

Temperature Dependence of the Structural Properties of Liquid Cu, Au and Fe Metals via RMC Method

Yisau A. Odusote^{1,*}, Lateef O. Mustapha²

¹Condensed Matter Physics Research Group, Department of Physics, Federal University of Technology, Akure, Nigeria

²Department of Physical Sciences, Al-Hikmah University, Ilorin, Nigeria

Abstract The structures of liquid metals of Cu, Au and Fe have been studied at temperatures close to their melting points and a few higher temperatures by reverse Monte Carlo (RMC) method using X-ray diffraction data. In each case, the positions of 4096 atoms placed in a configuration box were altered until the experimental diffraction data of the static structure factor $S(Q)$ was in agreement with the corresponding model static structure factor within the errors. From the simulations, useful information on the temperature dependence of the pair distribution function $g(r)$, the structure factor, $S(Q)$, the cosine of the bond angle distribution, $b\cos \theta$ and the average coordination number, $\langle N_c \rangle$, were extracted. Analysis of the results reveals that the structure of the liquids remains nearly close-packed as the density decreases. The calculated results agree quite well with the experimental $S(Q)$ data. It is reported that there is a gradual structural change from a more close-packed to a less close-packed structure in investigated liquid metals. Hence, the study indicates that as temperature increases many atoms have a small number of neighbours (i.e. atoms move further apart), showing that they are on the surface of clusters or on 'pathways' between them thereby causing a decrease in the average coordination number, $\langle N_c \rangle$ of the central atom.

Keywords Temperature, Structure factor, Coordination number, X-ray diffraction, Liquid metals

1. Introduction

The use of X-ray diffraction methods to describe the atomic structure of liquid metals and alloys in material science and, by extension, interpreting the experimental results are still complicated problems [1]. The knowledge of the detailed atomic structure of modern materials is the key to understanding their macroscopic properties and various kinds of techniques such as X-ray, neutron and electron diffractions have been proposed and used to obtain the structure of non-crystalline materials using both reflection and transmission experiments. It is widely acknowledged that the most efficient direct method of structural investigations is neutron diffraction with isotopic substitution. Unfortunately, this tool has proved to be prohibitively expensive and coupled with difficulty associated with the structural analysis of the diffraction data for liquid metals and binary liquid mixtures by way of separating the partial structure factors from the experimental total structure factor. To overcome these challenges one has to rely on the results of different experimental techniques as extended X-ray absorption fine

structure (EXAFS), X-ray and neutron diffractions. A number of recent studies [2-5] have confirmed that the reverse Monte Carlo technique provides a suitable framework for combining the information content of many different sorts of data.

Many studies of the potential based methods [6-9] reveal that a better understanding of the structure of liquid metals and alloys is essential for exact theoretical analysis of physicochemical properties like electron transport properties, atomic transport properties, to mention a few. This has prompted us to employ the reverse Monte Carlo method

(RMC) of simulation which has proved very useful in a number of cases [10-14] to model the structure of liquid copper, gold and iron at different temperatures close to their melting points and from a practical point of view find out how the properties of these liquid metals are affected with changes in density for some worthwhile reasons: firstly, liquid metals are two component systems, which are composed of valence electrons and ions and there is a strong correlation between electrons and ions. Secondly, the structural and electronic properties of liquid metals is strongly a function of the density due to the screening effect of conduction electrons [15], and it is believed that fluctuations in density are important in determining the physical properties of metals in the critical region [16]. Most metals have their critical point at such extremes of

* Corresponding author:

yaodusote@futa.edu.ng (Yisau A. Odusote)

Published online at <http://journal.sapub.org/ajcmp>

Copyright © 2017 Scientific & Academic Publishing. All Rights Reserved

temperature and pressure, where the temperature is too high to permit a liquid to be in stable state, and the pressure too high to sustain a gas and under such conditions it is very difficult to make accurate measurement of any steady-state properties. These are reasons why liquid metals are known to exhibit a number of distinguishing features in a wide range of density. It is also important to note that apart from the commercial values of these classes of materials, the unique chemical and physical properties offered by them are increasingly being studied in a growing number of applications. For instance, gold is used in the fields of nanotechnology and medicine for productions of smart cards, automotive, electronics, sensors, medical implants and drug delivery systems [17]. In addition, liquid metals are of practical importance from technological point of view, as liquid silver is being used as a doping agent in glassy semiconductor As_2Se_3 to make it an ionic conductor [18].

The RMC method [9] provides a general way of producing three dimensional structures of disordered materials on the atomic level based on experimental data. No input interatomic potential is required and the simulation can be performed to minimize the difference between calculated and measured total structure factors, instead of minimizing the system energy as is the case in Metropolis Monte Carlo (MMC) method [11, 19].

Although, the RMC method was initially developed for application to the structures of liquids and glasses, it has however been successfully applied to crystalline and magnetic structures [11, 19-21]. In the present study, the experimental structure factors taken from [22] are used as input data and the RMC method was used to give more detailed information on the structural properties of the selected liquid metals than can be obtained from pure structural measurements. The interesting results obtained from the simulations were analyzed for the pair distribution function, $g(r)$, the structure factor $S(Q)$, the ‘bond-angle’ distribution $b\cos\theta$ and the average coordination number, $\langle N_c \rangle$.

The layout of the paper is as follows: in section 2, a brief description of the RMC method algorithm is given. This is followed by results and discussion in section 3 and finally end the paper with the concluding remarks.

2. RMC Method

A brief description of the algorithm is given here, while details of the RMC method can be found in [10, 19, 23].

1. Starts with an initial configuration of N atoms placed in a cubic box of side L with periodic boundary conditions, that is, the box is surrounded by images of itself. The atomic number density ρ is expressed as:

$$\rho = \frac{N}{L^3} \quad (1)$$

2. The radial distribution functions, g_o^{calc} , for this old configuration is calculated by:

$$g_o^{calc} = \frac{n_o^{calc}(r)}{4\pi r^2 \rho \Delta r} \quad (2)$$

where $n_o^{calc}(r)$ is the number of atoms at a distance between r and $r + \Delta r$ from a central atom, averaged over all atoms as centers. Subscript o means ‘old’ and its significance will become clear in the following steps.

3. Fourier transform of g_o^{calc} to obtain the total structure factor:

$$S_o^{calc}(Q) = 1 + \frac{4\pi\rho}{Q} \int_0^\infty r(g_o^{calc}(r) - 1) \sin Qr dr \quad (3)$$

and calculate

$$\chi_o^2 = \sum_{i=1}^m (S_o^{calc}(Q_i) - S_o^{expt}(Q_i))^2 / \sigma^2(Q_i) \quad (4)$$

the difference between the experimental total structure factor $S^{expt}(Q)$ and the calculated structure factor from the configuration $S^{calc}(Q)$, where the sum is over all m experimental data points, each having an error $\sigma(Q_i)$.

4. Move one atom at random. Calculate the new radial distribution function, $g_n^{calc}(r)$ and total structure factor, $S_n^{calc}(Q)$ such that

$$\chi_n^2 = \sum_{i=1}^m (S_n^{calc}(Q_i) - S^{expt}(Q_i))^2 / \sigma^2(Q_i) \quad (5)$$

5. If $\chi_n^2 < \chi_o^2$, the move is accepted and the new configuration becomes the old configuration.

If $\chi_n^2 > \chi_o^2$, then move is accepted with probability $\exp(-(\chi_n^2 - \chi_o^2) / 2)$. Otherwise, it is rejected.

6. Repeated from step 4 until χ^2 becomes small enough.

As the number of accepted atom moves increases, χ^2 will initially decrease until it reaches an equilibrium value, about which it will then oscillate. The resulting configuration for which $S^{calc}(Q_i)$ agrees with $S^{expt}(Q_i)$ within the limits of experimental error should be a three dimensional structure.

3. Results and Discussion

The calculations in the present work were performed with a recent version of the RMC code [24]. The simulation box contained 4096 atoms at each temperature and density of the liquid metals studied as presented in table 1. In each

case, the atoms are arranged at random in a cubic box, but moved a minimum distance apart, corresponding to the closest approach of two atomic centers. The positions of atoms in the configuration box obeying periodic boundary conditions are altered until they give good agreement with experimental data.

Table 1. Temperatures and densities used for the RMC simulations in this work [22]

Metals	T(K)	ρ (g/cm ³)	ρ (Å ⁻³)
Cu	1150	7.97	0.07550
	1300	7.86	0.07446
	1500	7.69	0.07285
	1600	7.62	0.07219
Au	1150	17.20	0.05257
	1300	17.10	0.05226
	1500	16.90	0.05165
	1700	16.80	0.05136
Fe	1560	7.01	0.07556
	1600	6.95	0.07492
	1650	6.88	0.07416
	1750	6.52	0.07028

The structure factors $S(Q)$'s used as input data were taken from [22] and the $S(Q)$'s were modelled by adopting a modified version of an original code by McGreevy et al., [11] as described in the algorithm above. For each of the liquid metal, the RMC code was run using a small value of $\sigma = 0.01$ so as to get an excellent fit with the experimental data and varying the values of the distances of closest approach of pairs of atoms until a physically acceptable pair distribution function is achieved. In all cases, the results were obtained at convergence i.e. the simulation was run until the value of parameter χ^2 remains fairly constant. The functions $g(r)$, $S(Q)$ and $b\cos\theta$ as well as the average coordination number, $\langle N_c \rangle$ for the liquids were computed from the final configuration.

The pair distribution functions, $g(r)$'s, which gives useful information about the number of nearest-neighbour atoms were obtained from experimental $S(Q)$'s by Fourier transform for each of the liquid metal investigated at corresponding temperature, are shown in Figures 1, 2 and 3 for the set of cut-off distances finally adopted. The cutoff distances used in this study which gave the best results are presented in table 2 along with the characteristic parameters of $g(r)$'s, that is, the positions of the first and second peaks in $g(r)$, r_1^P and r_2^P as well as the positions of the first and second minima in $g(r)$, r_1^{min} and r_2^{min} used in the modelling, respectively, with the average coordination numbers $\langle N_c \rangle$ obtained. $\langle N_c \rangle$ is the average number of atoms within a distance r_1^{min} (position of first minimum in $g(r)$) from a central atom and it was calculated using the conventional method [22], that is the first peak area of $4\pi r^2 g(r)$ up to the first minimum.

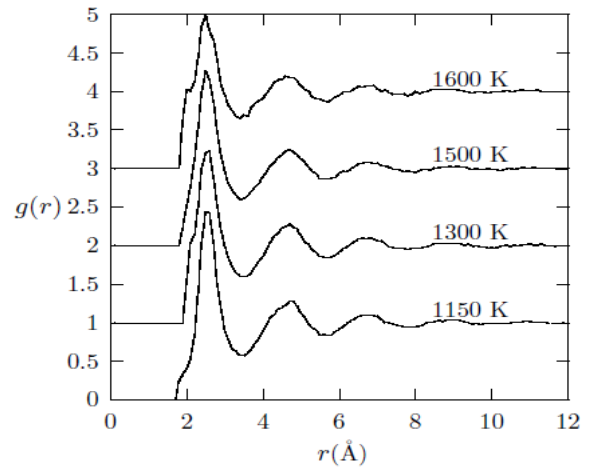


Figure 1. Temperature variation of $g(r)$ with $r(Å)$ as obtained for liquid Cu from the RMC

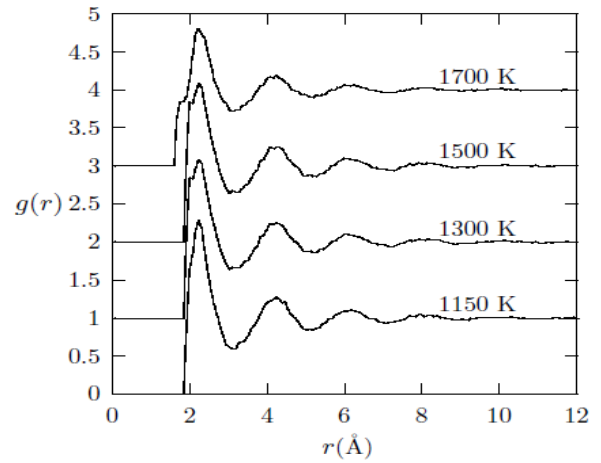


Figure 2. Temperature variation of $g(r)$ with $r(Å)$ as obtained for liquid Au from the RMC

From figures 1-3, it is evidently clear that the $g(r)$'s obtained are all physically consistent, while it was noted in the course of calculations that the cut-off distances did not give a better results by merely changing the values of the closest distance of approach. It can be seen from table 2 that the average values of r_c , r_1^P and r_1^{min} are 1.7 Å, 2.4 Å and 3.4 Å, respectively for liquid copper from Fig. 1 and these values are fairly constant despite considerable change in temperature. The lack of a significant change in the peak positions (r_1^P and r_2^P) indicates that the nature of the metallic bonding remains the same as temperature increases.

It is also noted that the heights of the first, second and third peaks of $g(r)$ practically do not differ as the densities of the liquid is lowered. However, one observes that only the positions of the first, second and third peaks shift towards increasing r values from about 2.4 Å to 4.7 Å and to 6.6 Å for the first, second and third peaks, respectively (see table 2).

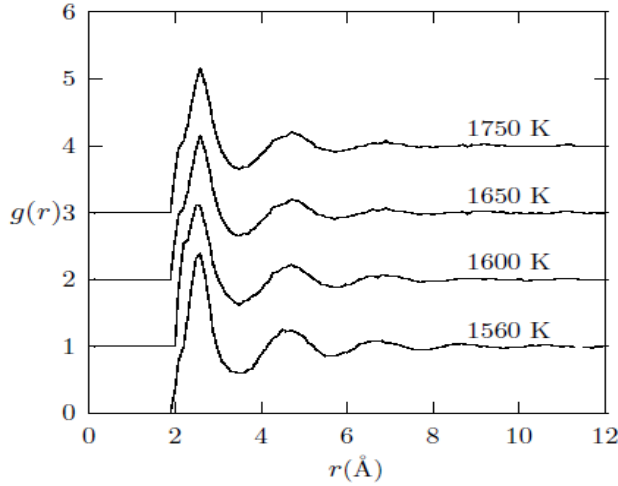


Figure 3. Temperature variation of $g(r)$ with $r(Å)$ as obtained for liquid Fe from the RMC

The position of second minimum r_2^{min} in $g(r)$ also remains fairly constant. Nonetheless, the slight observable shoulders on the left-hand side of the first peaks of the $g(r)$ at temperatures < 1600 K from the RMC simulations for the liquid metals would have been improved by increasing the cut-off by 0.05- 0.1 Å. The first peaks are very well separated from the remainder of $g(r)$'s and this, in principle, makes it possible to accurately calculate the average coordination number. A more careful perusal of table 2 reveals that the cut-off distances r_c somehow decrease for liquid gold as temperature is increased and has fairly constant first peak r_1^P and second peak r_2^P heights

(Fig. 2), while the positions of the first minimum r_1^{min} and second minimum r_2^{min} slightly vary with increasing temperature. Moreover, the cut-off distances, r_c for liquid iron show a slight variation as temperature increases. The heights of first peak r_1^P and second r_2^P are almost constant (Fig. 3), whereas the positions of the first minimum r_1^{min} and second minimum r_2^{min} in $g(r)$ were found to vary with increase in temperature. With regards to the structure of $g(r)$, the general effect of an increase in temperature in decreasing the heights of the first peak in $g(r)$ and reducing the depth of the first minimum is reproduced for all the liquid metals studied.

A comparison of our results with the RMC modelling of expanded liquid Cs, [25] reveals that Cs has a fairly constant first peak and first minimum in $g(r)$, with $r_1^P = 5.5$ Å and $r_1^{min} = 7.5$ Å (the r_1^{min} at the highest temperature of 1650°C is 7.8 Å). This simply implies that the metallic bond has a mean bond length of 5.5 Å and a maximum length of 7.5 Å. Therefore, the investigated liquid metals Cu, Au and Fe can be said to have their metallic bond lengths approximately within the range of 2.4 to 3.4 Å, 2.5 to 3.9 Å and 2.2 to 3.5 Å, respectively. In addition, we also compare the $g(r)$ obtained in the present study for liquid Cu at 1500 K with the result from the *ab initio* MD studies of Kresse et al., [26] and Pasquarello et al., [27] which further confirms that the heights of their first peaks agree well with our $g(r)$. But their peak positions are shifted slightly to the left of ours (ours is at 2.4 Å).

Table 2. Information about the data sets, including some characteristic parameters of the pair distribution functions, $g(r)$, the cut-off distance, r_c , the positions of the first and second peaks in $g(r)$ given as r_1^P and r_2^P , the positions of the first and second minima given as r_1^{min} and r_2^{min} with the average coordination number, $\langle N_c \rangle$ as obtained from the RMC

Metal	T(K)	r_c (Å)	r_1^P (Å)	r_2^P (Å)	r_1^{min} (Å)	r_2^{min} (Å)	$\langle N_c \rangle$
Cu	1150	1.7	2.4	4.7	3.4	5.6	12.4
	1300	1.8	2.5	4.6	3.4	5.6	12.2
	1500	1.7	2.4	4.6	3.4	5.6	11.9
	1600	1.7	2.4	4.6	3.4	5.6	10.8
Au	1150	2.3	2.8	5.3	3.9	6.3	12.8
	1300	2.2	2.8	5.2	3.8	6.3	12.6
	1500	2.3	2.7	5.2	3.9	6.5	12.6
	1700	2.0	2.8	5.2	3.8	6.4	11.6
Fe	1560	1.8	2.5	4.5	3.5	5.5	13.1
	1600	2.0	2.5	4.6	3.4	5.7	12.2
	1650	1.8	2.5	4.6	3.5	5.7	12.2
	1750	2.0	2.4	4.5	3.5	5.6	12.2

The curves in Figures 4, 5 and 6 show the quality of the RMC fits to the experimental $S(Q)$'s data for the liquid Cu, Au and Fe, at respective investigated temperatures. As it can be seen from the figures, the calculated $S(Q)$ from RMC compares well with the experiment at all values of Q such that it is almost impossible to distinguish between the RMC fits and the experimental data. This agreement gives us confidence to use the configuration files for the liquid metals. Investigation by previous studies of a number of pure liquid metals and alloys [28, 29] has shown that the $S(Q)$'s curves obtained in the present study are reliable and follow the general trend in that variation of the sample temperature is accompanied mainly by change in the amplitude of the peaks, while the position of the peaks practically does not change with respect to Q [1].

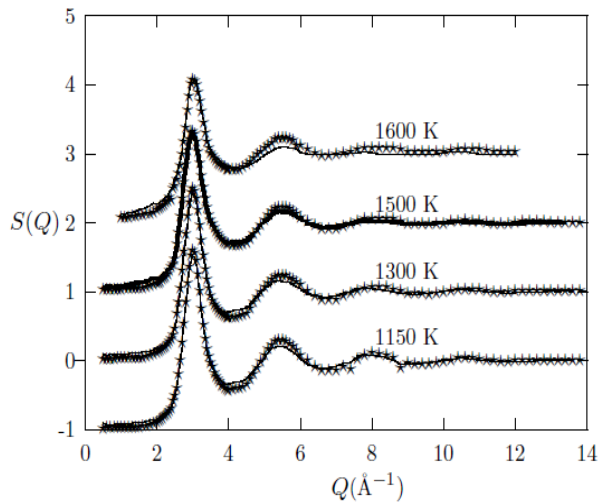


Figure 4. Temperature variation of the static structure factor, $S(Q)$, as obtained for liquid Cu from RMC. The solid line denotes theoretical models and the stars denote experimental data. The experimental $S(Q)$ were taken from [22]

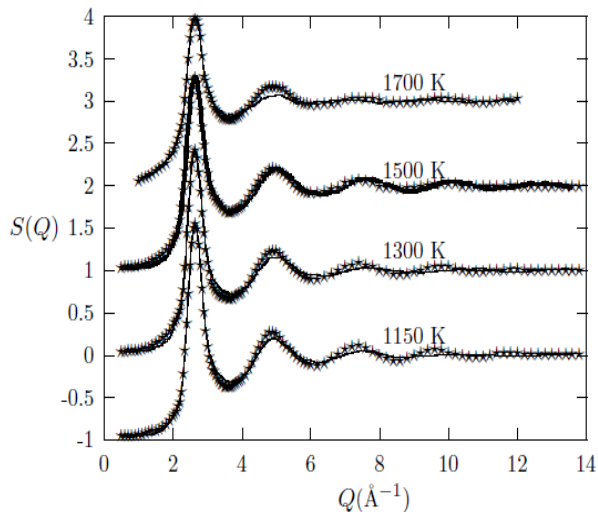


Figure 5. Temperature variation of the static structure factor, $S(Q)$, as obtained for liquid Au from RMC. The solid line denotes theoretical models and the stars denote experimental data. The experimental $S(Q)$ were taken from [22]

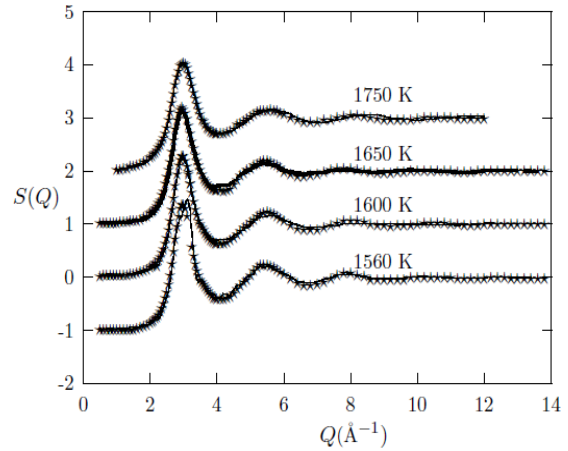


Figure 6. Temperature variation of the static structure factor, $S(Q)$, as obtained for liquid Fe from RMC. The solid line denotes theoretical models and the stars denote experimental data. The experimental $S(Q)$ were taken from [22]

It is known that orientational correlations in disordered structures could be well represented by the distribution of the cosine of the bond angles, $b(\cos \theta)$. This is defined as the probability of two neighbours within r_1^{min} from a central atom forming an angle θ with the central atom. For this reason the bond-angle distributions for liquid Cu, Au and Fe were calculated by using the results of the RMC simulations which are shown in Figures 7, 8 and 9. As seen from the figures, each of the liquid metal exhibits existence of two peaks irrespective of the cut-off radius r_c , one ranging between $\cos \theta \approx -0.241$ to -0.406 and other between $\cos \theta \approx 0.569$ to 0.620 , as seen in Table 3.

Table 3. Temperature variation of the bond angle distribution obtained from RMC simulations. Subscripts 1 and 2 denote first and second peaks, respectively

Metals	T(K)	$\cos(\theta)_1$	$\cos(\theta)_2$
Cu	1150	-0.330	0.581
	1300	-0.384	0.572
	1500	-0.406	0.590
	1600	-0.372	0.581
Au	1150	-0.296	0.614
	1300	-0.284	0.620
	1500	-0.330	0.602
	1700	-0.278	0.590
Fe	1560	-0.305	0.605
	1600	-2.241	0.596
	1650	-0.391	0.569
	1750	-0.354	0.587

The area under the first peak is much larger than that of the second peak, and with increase in temperature, the first peak broadens out becoming nearly structureless at higher temperatures while the second peak is still observable. This shows a distortion in the body-centered cubic (bcc) crystal structure of these metals at temperatures approaching their melting points and temperatures above the melting points. The distribution of the number of nearest neighbours of an

atom at a distance less than a certain value from the reference atom for all the metals at various temperatures studied were also considered. In this study, the distance was taken to be the value corresponding to the value of the position of the first minimum, r_1^{min} , in $g(r)$ (see Table 2).

In addition, $b\cos\theta$ looks very similar for all the liquid metals studied with some variation in the heights of the main peak with a distinct well pronounced maximum at $\cos\theta$ in the range of 0.569 to 0.620. These features indicate a presence of a bond-angle of nearly 60 degrees. This angle ($\theta \approx 60^\circ$) is characteristic of close-packed bonding in the systems. Since $b\cos\theta$ provides valuable information regarding local structural units and their connectivity in the liquid structures. The distribution for the central atom of an ideal 13-atom icosahedra cluster shows peaks at 63.4° , 116.4° and 180.0° [6]. Other crystallographic clusters, like hcp, fcc and bcc, we see peaks at 60° , 90° and 120° . Angles around 60° indicate nearly equilateral triangles that may well belong to tetrahedral. One might feel that the existence of 60° peaks is indicative of triplets of Cu, Au and Fe hard spheres, respectively. An interesting question pose here is whether triplets with a bond angle of 60° really exist naturally for these liquid metals. However, it is important to note that the experimental data allows a diversity of bond angles and coupled with the fact that RMC simulation always produces the structure with the highest degree of disorder that a particular set of data allows. Therefore, the clear peaks around 60° in all the metals investigated is presumed to indicate a close packed bonding, a feature typical of simple liquid structure [30]. The overall similarity in $g(r)$, $S(Q)$ and $b\cos\theta$ shows that the local structure of the liquids may be described as a distortion of the bcc crystal structures of the liquids at their melting points and temperatures above the melting points [6, 8]. It is also observed that the bond angle distribution curves obtained in this work are similar to that obtained by Howe *et al.*, [30] for molten Rb, which further corroborates our submission of possibility of the local structure of the liquid metals being that of distorted bcc crystals.

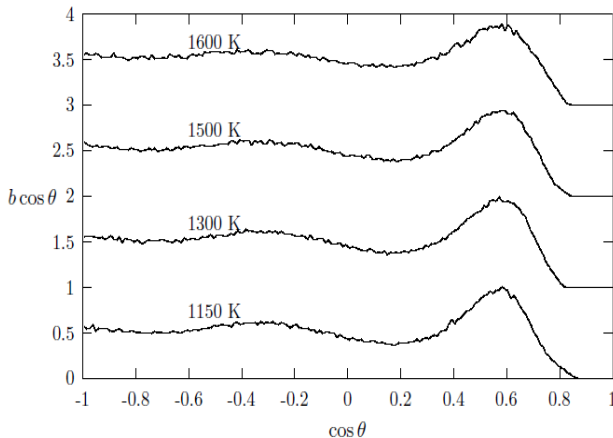


Figure 7. The bond-angle distribution, $b\cos\theta$ against $\cos\theta$ as obtained for liquid Cu at 1150 K, 1300 K, 1500 K and 1600 K, respectively

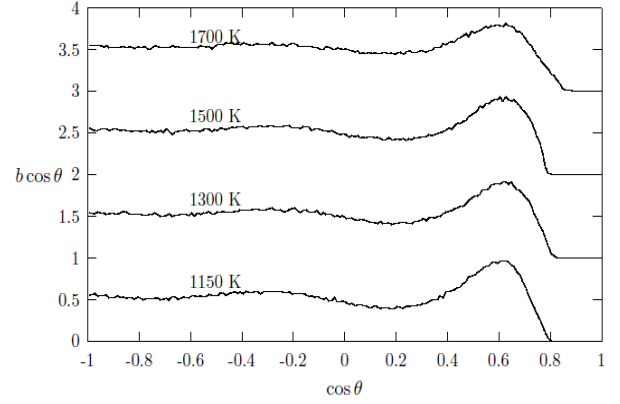


Figure 8. The bond-angle distribution, $b\cos\theta$ against $\cos\theta$ as obtained for liquid Au at 1150 K, 1300 K, 1500 K and 1700 K, respectively

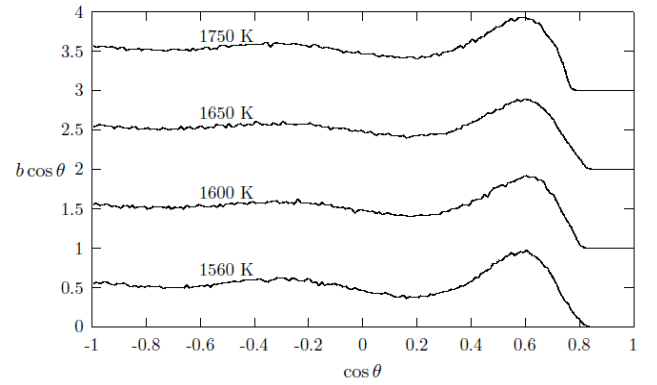


Figure 9. The bond-angle distribution, $b\cos\theta$ against $\cos\theta$ as obtained for liquid Fe at 1560 K, 1600 K, 1650 K and 1750 K, respectively

From the results of $\langle N_c \rangle$, calculated from the pair distribution functions $g(r)$ of the final atomic configuration shown in table 2, one can see that the $\langle N_c \rangle$ decreases considerably with decrease in density. This should however be expected because as temperature increases, the nearest neighbours of a central atom move further apart thereby leading to a decrease in the average coordination number of the central atom i.e. on average each atom has fewer neighbours. This observation is in line with the result of Nield *et al.*, [25] for expanded Cs which shows that the average coordination number changes directly with density.

However, for simple liquid metals and most of the weakly covalent liquids, the $\langle N_c \rangle$ is found to be ≈ 13.0 [29]. While fitting the highest temperature data for liquid metals of Cu, Au and Fe, where the density is lowest, we found that the $\langle N_c \rangle = 10.8, 11.4$ and 12.2 , respectively, which indicates that there is a decrease in $\langle N_c \rangle$ as the temperature increases. Thus, there is a gradual change from a more close-packed to a less close-packed structure. It is of considerable interest to note that the density under consideration here is around melting points corresponding to the experimental temperature in x-ray diffraction, which thus infer that local crystallization may occur in the liquid metals [8], even fast transition between crystallization and liquefaction due to the fact that the structure factor cannot distinguish between the local orders of the systems.

The study shows that the feasibility usage of RMC crosses over the phase transitions between liquid and solid. Whereas from the analysis of the structure factors and the pair distribution functions together with the positions, heights of first and second peaks of the $g(r)$, the nearest neighbour distance and the average coordination number of the liquids investigated, it is evident that [30, 31] the structure of the liquids remains nearly close-packed. Thus, as the temperature increases and density decreases, there will be a gradual change in structure of the liquids because some atoms adopt arrangements with a slightly larger near-neighbour distance, resulting in many atoms having a small number of neighbours (i.e. atoms move further apart), suggesting that they are on the surface of clusters or on 'pathways' between them thereby causing a decrease in the average coordination number of the central atom. Also, the results obtained in this study compare well with [6, 32] which were obtained using the classical methods, as the general trend that average coordination number, $\langle N_c \rangle$ of nearest neighbour atoms decreases when the density is lowered is reproduced.

4. Conclusions

Structural properties of three liquid metals Cu, Au and Fe at various temperatures close to their melting points and above, have been carried out using the reverse Monte Carlo method. The results obtained gave useful insights into the atomic configurations of the liquid metals studied. The study confirms the general trend that variation of the sample temperature is accompanied mainly by change in the intensity of the diffraction peaks, while the position of the peaks practically does not change. The overall agreement between the modeled data and experiment is good enough for a better understanding of the three dimensional structures of liquid metals, but not their dynamic properties. In addition, the observed similarity in $g(r)$, $S(Q)$, $b\cos\theta$ and $\langle N_c \rangle$ have been discussed. It is observed that the average coordination number changes directly with density throughout the whole of the density regions investigated. Therefore, it can be concluded that the position of the first peak in $g(r)$ and $\langle N_c \rangle$ indicate that the local structures in the liquid metals change from the high-coordinated state to the low-coordinated state as density decreases, and hence, there is a gradual change from a close-packed structure to a less close-packed structure in the systems investigated.

ACKNOWLEDGEMENTS

One of the authors Y. A. is grateful to Prof. O. Akinlade, Department of Physics, Federal University of Agriculture, Abeokuta, Nigeria for the data used in this study.

REFERENCES

- [1] I. Kaban, W. Hoyer, A. Il'inskii, O. Slukhovskii and S. Slyusarenko, Short-range order in liquid Silver-tin alloys, *J. Non-Cryst. Solids* 331 (2003) 254-262.
- [2] A. Mellergard and R. L. McGreevy, Reverse Monte Carlo modelling of neutron powder diffraction data, *Acta Crystallogr. A* 55 (1999) 783.
- [3] T. Petkova, P. Petkov, P. J  v  ri, I. Kaban, W. Hoyer, A. Sch  ps, A. Webb and B. Beuneu, *J. Non-Cryst. Solids* 353 (2007) 2045.
- [4] P. J  v  ri, I. Kaban, J. Steiner, B. Beuneu, A. Sch  ps and A. Webb, 'Wrong bonds' in sputtered amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$, *J. Phys.: Condens. Mat.* 19 (2007) 335212.
- [5] K. Saksl, P. J  v  ri, H. Franz, Q. S. Zeng, J. F. Liu and J. Z. Jiang, Atomic structure of $\text{Al}_{89}\text{La}_6\text{Ni}_5$ metallic glass, *J. Phys.: Condens. Mat.* 18 (2006) 7579-7592.
- [6] P. Ganesh and M. Widom, Signature of nearly icosahedral structures in liquid and supercooled liquid copper, *Phys. Rev. B* 74 (2006) 134205.
- [7] T. Tomida and T. Egami, Molecular-dynamics study of orientational order in liquids and glasses and its relation to the glass-transition, *Phys. Rev. B* 52 (1995) 3290-3308.
- [8] P. R. ten Wolde, M. J. Ruiz-Montero and D. Frenkel, Numerical calculation of the rate of crystal nucleation in a Lennard-Jones system at moderate undercooling, *J. Chem. Phys.* 104 (24) (1996) 9932.
- [9] T. Itami, S. Munejiri, T. Masaki, H. Aoki, Y. Ishii, T. Kamiyama, Y. Senda, F. Shimojo and K. Hoshino, Structure of liquid Sn over a wide temperature range from neutron scattering experiments and first-principles molecular dynamics simulations: A comparison of liquid Pb, *Phys. Rev. B* 67 (2003) 064201-12.
- [10] R. L. McGreevy and L. Pusztai, Reverse Monte Carlo simulation: A new technique for the determination of disordered structures, *Mol. Sim.* 1 (1988) 359-367.
- [11] R. L. McGreevy, M. A. Howe and J. D. Wicks, RMCA Version 3.14, A General Purpose Reverse Monte Carlo Code, June, 2005.
- [12] M. A. Howe and R. L. McGreevy, Determination of three body correlations in liquid by RMC modeling of diffraction data. I. Theoretical tests. *Phys. Chem. Liq.* 24 (1991) 1-12.
- [13] P. J  v  ri, L. Pusztai, Structure of disordered forms of selenium close to the melting point, *Phys. Rev. B* 64 (2001) 014205.
- [14] P. J  v  ri, R. G. Delaplane and L. Pusztai, Structural models of amorphous selenium, *Phys. Rev. B* 67 (2003) 172201.
- [15] K. Hoshino and F. Shimojo, Structure and electronic states of expanded and compressed liquid alkali metals by ab initio Molecular dynamics Simulation, *High Temp. Mater. Processes* 18(1-2) (1999) 79-85.

- [16] V. M. Nield and P. T. Verronen, The structure of expanded mercury, *J. Phys.: Condens. Mat.* 10 (1998) 8147-8153.
- [17] M. Mahladisa, L. Ackermann and P. E. Ngoepe, Structural properties of gold clusters at different temperatures, *South African J. Sci.* 101 (2005) 471.
- [18] I. Kaban, W. Hoyer, T. Petkova, B. Beuneu, A. Schöps and A. Webb, Atomic structure of $\text{As}_{34}\text{Se}_{51}\text{Ag}_{15}$ glass, *J. Ovonic Research* 3 (4) (2007) 67-70.
- [19] G. Evrard and L. Pusztai, Reverse Monte Carlo modelling of the structure of disordered materials with RMC++: a new implementation of the algorithm in C++, *J. Phys.: Condens. Mat.* 17 (2005) S1-S13.
- [20] R. L. McGreevy, RMC – progress, problems and prospects. *Nucl. Instrum. Methods Phys. Res., A, Accel. Spectrum. Detect. Assoc. Equip.*, 354 (1995) 1–16.
- [21] R. L. McGreevy, *Computer Modelling in Inorganic Crystallography* ed C. R. A. Catlow (New York: Academic) p151, 1997.
- [22] Y. Waseda, *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York, 1980.
- [23] R. L. McGreevy, Reverse Monte Carlo modelling, *J. Phys.: Condens. Mat.* 13 (2001) R877.
- [24] O. Gereben, G. Evrard, L. Pusztai, RMC++ version 2 (2005); available at: <http://www.szfki.hu/nphys/rmc++/opening.html>
- [25] V. M. Nield, M. A. Howe and R. L. McGreevy, The metal-non metal transition in expanded cesium. *J. Phys: Condensed Matter* 3 (1991) 7519-7525.
- [26] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for open-shell transition metals, *Phys. Rev. B* 48 (1993) 13115.
- [27] A. Pasquarello, K. Laasonen, R. Car , C. Lee and D. Vanderbilt, *Ab initio* Molecular Dynamics for d - Electron Systems: Liquid Copper at 1500 K, *Phys. Rev. Lett.* 69 (1992) p1982.
- [28] A. Il'inskii, I. Kaban, S. Slyusarenko, W. Hoyer, *Phys. Met.* 14 (8) (1995) 927.
- [29] A. G. Il'inskii, I. G. Kaban, S. I. Slyusarenko, W. Hoyer, *Metallofizika* 15 (8) (1993) 42.
- [30] M. A. Howe, R. L. McGreevy, L. Pusztai and I. Borzsak, Determination of three body correlations in simple liquids by RMC modelling of diffraction data. II. Elemental liquids, *Phys. Chem. Liq.* 25 (1993) 204.
- [31] A. Il'inskii, S. Slyusarenko, O. Slukhovskii, I. Kaban, W. Hoyer, Structural properties of liquid Fe-Si alloys, *J. Non-Crystal. Solids* 306 (2002) 90-98.
- [32] M. M. G. Alemany, J. L. Martins and B. J. Costa Cabral, First-principles molecular dynamics of liquid rubidium at low density, *J. Non-Cryst. Solids* 347 (2004) 100.