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An ab initio molecular dynamics calculation of the density of the liquid metallic alloy Al–Si₁₂at% as a function of temperature

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ABSTRACT

The study of liquid metallic alloys using first principles Molecular Dynamic (MD) requires the knowledge of the liquid phase density that is not easy to obtain experimentally. In this work we calculate the densities for the liquid phase of eutectic Aluminium–Silicon alloy in the range of temperature from 856 K to 1270 K (The melting point for this alloy is 850 K). We build an atomic model in a periodic cubic cell with 125 atoms, 110 aluminium atoms and 15 silicon atoms. We then heat it from room temperature to the temperature of calculation T_{\max} , above the melting temperature, in 100 computational steps and we maintain the cell at this temperature (*plateau*) during 100 computational steps. Finally we apply a volume optimization of the structure to find the desired density. This process is carried out several times until a minimum energy structure is reached. The results are compared with the experimental values.

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1. Introduction

The structures of disordered solid can be generated in different ways. One method to generate them is from the molten state but their disordered properties are modified by the quench process [1–3]. Understanding the atomic structure of liquid alloys or pure elements has been a challenge in materials science. In the last decades the computational study of the structures and their properties has been carried out with *ab initio* methods [4–13], these results have provided a quantitative picture about the microstructure of the liquid. Experimental knowledge of the structure of the liquid phase of pure and alloyed elements has been scarce [14–16]; the information about the structure is obtained from the structure factor which when Fourier transformed leads to Radial Distribution Functions. From the simulational viewpoint we can observe their atomic environment so that the contribution of each element to the RDFs can be discerned. Since the *ab initio* methods often need some experimental parameters like the atomic density, and since this parameter is difficult to measure it becomes necessary to find a way to determine the density theoretically or simulationally. In this work we present a calculation of the liquid atomic density for the Aluminium–Silicon (Al–Si) eutectic alloy in

the liquid state, for the temperature range from 856 K to 1270 K (the melting temperature is 850 K) and compare our results with some existing experimental data [17,18].

2. Methodology

Using the DMol³ code in the Materials Studio suite produced by Accelrys (Version 3.2) [19], we perform a molecular dynamics process that implements the Harris functional [20] and a Linear Combination of Atomic Orbitals (LCAO) as the basis set. We also use the Local Density Approximation (LDA) of Vosko-Wilk-Nusair [21] to generate the liquid structure. The electronic parameters utilized are as follows: the core was treated as full electron, the basis set were taken as double numeric (dn), the cut-off for the wave functions is 5 Å and the time step used was 9.29 fs.

To do the calculations we applied the following *ab initio* MD process to 8 cubic supercells with 125 atoms which contained 110 Al and 15 Si atoms to form the Al–Si₁₂at% alloy. Each process started at room temperature (300 K) and with an initial density of 2.70 g cm⁻³, the density of the crystalline eutectic alloy [22]. Then the sample was linearly heated in 100 computational steps to reach the maximum temperature (T_{\max}) above the melting point and within the range of 856 K–1270 K. Next the sample was maintained at a constant temperature T_{\max} during 100 computational steps and then cooled down to 0 K in 2 computational steps. By analogy with the computational process that we have

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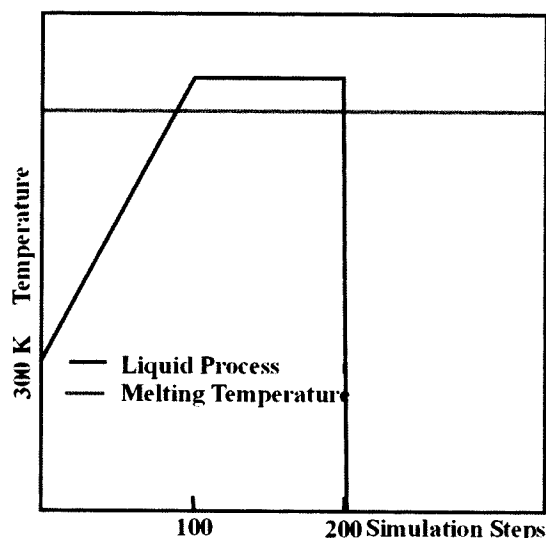


Fig. 1. Diagram of the Truncated San Diego Process (TSDP). The supercell is linearly heated in 100 steps from 300 K to T_{max} , then maintained at this temperature during 100 steps (plateau) and finally cooled down to 0 K in 2 steps.

developed to amorphize solids, the *undermelt-quench* approach, or the San Diego approach [23], we call this process the “Truncated San Diego Process” (TSDP) (Fig. 1).

We calculate the total energy of each structure generated after the first 200 steps (at the temperature T_{max}) and then minimize the cell volume several times until the final energy does not diminish any longer. This minimization is done by varying the lattice parameters, but not the angles, in a manner similar to the method of Parinello–Rahman [24] except that we do it manually by expanding and contracting the cell symmetrically along the x, y and z axis, keeping the fractional coordinates of the atoms fixed during the process. We use the Harris approximation avoiding the self-consistency issue of other approximations. The lattice parameter of the minimized volume is used in a new *ab initio* MD simulation in the TSDP process at the T_{max} plateau and then again we minimize the energy of each supercell until the final energy seems to fluctuate but does not openly diminish any longer, Fig. 2. The process is applied around seven times to each supercell, and we show the results below.

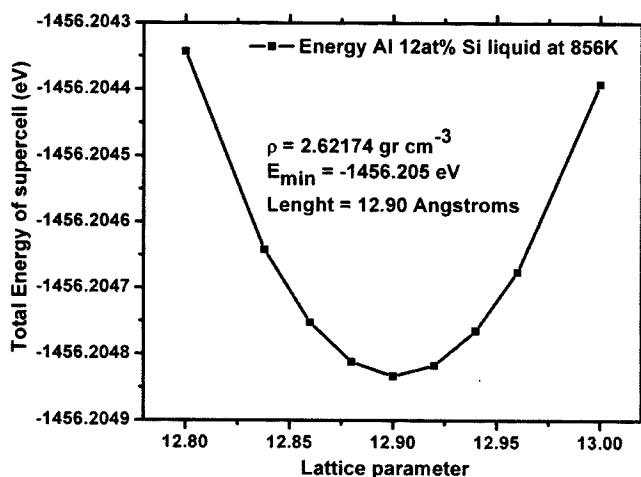


Fig. 2. Variation of the total energy of a structure obtained after 200 MD steps of the TSDP at $T_{max} = 856$ K, as a function of the lattice parameter maintaining the atomic fractional coordinates fixed. The value that minimizes the total energy is used in the new MD.

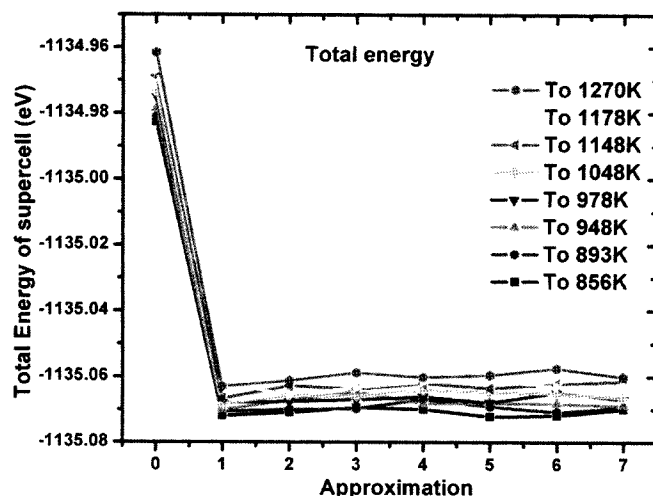


Fig. 3. Total energy for each minimization process at the 8 liquid temperatures studied (T_{max}). The energy difference between the zero and the first approximation is drastic but the difference between the first and the next approximations is minimal.

3. Results

We calculate the volume (lattice parameter) that minimizes the total energy and use it in the next MD run until the final energy is essentially constant. *Grosso modo* seven different MDs are needed to approach the “correct” density of the liquid metallic alloy Al–Si₁₂at% for each T_{max} . We plot the minimized energy for each of the seven supercell volume optimizations at each temperature and these are shown in Fig. 3. Looking at all seven approximations we see that the first supercell volume optimization gives us a very good density approximation as can be seen if we plot all seven approximations for the 8 liquid temperatures studied (Fig. 4). The change in energy between the initial structure (zero approximation) and the first structure (first approximation) is drastic but no radical changes are observed for the subsequent structures. We compare the density values that we obtained with the experimental results and this is shown in Fig. 5. Simulation and experimental values agree quite well when the values in Reference [18] by Xiufang et al. (published in 2006) are considered. The values

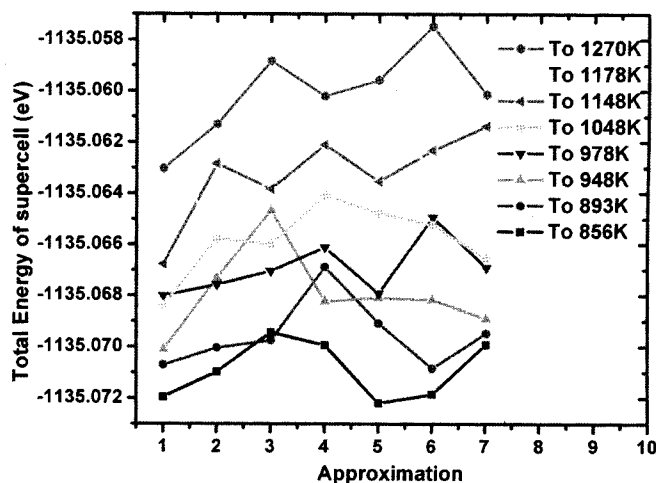


Fig. 4. In almost all cycles of the volume optimization, the first approximation is lower in energy. Had we done more cycles, perhaps lower energies could have been found but the computational cost would have been higher.

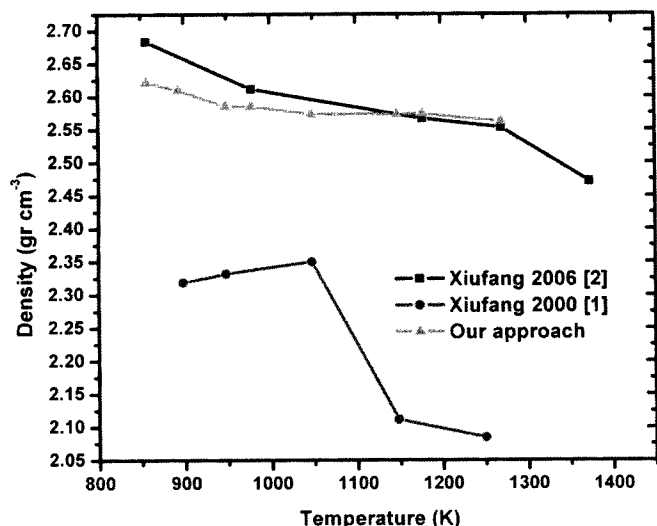


Fig. 5. Density values obtained in the first approximation (green triangles) compared with the 2006 data of Xiufang et al. [18] (black squares) and the 2000 data of Xiufang et al. [17] (red circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

The column "Experimental values" shows the density values obtained by Xiufang et al. The "Computational values" are our results. The experimental and computational values agree to within 2.4%.

Temperature (K)	Experimental values (g cm ⁻³)	Computational values (g cm ⁻³)	Difference between experimental and theoretical values (g cm ⁻³)	Percent difference (%)
856	2.6835	2.62174	0.06176	2.356
898		2.60958		
948		2.58550		
978	2.6114	2.58550	0.02590	1.002
1048		2.57356		
1148		2.57356		
1178	2.5664	2.57356	-0.00716	0.278
1270	2.5529	2.56170	-0.0088	0.344

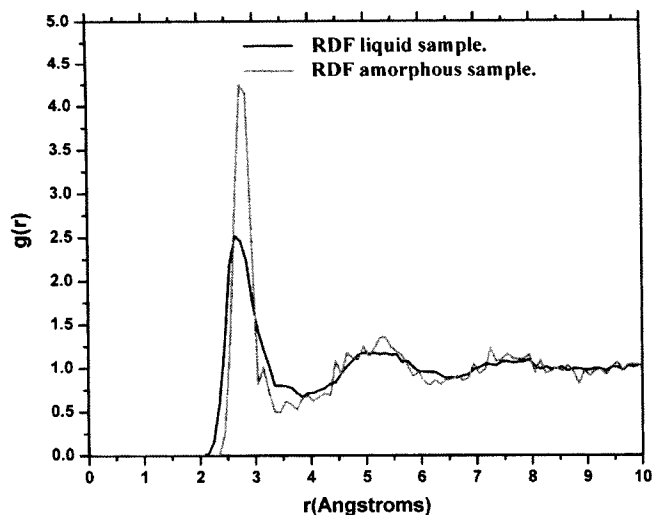


Fig. 6. Radial Distribution Functions (RDFs) of disordered samples. The RDF of the liquid sample (Red line) was obtained for a 1270 K temperature, whereas the black line corresponds to an amorphous sample. The difference is evident (see text) and points at the fact that our present sample is indeed liquid. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported in Reference [17], also by Xiufang et al. (2000), disagree markedly with our calculations. So our results for the density values of the liquid phase of the Al–Si eutectic alloy based on the first approximation of the energy minimization is a good estimate for the density in the liquid phase. The density values are shown in Table 1.

We calculated the Radial Distribution Functions (RDF) for the highest temperature in the liquid phase, 1270 K, and compared it with the RDF of the Al–Si_{12at%} amorphous system [3]. The liquid curves show a spread in the first peak, whereas the corresponding peak for the amorphous is more localized. The second and third peaks of the liquid are smoother than the corresponding ones for the amorphous, Fig. 6. This behaviour, together with the less pronounced valleys in the RDFs point at the existence of a liquid [25] in our simulations.

4. Conclusions

The method presented here to calculate the density of the liquid eutectic metallic alloy Al–Si_{12at%} based on the minimization of the total energy of the samples as a function of the volume of the supercells seems to give good results. Our seven minimizations manifest something interesting: The fact that the first approximation is good enough to give confident results for the atomic density. Since the experimental results are scarce it seems reasonable to stop here and try to do more refined calculations when experiment demands.

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