20)$$

$$S_{14}(k) = [((1 - n_2 c_{22}(k))(1 - n_3 c_{33}(k)) c_{14}(k) + n_3 (1 - n_2 c_{22}(k)) c_{13}(k) c_{34}(k) + n_2 n_3 c_{12}(k) c_{23}(k) c_{34}(k) + n_2 n_3 c_{13}(k) c_{23}(k) c_{24}(k) + n_2 (1 - n_3 c_{33}(k)) c_{12}(k) c_{24}(k) - n_2 n_3 c_{14}(k) c_{23}^2(k) \sqrt{n_1 n_4})] / D(k), \quad (21)$$

$$S_{23}(k) = [((1 - n_1 c_{11}(k))(1 - n_4 c_{44}(k)) c_{23}(k) + n_1 (1 - n_4 c_{44}(k)) c_{12}(k) c_{13}(k) + n_4 (1 - n_1 c_{11}(k)) c_{24}(k) c_{34}(k) + n_1 n_4 c_{12}(k) c_{14}(k) c_{34}(k) + n_1 n_4 c_{13}(k) c_{14}(k) c_{24}(k) - n_1 n_4 c_{23}(k) c_{14}^2(k) \sqrt{n_2 n_3})] / D(k), \quad (22)$$

$$S_{24}(k) = [((1 - n_1 c_{11}(k))(1 - n_3 c_{33}(k)) c_{24}(k) + n_3 (1 - n_1 c_{11}(k)) c_{23}(k) c_{34}(k) + n_1 (1 - n_3 c_{33}(k)) c_{12}(k) c_{14}(k) + n_1 n_3 c_{12}(k) c_{13}(k) c_{34}(k) + n_1 n_3 c_{13}(k) c_{14}(k) c_{23}(k) - n_1 n_3 c_{24}(k) c_{13}^2(k) \sqrt{n_2 n_4})] / D(k), \quad (23)$$

$$S_{34}(k) = [((1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k)) c_{34}(k) + n_2 (1 - n_1 c_{11}(k)) c_{23}(k) c_{24}(k) + n_1 (1 - n_2 c_{22}(k)) c_{13}(k) c_{14}(k) + n_1 n_2 c_{12}(k) c_{23}(k) c_{14}(k) + n_1 n_2 c_{12}(k) c_{13}(k) c_{24}(k) - n_1 n_2 c_{34}(k) c_{12}^2(k) \sqrt{n_3 n_4})] / D(k), \quad (24)$$

where $D(k)$ is the determinant of the matrix and is given by

$$\begin{aligned}
 D(k) = & (1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k))(1 - n_3 c_{33}(k))(1 - n_4 c_{44}(k)) \\
 & - n_2 n_3 (1 - n_1 c_{11}(k))(1 - n_4 c_{44}(k)) c_{23}^2(k) \\
 & - n_2 n_4 (1 - n_1 c_{11}(k))(1 - n_3 c_{33}(k)) c_{24}^2(k) \\
 & - n_1 n_3 (1 - n_2 c_{22}(k))(1 - n_4 c_{44}(k)) c_{13}^2(k) \\
 & - n_3 n_4 (1 - n_1 c_{11}(k))(1 - n_2 c_{22}(k)) c_{34}^2(k) \\
 & - n_1 n_2 (1 - n_3 c_{33}(k))(1 - n_4 c_{44}(k)) c_{12}^2(k) \\
 & - n_1 n_4 (1 - n_2 c_{22}(k))(1 - n_3 c_{33}(k)) c_{14}^2(k) \\
 & - 2n_2 n_3 n_4 (1 - n_1 c_{11}(k)) c_{23}(k) c_{24}(k) c_{34}(k) \\
 & - 2n_1 n_2 n_3 (1 - n_4 c_{44}(k)) c_{12}(k) c_{13}(k) c_{23}(k) \\
 & - 2n_1 n_3 n_4 (1 - n_2 c_{22}(k)) c_{13}(k) c_{14}(k) c_{34}(k) \\
 & - n_1 n_2 n_4 (1 - n_3 c_{33}(k)) c_{12}(k) c_{14}(k) c_{24}(k) \\
 & + n_1 n_2 n_3 n_4 [c_{12}^2(k) c_{34}^2(k) + c_{13}^2(k) c_{24}^2(k) \\
 & + c_{23}^2(k) c_{14}^2(k)] - n_1 n_2 n_3 n_4 [2c_{12}(k) c_{13}(k) c_{24}(k) \\
 & + 2c_{12}(k) c_{14}(k) c_{23}(k) c_{34}(k) + 2c_{13}(k) c_{14}(k) c_{23}(k) c_{24}(k)]. \quad (25)
 \end{aligned}$$

The total structure factors for quaternary liquid alloys have been obtained through the following empirical relation:

$$\begin{aligned}
 S(k) = & x_1 S_{11} + x_2 S_{22} + x_3 S_{33} + x_4 S_{44} + 2\sqrt{x_1 x_2} S_{12} + 2\sqrt{x_1 x_3} S_{13} \\
 & + 2\sqrt{x_1 x_4} S_{14} + 2\sqrt{x_2 x_3} S_{23} + 2\sqrt{x_2 x_4} S_{24} + 2\sqrt{x_3 x_4} S_{34}. \quad (26)
 \end{aligned}$$

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