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***Ab initio* molecular dynamics simulation on temperature-dependent properties of Al–Si liquid alloy**

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Abstract

We have carried out *ab initio* molecular dynamics simulations on Al–15% Si liquid alloy at different temperatures. The temperature dependences of energy, volume, diffusion coefficient and structure factor have been studied. The theoretical structure factors are in agreement with the experimental data. The obtained results suggest that the structure properties near 1100 K have different behaviour from that at higher temperature.

1. Introduction

Understanding the structure of a liquid has been a challenge in materials science and condensed matter physics. The invention of the *ab initio* molecular dynamics method, in which the interatomic forces are calculated based on the density functional theory, has uniquely made it possible to theoretically predict the liquid structure. Over the past two decades, the structures and properties of many elementary liquids have been studied by the *ab initio* molecular dynamics method [1–9], and the results obtained have provided a quantitative picture for the microstructure of the liquid. However, the structure of a liquid alloy is usually more complicated than that in an elementary liquid. Recently, it has been reported that liquid alloys can have structural changes or phase transitions at temperatures well above the melting temperature [10, 11]. Such a discovery has added a new ingredient to condensed matter physics and will be important to material science.

The Al–12.6% Si binary alloy is a eutectic system in which silicon doping reduces the thermal expansion coefficient, increases corrosion and wear resistance and improves the casting and machining characteristics of the alloy, and thus it attracts much attention in materials science and has been commercially used in engine applications [13]. Studies of the liquid state of Al–Si alloys also have primary importance in the understanding of the physical properties of Al–Si alloys in the solid state. In fact, experiments have suggested that Al–12.6% Si shows structure changes near 1100 K [11]. Liquid Al is a simple metal with a coordination number of 11.5 [12]. Liquid Si is also metallic, but has a complicated structure with a coordination number

of 6.4 [12], where the covalent bonding is still playing an important role. It is interesting to know how the small amount of Si doping changes the properties of the liquid Al.

In this paper, motivated by experimental data and general interests in this binary alloy, we have studied Al–15% Si liquid alloy from 930 to 2173 K using the *ab initio* molecular dynamics method.

2. Computational details

Our calculations are based on the density functional theory with the local density approximation (LDA); the interaction between the core and the valence electrons of the atom is modelled by the ultrasoft pseudopotential, as implemented in the Vienna *Ab initio* Simulation Package (VASP) [14]. The wavefunctions are expanded in plane waves, with an energy cutoff of 188 eV, which can correctly predict the lattice constant of solid Al and Si with an error of 1%. The simulation cell contains 54 Al atoms and 10 Si atoms, which approximately corresponds to an Al–15% Si alloy. Four special *k*-points are used in the Brillouin zone sampling. All 64 ions are put in a simple cubic box with periodical boundary condition. The temperature-dependent box size is adjusted to make the internal pressure approximately equal in all the simulations. Our microcanonical ensemble simulations have been performed at seven different temperatures from 930 to 2173 K. We use the Verlet algorithm to integrate Newton's equations of motion and the time step of ion motion is 4 fs. At each temperature, after equilibrating for about 4 ps, the simulation is performed for another 16 ps to collect the trajectories for analysing structural properties.

The sample was prepared as following. At first, we put 64 Al atoms in a simple cubic cell with fcc structure and then randomly substitute 10 Al atoms with Si atoms. After giving a small displacement to each atom, micro-canonical simulation was performed for more than 8 ps. Then we got a liquid with very high temperature. By gradually decreasing the hot liquid and adjusting the box size, we arrived at a liquid with 930 K, at which the structure of the liquid was simulated and analysed. To get a higher temperature sample, we simply scale the velocities of atoms and box size, then the system is equilibrated for about 4 ps. In order to study the temperature-dependent properties of the Al–15% Si alloy, we repeated this procedure and performed simulation at seven temperatures: 930, 1138, 1313, 1444, 1758, 1916 and 2173 K.

3. Results and discussion

3.1. Dynamical properties

We have studied the dynamical properties of the liquid alloy by calculating the mean square displacement (MSD), defined in the conventional way,

$$\langle \Delta \vec{r}_\alpha(t)^2 \rangle = \frac{1}{N_\alpha} \langle |\vec{r}_{i\alpha}(t + t_0) - \vec{r}_{i\alpha}(t_0)|^2 \rangle \quad (1)$$

where the summation goes all over N_α of the α species, \vec{r}_i is the coordinates of atom i , t_0 is the arbitrary origin of time; the average is taken for all possible t_0 . In the liquid state, the behaviour of the MSD in the limit of long time is proportional to time, which is correlated to the diffusion coefficient D by the so-called Einstein relationship:

$$D = \frac{1}{6t} \langle \Delta \vec{r}_\alpha(t)^2 \rangle. \quad (2)$$

Figure 1(a) shows the calculated MSD for Al atoms at 930 K, it clearly shows a linear behaviour with simulation time, which also confirms that our sample is well in the liquid state.

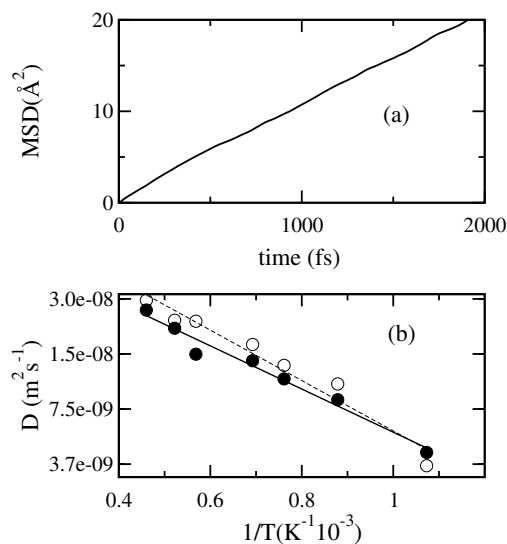


Figure 1. (a) Mean square displacement (MSD) of Al–Si liquid at 930 K. (b) Diffusion constant of Al (black circle) and Si (empty circle) atoms in the Al–Si alloy, the solid line and dashed line are the fitted results, respectively. D is plotted in logarithmic scale.

In fact we also checked our sample below 850 K and found that the linear relation of the MSD with time does not hold, and the atoms are moving around the equilibrium position, which indicates the sample is in solid state. According to the Einstein relationship, we can easily calculate the diffusion coefficient of the Al atoms and the Si atoms in Al–Si alloys. In figure 1(b), we show the diffusion coefficient of the Al and Si atoms at various temperatures. One can see that the temperature dependent diffusion coefficient follows the Arrhenius relationship

$$D = D_0 e^{-E_a/k_B T} \quad (3)$$

where E_a is called the activation energy, T is the temperature, D_0 is the pre-exponential factor and k_B is the Boltzmann constant. By a linear least squares fit of $\ln D$ via $1/T$ (figure 1(b)), the obtained E_a and D_0 are 0.23 eV and $8.42 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, respectively for Al atoms (figure 1(b)). To our knowledge, there is no direct experimental data for the diffusion coefficient in Al liquid, but we can compare with other simulation results. From the fitted results of D_0 and E_a , one can get the diffusion coefficient of $5.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for Al atoms at 1000 K, which is in agreement with previous *ab initio* results, $5.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [15]. We have also calculated the diffusion coefficient for Si atoms in the Al–Si alloy, as shown in figure 1(b). The obtained D_0 and E_a are $1.35 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and 0.27 eV, respectively, in excellent agreement with experimental values $1.34 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and 0.31 eV [16] for Si atoms as an impurity in the liquid Al. One can note that the activation energy for the diffusion of Si atoms is about 15% larger than that for Al atoms, and also the coefficient D_0 , proportional to the jumping frequency, is about 20% larger than that for Al atoms; all these results indicate that bonding of Si atoms to their neighbours is different from the counterparts of Al atoms, the residual covalent bonding could probably exist in such an alloy.

The size of the simulation cell was adjusted at each temperature by approximately keeping internal pressure as a constant. Figure 2(a) shows the calculated internal pressure statistically averaged over the simulated trajectories. The variation at different temperatures is within

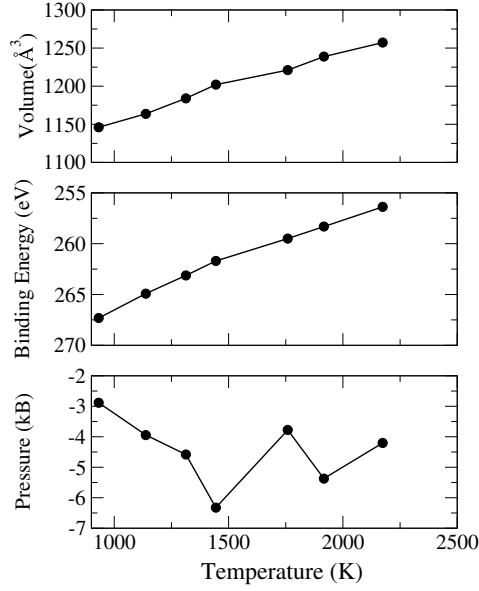


Figure 2. Calculated properties of Al-15% Si alloy at different temperatures. Lower panel: the internal pressure; middle panel: total binding energy for all atoms in the simulation cell; upper panel: the volume of the simulation cell.

5 kbar, corresponding to 0.1% volume change or less. We believe such a small pressure variation will not bring significant errors for the comparison of structural properties at different temperatures. On the other hand, as is well known, the calculated value of the pressure is also very sensitive to the choice of the energy cut-off in the plane-wave scheme, and we find that in our sample the higher the energy cutoff is, the larger the internal pressure. If we repeat the calculation with higher energy cut-off, the internal pressure is very close to zero, but the structural properties do not change. Figure 2 also shows the temperature-dependent energy and volume. The total binding energy of the simulation cell decreases monotonically with increasing temperature. One can approximately consider that the volume has a linear relation with temperature. It is known that the liquid density (ρ) and temperature (T) satisfy the following equation:

$$\rho = \rho_m - \Lambda(T - T_m) \quad (4)$$

where ρ_m is the density at the melting point, T_m is the melting point and Λ is the isobaric expansion coefficient. From our calculated results as shown in figure 2(c), we can get $\Lambda = 0.18 \text{ kg m}^{-3} \text{ K}^{-1}$, which is comparable to the experimental value of $0.35 \text{ kg m}^{-3} \text{ K}^{-1}$ for pure liquid Al [17].

3.2. Structural properties

The structure factor is the most common quantity to statistically show the structural information, which is defined as following,

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \left| \sum_{\mu=1}^N e^{-\mathbf{k} \cdot \mathbf{r}_\mu} \right|^2 \right\rangle \quad (5)$$

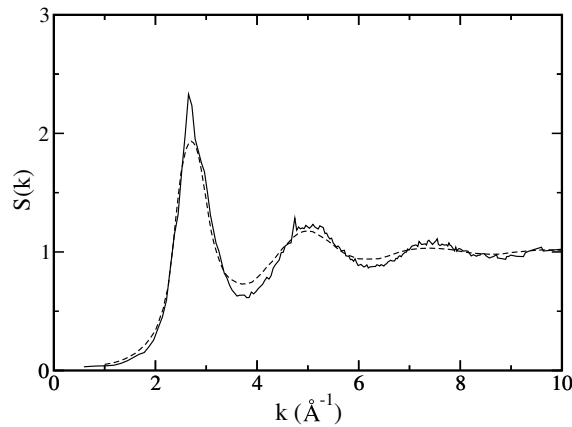


Figure 3. The calculated structure factor $S(k)$ of pure Al liquid at about 1250 K. The dashed curve is the experimental result at 1332 K [18]. The simulated results are in satisfactory agreement with experimental data.

where N is the total number of atoms in the simulation cell, \mathbf{r}_μ is the coordinates of the μ th atom and \mathbf{k} is the reciprocal vector. One can easily get the pair correlation function by Fourier transformation of structure factor, or directly calculate it through the following definition:

$$g(r) = \frac{1}{\rho_0 N} \left\langle \sum_{i \neq j}^N \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle \quad (6)$$

where ρ_0 is the number density of the liquid, and \mathbf{r}_{ij} is the interatomic distance between atom i and j . Figure 3 compares the experimental and calculated structure factor of pure Al liquid. One can find that the agreement is quite good, especially the position of the peaks, although a slight difference can be found in the height of the peaks which is a systematic error caused by the LDA approximation.

We have calculated the structure factor and pair correlation function of Al–Si alloys, as shown in figure 4, the experimental data at 1148 K are also shown. Comparing the calculated results ($T = 1138$ K) and experimental data ($T = 1148$ K), one can see that the agreement is reasonably good. However, we have noticed that the obtained position of the first peak is in good agreement with experimental data, but there is a small difference in position of the second peak, the calculated value is slightly smaller. From the low temperature to high temperature, there is no dramatic change in the structure factor. Even so, one can find that the position of the second peak has a slight shift to the right side and the height of the peaks decreases with the increasing temperature. Figure 5 plots the height of the first peak at various temperatures. As one can expect, the height of the peak monotonically decreases with temperature. However, it does not show a linear behaviour, it drops very quickly from 900 to 1200 K. Experiment has shown a sharp drop in the height of the first peak in the structure factor near 1100 K [11], which implies that structural change at this temperature range is quicker. Thus, our calculations have qualitatively confirmed the experimental observation. However, more theoretical evidence is needed to conclude that this is a structural change of the liquid.

Figure 6 shows the variation of the pair-correlation function ($g(r)$) with temperature. The position of the first peak is 2.75 Å, very close to the experimental value 2.78 Å [17]. To further demonstrate the local structure of the liquid, we have calculated the partial pair correlation function for Al and Si atoms, as shown in figure 7. The first peak position of the Si partial

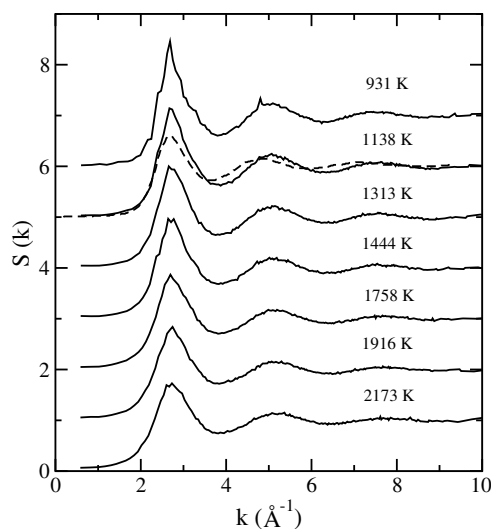


Figure 4. The total structure factor $S(k)$ of the simulated Al–15% Si alloy. The dashed curve is the experimental result of the Al–12.6% Si liquid at 1148 K.

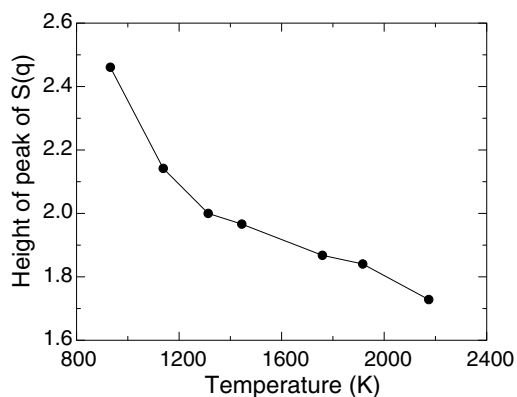


Figure 5. Temperature-dependent height of the first peaks in $S(k)$ of the simulated Al–15% Si alloy.

$g(r)$ is about 0.2 \AA smaller than that in the Al partial $g(r)$. The shape of the first peak for Si is sharper than that for Al in the low temperature, and becomes similar as the temperature increases. In coordination number calculation we chose 3.6 and 3.3 \AA as the cutoff for Al–Al bond length and Si–Al bond length, respectively. At about 930 K , Al atoms have about 11.5 neighbours, very close to what is observed in the pure Al liquid. As the temperature increases, the number of neighbours decreases monotonically and, up to 2173 K , it becomes only 10 . It is known that Si atoms have about 6.4 neighbours in the pure liquid Si, while in the Al–15% Si alloy, Si atoms have about two neighbours more, but it is about three neighbours fewer than that of Al atoms, which further indicates that the intrinsic bonding of Si partially remains in the Al–Si alloys. We have also noticed that the changes of coordination number for both Al and Si atoms in the range 930 – 1450 K is faster than that at higher temperature. This is consistent with what has been found in the structure factor (as shown in figure 5).

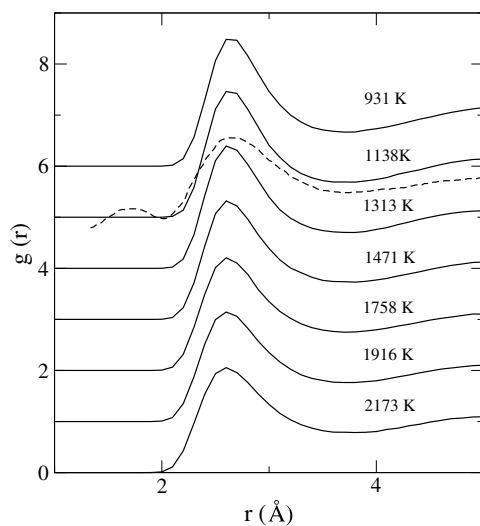


Figure 6. The pair correlation function $g(r)$ of the simulated Al–15% Si alloy. The dashed curve is the experimental result of Al–12.6% Si liquid at 1148 K.

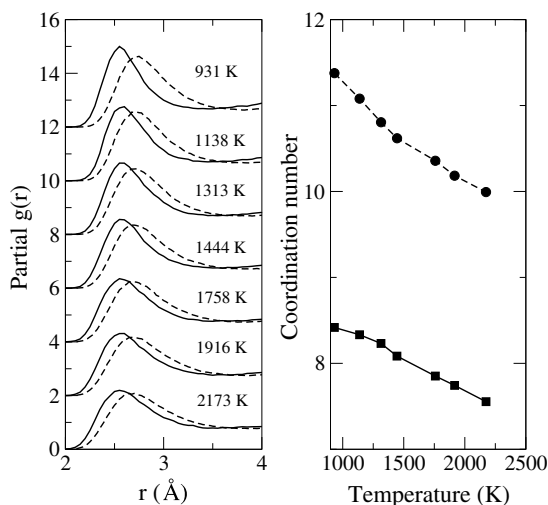


Figure 7. Left panel: temperature dependence of partial pair-correlation functions in Al–15% Si for Al–Al atoms (dashed line) and for Si–Al atoms (solid line); right panel: temperature dependence of the coordination numbers for Al atoms (solid circles) and Si atoms (solid squares), where the cutoff of the bond length is 3.6 and 3.3 Å for Al and Si, respectively.

4. Summary

By using the *ab initio* molecular dynamics method, we have simulated the structure of Al–15% Si alloy and its temperature dependence. The diffusion coefficient, activation energy, structural factor and pair-correlation function have been calculated. We find that the temperature dependence of the diffusion coefficient from 930 to 2173 K for both Al and Si atoms follows the Arrhenius relationship, with activation energy of 0.23 and 0.27 eV for Al and Si atoms, respectively. The larger activation energy and smaller coordination number for Si atom than

that for Al atoms indicates that the residual directional bonds of Si atoms can exist in the Al–Si alloy. From the coordination number and the structure factor, we do find that the change around 1100 K is faster than that at the higher temperature, which is qualitatively in agreement with experimental observation. However, to conclude that this is a liquid–liquid phase transition in this temperature range of Al–Si alloys, further theoretical and experimental studies are needed.

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