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1990 J. Phys.: Condens. Matter 2 SA227

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***Ab initio* molecular dynamics simulation of molten KSi**

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Received 3 September 1990

Abstract. We describe a recently proposed molecular dynamics scheme, which allows simulations using forces obtained from accurate quantum mechanical calculations. We apply this scheme to molten KSi, which is known to form Zintl-like ions $(\text{Si})_4^{4-}$ in the solid state. It is shown that these complexes tend to lose their identity in the liquid phase, and that Si atoms form an extended network with threefold-coordinated sites.

1. Introduction

Liquid semiconductors pose a special challenge to conventional computer simulation techniques. Indeed, it is very difficult to represent, with an effective potential, the complex interactions and subtle quantum mechanical effects characterizing the chemical bonding in these systems. These difficulties are exaggerated in liquid alloys, where one needs to describe the delicate chemical balance between different species.

Recently [1], a unified approach to molecular dynamics (MD) and density functional theory [2] (DFT) was proposed, which allows one both to overcome the need for effective potentials, and to avoid the calculation of all of the quantum mechanical interactions between atoms at every step of an MD simulation. We shall refer to this computational scheme as *ab initio* MD. A growing body of experience has proven *ab initio* MD to be a viable and highly accurate tool [3–7].

In this work we review the theoretical basis of the method and apply it to a rather complex system, namely molten KSi. This is a member of a very interesting class of alloys obtained by mixing alkali metals with group-IV elements. Extensive studies of Sn and Pb liquid alloys have shown several anomalies in their thermodynamical [8, 9] and transport properties [10, 11], as well as a pronounced first diffraction peak at $\sim 1 \text{ \AA}^{-1}$ [12, 13]. These anomalies have been connected [14] with the possible formation of Zintl ions in the melt, namely of polyionic complexes such as $(\text{Pb})_4^{4-}$ or $(\text{Sn})_4^{4-}$, which are known to be present in the solid phases of these alloys. It would be interesting to simulate directly Sn and Pb alloys, for which a complete set of experimental data is available. Although feasible, such a project is complicated by technical difficulties, such as the need to treat explicitly the effect of the uppermost *d* core levels, and to include relativistic effects. For these reasons we have chosen to study KSi which does not present such complications, although no experimental data are yet available. Our study will allow us to explore the feasibility of first-principles simulation of I–IV compounds, and for once we will allow theory to precede experiment.

Furthermore, as we shall show, our results may also have some bearing on the understanding of the heavier alloys. The pair correlation functions computed for KSi are apparently consistent with the picture of a liquid composed of Zintl ions. Yet the structure attained by Si atoms in the system is much more complex, with Zintl ions only partially surviving as independent entities.

2. *Ab initio* molecular dynamics

In our MD simulation the ionic forces are derived from the many-body potential $\Phi[\{\mathbf{R}_I\}]$ calculated from the electronic ground state within DFT. $\Phi[\{\mathbf{R}_I\}]$ defines the Born–Oppenheimer (BO) potential energy surface for the ions. The electronic ground state is attained by minimizing the energy functional $E[\{\psi_i\}, \{\mathbf{R}_I\}]$ with respect to the ‘electronic degrees of freedom’ $\{\psi_i\}$

$$\Phi[\{\mathbf{R}_I\}] = \min_{\{\psi_i\}} E[\{\psi_i\}, \{\mathbf{R}_I\}].$$

The functional $E[\{\psi_i\}, \{\mathbf{R}_I\}]$ is given by [2] (using atomic units $e = \hbar = m_e = 1$):

$$E[\{\psi_i\}, \{\mathbf{R}_I\}] = \sum_i^{\text{occ}} \int d\mathbf{r} \psi_i^*(\mathbf{r}) (-\frac{1}{2}\nabla^2) \psi_i(\mathbf{r}) + \int d\mathbf{r} V^{\text{ext}}(\mathbf{r}) \rho_e(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho_e(\mathbf{r}) \rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\text{xc}}[\rho_e] + \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (1)$$

Here

$$\rho_e(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

denotes the valence electron pseudo-charge density, $V^{\text{ext}}(\mathbf{r})$ is the total ionic pseudo-potential acting on the valence electrons, Z_I are ion core charges and the state sum extends over the occupied (valence) states. $E^{\text{xc}}[\rho_e]$ is the exchange–correlation energy functional [2], for which we adopt the local density approximation (LDA). The single-particle states $\{\psi_i\}$ are subject to orthonormality constraints ($\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij}$). The minimization in equation (1) can be carried out in different ways: We find it most convenient to follow the generalized Lagrangian formulation of [1]. In this approach, the interparticle potential is optimized dynamically via a fictitious classical equation of motion for the electrons. The system is prepared in a long-lasting metastable state, in which ions and electrons are not in thermal equilibrium, with the ‘electronic’ temperature being much less than that of the ions. Under these conditions ionic trajectories, initially lying on the BO surface, deviate from it very slowly on the time scale of MD simulations. In general, for systems with a gap, very few electron quenches are necessary during an MD run. This is the case for the system studied here.

We have investigated KSi with a constant-volume MD simulation. The macroscopic density (ρ) has been chosen to be about 10% smaller than that of the crystal, consistent with what is found for most of the I–IV alloys. The MD cell contained 32 K and 32 Si atoms, with periodic boundary conditions of the simple cubic type. The average temperature was kept at $T = 1700$ K, close to the experimental melting point of Si ($T_m = 1680$ K). In the absence of direct experimental data, these appeared to be reasonable guesses for the

relevant thermodynamic parameters of molten KSi. We used non-local norm-conserving pseudopotentials [15] for Si, expressed in the Kleinman–Bylander factorized form [16]. *s*-only non-locality was considered. Instead, we adopted a local pseudopotential of the Harris–Jones type [17] for potassium. The electronic orbitals were expanded in plane waves with an energy cut-off of 8.8 Ryd. Only the Γ point, $\mathbf{k} = (0, 0, 0)$, was used to sample the Brillouin zone of the MD supercell. The integration time step was 8 au (1.9×10^{-16} s), while the fictitious ‘mass’ μ [1] was taken to be 300 au. This choice of parameters guarantees an accurate adiabatic evolution of the system over a relatively long MD run.

3. Results and discussion

As a preliminary test of the accuracy of our calculation we have determined the equilibrium lattice constant of the solid at $T = 0$. This is a complicated crystal structure [18] with 64 atoms in the cubic unit cell. Its most striking feature is the presence of almost tetrahedral $(\text{Si})_4$ units. Each Si has three first neighbours at approximately the same distance. The value obtained for the equilibrium lattice constant is about 6% smaller than the experimental one. This discrepancy is larger than that normally found in LDA calculations. In our opinion it is mainly due to the neglect of non-linear core corrections [19] for K, which is known to lead to shorter bond lengths. The initial configuration for our calculation has been obtained by imposing a small random displacement on the perfect crystal positions. We then melted the system and brought it to a temperature of 1700 K. After a long equilibration (≈ 1 ps), we collected statistics for about 3.3 ps. The resulting pair correlation functions are displayed in figure 1. The radial distributions $g_{\text{Si-K}}(r)$ and $g_{\text{K-K}}(r)$ have little structure, whereas $g_{\text{Si-Si}}(r)$ exhibits a very strong first peak. Si atoms are found to have an average coordination number of about 3, in conformity with what one would expect from systems forming Zintl-like ions. A closer examination of the ionic coordinates, however, reveals that this is not necessarily the case. Using the first minimum of $g_{\text{Si-Si}}(r)$ (≈ 6 au) as a cut-off distance to distinguish between bonded and non-bonded atoms, we have made a further analysis. This shows that:

- (i) 50% of the Si atoms are threefold coordinated, and the remaining are twofold (30%) and fourfold coordinated (20%);
- (ii) only a fraction of the Zintl ions survives as separate entities in the liquid.

In fact, the majority of atoms tend to form a large extended network. The number of atoms in the cluster vary in time when individual Zintl ions leave or join the network. The number of isolated Zintl ions oscillates between zero and three in our small sample. At this stage, we cannot quantitatively predict the free Zintl concentration; we also expect that this may be altered by changing the thermodynamic parameters of the alloy. We note that even when Si atoms belong to the cluster, a Zintl-like coordination is maintained, as is apparent from the pair correlation function. The Si–Si bond angle distribution, $A(\theta)$, also reflects this property. As shown in figure 2, $A(\theta)$ has a very sharp maximum centred at 60° , plus a broader secondary maximum roughly centred around the tetrahedral angle. The secondary maximum is absent in the crystal structure, and reflect the presence of a larger variety of bonding configurations in the liquid.

From an analysis of the electronic distribution of the system, we find maxima of the charge density in the Si–Si bonds, which indicate that the chemical bond is prevalently covalent.

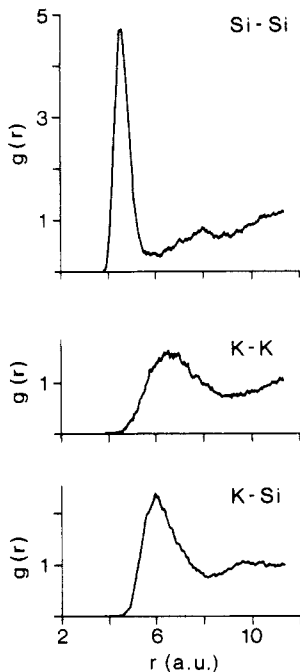


Figure 1. Computed radial distribution functions $g(r)$ for molten KSi.

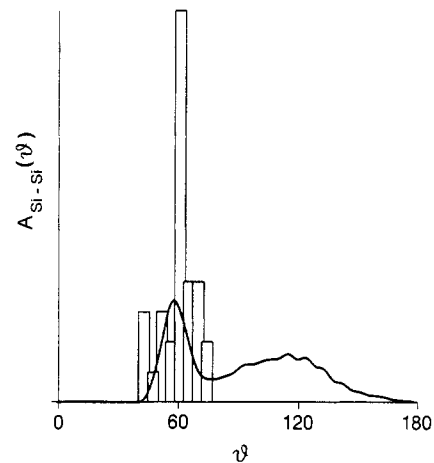


Figure 2. Angular distribution ($A_{\text{Si-Si}}(\theta)$) of Si atoms in solid and liquid KSi. In order to make the comparison homogeneous, $A_{\text{Si-Si}}(\theta)$ for the solid has been computed with the same resolutions as that used for the liquid.

Our results are still preliminary and need a more thorough analysis. Furthermore it is not clear, at this stage, whether the picture obtained for KSi can be generalized to Sn and Pb alloys. However, a lesson of caution should be learned. At first sight, the computed $g_{\text{Si-Si}}(r)$ appears to reflect all the expected features of a Zintl-forming liquid. The underlying picture, however, is much more complex. Therefore the assumption of the existence of Zintl ions as stable constituents when modelling these compounds may be inappropriate.

Acknowledgments

It is a pleasure to thank M L Saboungi and D Price for having suggested the study of this system.

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