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ABSTRACT

Diffusion of Ga and As ions in simulated liquid gallium arsenide, GaAs, have been studied in a model containing 3000 ions under periodic boundary conditions via molecular dynamics simulation (MD). Diffusion constant D in system has been calculated over temperatures ranged from 5000 K down to 1400 K. Calculations of liquid GaAs model with a real density at 5.3176 g cm^{-3} show that the temperature dependence of the diffusion constant D show an Arrhenius law at relatively low temperatures above the melting point and show a power law, $D \sim (T - T_c)^{\gamma}$, at higher temperatures. And upon cooling the system from relatively high temperatures to low temperatures, we found across over from non-Arrhenian to Arrhenian dynamics in the liquids, i.e. corresponding to a transition from fragile to strong liquid behaviours in the system. Furthermore, we also found the glass phase transition temperature T_g for the GaAs system is anywhere around 1050 K.

1. Introduction

In recent years, structure and dynamics of liquid and amorphous GaAs has attracted great interest and has been under intensive investigation by both experiment and computer simulation [1,2]. Isotopically controlled GaAs heterostructures have been used to study Ga self-diffusion with secondary-ion mass spectrometry. The Ga self-diffusion coefficient in intrinsic GaAs has been well described with $D = (43 \pm 25)\exp[(4.24 \pm 0.06 \text{ eV})/k_B T]$ over 6 orders of magnitude between 800 and 1225 °C under As-rich condition [3]. However, authors used another method with temperatures lower than melting temperature to calculate diffusion constant. It was found that the temperature dependence of the diffusion constant of ions in liquid silica models D shows an Arrhenius law at low temperatures with an activation energy that is very close to the experimental data in [4,5], and this dependence shows a power law, $D \sim (T - T_c)^{\gamma}$, at higher temperatures, as predicted by mode-coupling theory (MCT) [6]. A power law behaviour for the dynamics in other tetrahedral network structure liquids such as GeO$_2$ or H$_2$O has also been found [7,8]. The temperature dependence of the diffusion constant in water has been observed by both experiment and computer simulation [9,10]. Measurements of the self-diffusion constant in super cooled water under high pressure up to 300 MPa have been reported where the temperature dependence of the self-diffusion constant in H$_2$O showed a power law, $D = D_0 T^{1/2}(T/T_c - 1)^{\gamma}$, with the value for γ ranging from 1.80

to 2.46 [7]. The power law behaviour of the dynamics in water has been tested later by MD simulation. Starr et al. calculated the isochors of the diffusion constant in water over a wide temperature range at densities ranging from 0.95 to 1.40 g cm^{-3} using the extended simple point-charge potential [9]. Also, at each density studied, they found a good fitting of a power law, $D \sim (T/T_c - 1)^{\gamma}$. Moreover, they found that γ decreases under pressure for their model whereas it increases experimentally [9] and, as suggested, this disagreement indicated the need to improve the dynamic properties of water models. Similar simulation results for water at temperatures from 350 K down to 190 K and at pressures from 2.5 GPa down to −300 MPa also confirmed the prediction of MCT for the dynamics of weakly super cooled liquids, i.e. the calculated data of each isochrones showed a power law: $D \sim (T/T_c - 1)^{\gamma}$ [10]. Power law behaviour for diffusion in liquid simulated GeO$_2$ and SiO$_2$ at ambient pressure has been observed [6,11]. However, a possible appearance of the power law behaviour for diffusion in liquid GaAs has not been tested yet, and it motivates us to carry out present work in this direction.

2. Calculation

It is important to choose appropriate interatomic potentials for the system to be simulated. A new approach to developing interatomic pair potentials for III–V compound semiconductors has been presented. By using Chen–Mobius multiple lattice inversion technique, the interatomic potentials of GaAs are extracted from a set of ab initio total energy curves of zincblende GaAs as well as of some related virtual structures [12]. The shape of pair potential curve indicates the Morse function form well expresses the Ga–

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As short-range interaction, and the total Ga–As, As–As, Ga–Ga pair potential becomes:

$$\Phi_{Ga-As}(r) = D_{+-}(e^{\gamma_{+-}(1-r/R_{+-})} - 2e^{\gamma_{+-}(1-r/R_{+-})/2}) + \frac{q_+ q_-}{4\pi\varepsilon_o r} \qquad (1)$$

$$\Phi_{As-As}(r) = D_{--}(e^{\gamma_{--}(1-r/R_{--})}) + \frac{q_- q_-}{4\pi\varepsilon_o r} \qquad (2)$$

$$\Phi_{Ga-Ga}(r) = D_{++}(e^{\gamma_{++}(1-r/R_{++})}) + \frac{q_+ q_+}{4\pi\varepsilon_o r} \qquad (3)$$

All three kinds of pair potentials and their parameters can be found in [12].

Simulations have been done in the basic cube containing 3000 ions under periodic boundary conditions. Use the Verlet algorithm with the MD time step of 2.125 fs. Initial well-relaxed 100,000 MD steps liquid GaAs model at 5000 K and at density of 5.3176 g cm^{-3} have previously been obtained [13]. The new model has been subsequent cooled down to 250 K at fixed density at a cooling rate of 2.353×10^{13} K s^{-1}. The model obtained at each temperature above the melting point has been relaxed for 100,000 MD steps (or 212.5 ps) in order to calculate the diffusion constant and static properties.

Because the simulations were carried out at constant volume, this could lead to negative pressures at low temperatures or high pressures at high temperature. Therefore, we only calculated the model over temperatures ranged from 5000 K down to 250 K.

3. Results and discussion

If the interatomic potential is known, it is easy to calculate self-diffusion constants of a liquid by molecular dynamics method. In the process of molecular dynamics relaxation of liquid phase, the particles of model at each temporal step perform small displacements correlated with displacements of neighbouring atoms. Hence, the cooperative diffusion mechanism is realized. The self-diffusion constants of ions in the liquid GaAs model can be determined through the mean squared atomic displacement $\langle r^2 \rangle$ via the Einstein relation:

$$D = \lim_{t\to\infty} \frac{\langle r^2(t) \rangle}{6t} \qquad (4)$$

The time dependence of $\langle r^2 \rangle$ was presented in Fig. 1, and the diffusion constant with error bars at different temperatures has been presented in Table 1.

The diffusion constant of atomic species has been studied in the liquid state of the system (at temperatures above the melting point, T_m = 1237 K [13]), i.e. at temperatures ranging from 1400 K to 5000 K for models at 5.3176 g cm^{-3}. The obtained diffusion constant D for Ga ions ranged from $(0.05 \pm 0.01) \times 10^{-5}$cm^2/s to

Table 1
Diffusion constant, D in 10^{-5} cm^2 s^{-1}, of atomic species in liquid GaAs models at density of 5.3176 g cm^{-3}.

T (K)	D_{Ga} (in 10^{-5} cm^2/s)	D_{As} (in 10^{-5} cm^2/s)
1400	0.05 ± 0.01	0.05 ± 0.01
1500	0.10 ± 0.005	0.10 ± 0.01
1700	0.34 ± 0.01	0.33 ± 0.01
1800	0.56 ± 0.02	0.58 ± 0.01
2000	1.05 ± 0.01	1.09 ± 0.01
2500	2.80 ± 0.01	2.79 ± 0.01
2800	4.16 ± 0.02	4.11 ± 0.02
3000	4.89 ± 0.01	4.99 ± 0.02
3500	7.29 ± 0.02	7.36 ± 0.03
3800	8.41 ± 0.05	8.87 ± 0.03
4000	9.51 ± 0.03	9.55 ± 0.02
4500	12.22 ± 0.03	12.02 ± 0.03
4800	14.26 ± 0.02	13.10 ± 0.05
5000	13.98 ± 0.02	14.07 ± 0.04

$(13.98 \pm 0.02) \times 10^{-5}$cm^2/s at the temperatures from 1400 K to 5000 K, respectively. Meanwhile, those numbers for the As ions ranged from $(0.05 \pm 0.01) \times 10^{-5}$cm^2/s to $(14.07 \pm 0.04) \times 10^{-5}$ cm^2/s for the same temperature range (see Table 1). This means that they have reasonable values and close to the calculated values D for ions Al$^{1.8+}$ and O$^{1.2-}$ in liquid aluminum silicate $(Al_2O_3)2SiO_2$ in Ref. [14] and for ions Si^{4+} and O^{2-} in liquid SiO$_2$ models [15,16]. Furthermore, we can see that the diffusion constants of As and Ga ions are close with each other.

The temperature dependence of self-diffusion constants D in liquid GaAs models shows an Arrhenius law in the low temperature region above melting point (see Fig. 2) as given below:

$$D = D_o \exp\left(-\frac{E}{k_B T}\right) \qquad (5)$$

We can determine parameters in Eq. (5) through temperature dependence of diffusion constant. For Ga and As ions, the pre-exponential constant and activation energy at constant volume almost has the same value (see Table 2).

For liquid SiO$_2$ (see Ref. [15]), they found that the activation energies are 4.66 eV and 5.18 eV for oxygen and silicon, respectively. These numbers compare well with the ones determined in experiments at significantly lower temperatures, namely, 4.7 eV for oxygen [17] and 6 eV for silicon [4]. For liquid gallium arsenide the experimental data was found that the activation energies are 4.24 ± 0.06 eV, but the authors had carried out with temperatures from 800 to 1225 °C. And the experimental data for liquid GaAs with temperatures above melting point was not found, but we can see that the calculated data have reasonable values. Such an
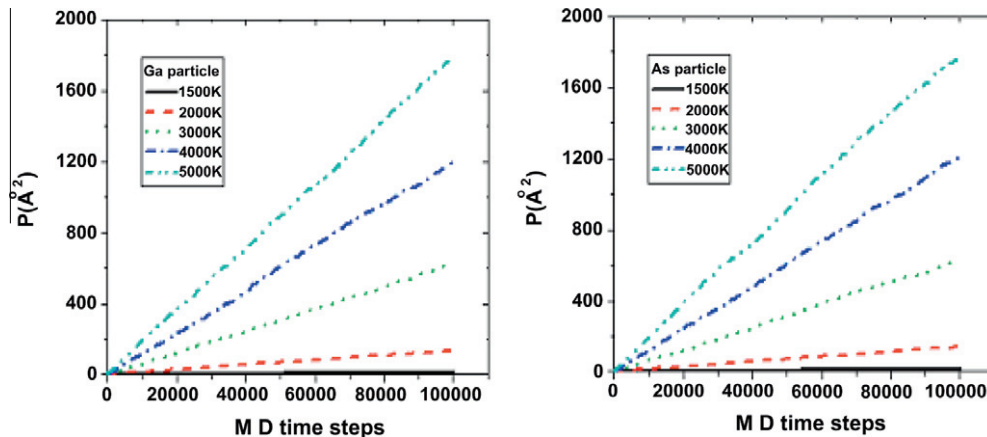

Fig. 1. Mean-squared atomic displacement $\langle r^2 \rangle$ of As and Ga particles in liquid GaAs models obtained at different temperatures and at a density of 5.3176 g cm^{-3}.
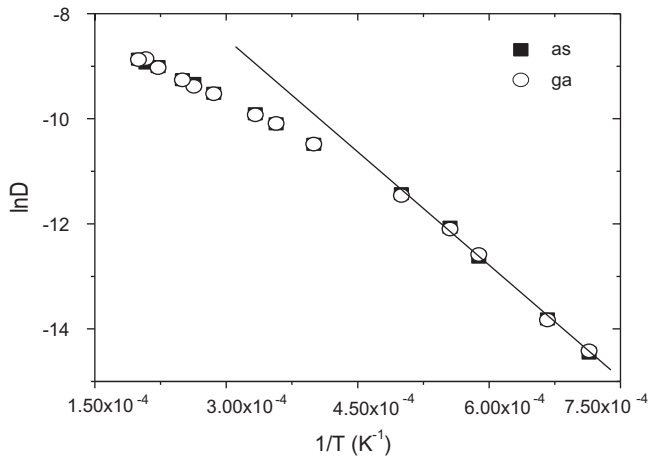
Fig. 2. $1/T$ dependence of logarithm of the diffusion constants of Ga and As ions in liquid GaAs.

Table 2
Parameters of power law, $D \sim (T/T_c - 1)^\gamma$, and Arrhenius law, $D = D_0 \exp(-E/k_B T)$, in liquid GaAs model.

T_c (K)		γ		D_0 (in 10^{-4} cm²/s)		E (eV)	
Ga	As	Ga	As	Ga	As	Ga	As
2100	2050	0.86	0.90	138.13	163.62	1.23	1.25

And several important remarks related to the temperature dependence of diffusion constant in liquid GaAs can be made here. First, the temperature dependence of diffusion constant in liquid GaAs has also been observed by MD simulation (Fig. 2). Second, the deviation from an Arrhenius law behaviour has been observed in that the diffusion constants decrease slower with decreasing temperatures than that expected from an activated process (Fig. 2). This is totally similar to the data obtained previously for diffusion constant in both liquid GeO₂ and SiO₂ [6,15,21]. As discussed above, the transition from a non-Arrhenius law to an Arrhenius law behaviour for the dynamics in liquids is related to the structural evolution in the system with decreasing temperature. It means that there is evidence of a transition from a fragile liquid to a strong liquid upon cooling the system from 5000 K to 250 K. As SiO₂, there is clear evidence of a transition from a strong liquid to a fragile liquid upon heating the system from 3000 K to 7000 K if one considers that strong liquids show Arrhenius relaxation process and typically have a three-dimensional network structure of covalent bonds while fragile liquids have non-Arrhenius relaxation properties with non-directional and non-covalent interaction like those stated in Ref. [22]. Such structural changes in liquid SiO₂ are accompanied by changes in the diffusion of atomic species from an Arrhenius law behaviour to a power-law one in that the diffusion constants increase
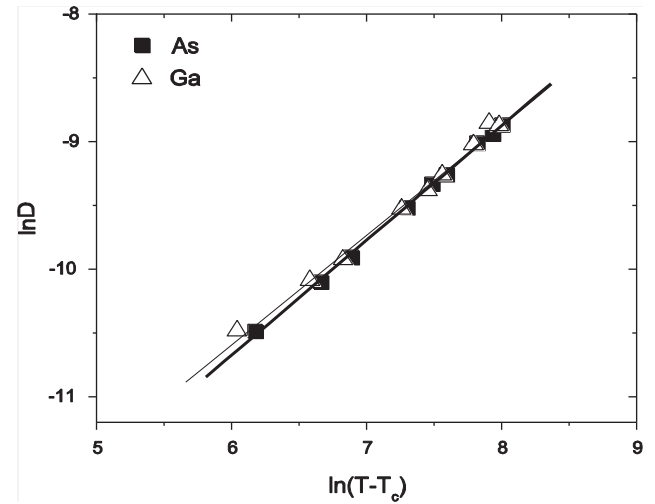
excellent agreement between the theoretical and experimental activation energies for liquid SiO₂ is not trivial as it has recently been demonstrated by Hemmati and Angell [18], who showed that various models for silica can give rise to quite different activation energies. These authors showed that different models predict diffusion constants which differ by up to two decades at temperatures as high as 3000 K, which show that dynamical quantities such as D depend much more sensitively on the potential than structural quantities. For higher temperatures, significant deviations from the Arrhenius law were obtained for liquid SiO₂ (see Ref. [14]) that the diffusion constants increase more slowly with increasing temperature than expected from an activated process. Recently, Hess et al. have reported the analysis of experimental viscosity data of SiO₂ at high temperatures and find that deviations from a pure Arrhenius law are present [19]. Such phenomenon has been also observed for our liquid GaAs, we can see in Fig. 2 that at $T \geqslant 2100$ K the curve starts to deviate from a pure Arrhenius law.

One explanation for the observed deviations from the Arrhenius behaviour is offered by mode-coupling theory (MCT) (see Ref. [20]), since the so-called ideal version of this theory predicts that the temperature dependence of the diffusion constant, as well as the inverse of the α-relaxation time $\tau(T)$, is given by a power law, i.e.,

$$D \propto \tau^{-1} \propto (T - T_c)^\gamma \tag{6}$$

where the critical temperature T_c and the critical exponent γ can be calculated from the temperature dependence of the partial structure factor.

In practice, however, the two quantities are usually taken as fit parameters [20]. From Fig. 2, we calculated the critical temperature T_c and from Fig. 3 the critical exponent γ has been found (see Table 2). Note that the theory predicts that the value of γ should be independent of the species and the fact that the two values we find are close together supports this prediction.

Fig. 3. Fit of each isochore to the power law, $D \sim (T/T_c - 1)^\gamma$, predicted by MCT.
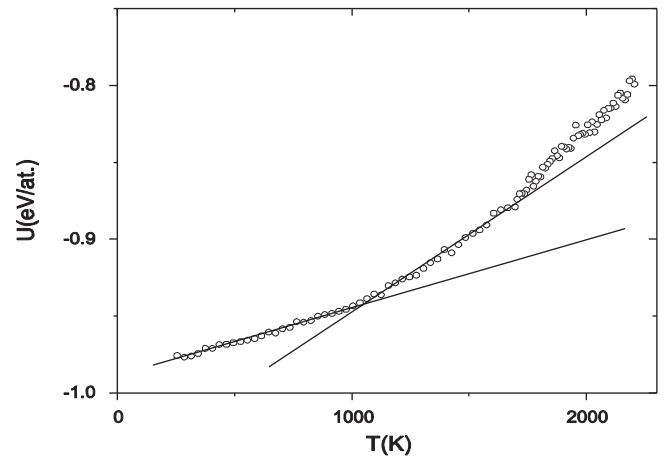

Fig. 4. Temperature dependence of potential energy of GaAs system.

slower with increasing temperature than that expected from an activated process [6].

Moreover, the glass transition temperature T_g for the system has been also determined from the intersection of a linear high- and low temperature extrapolation of the system potential energy (Fig. 4) and it is anywhere around 1050 K.

4. Conclusion

(i) We found that the temperature dependence of the diffusion constant in simulated GaAs shows an Arrhenius law at temperatures above the melting point and shows a power law, $D \sim (T/T_c - 1)^\gamma$, at higher temperatures for models at density of 5.3176 g cm^{-3}. And upon cooling the system from relatively high temperature to low temperature, we found across over from non-Arrhenian to Arrhenian dynamics in the liquids, i.e. corresponding to a transition from fragile to strong liquid behaviour in the system. Also, this is related to structural evolution in the system when the temperature decreases.

(ii) The glass phase transition temperature T_g for the GaAs system is anywhere around 1050 K.

Acknowledgments

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