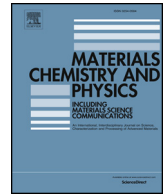




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## Thermophysical properties and atomic structure of liquid Si-Ge alloys

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## HIGHLIGHTS

- The temperature range is much broader, including 600–2500 K for Ge.
- The difference between calculated and reported density for Si and Ge is less than 4%.
- The structure change between normal and undercooled liquid was observed.

## ARTICLE INFO

## Keywords:

Phase change materials  
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## ABSTRACT

The thermophysical properties and atomic structure of liquid Si-Ge alloys were investigated by the molecular dynamic simulations with Stillinger-Weber potential over a broad temperature range, including both superheating and undercooled regime. The maximum undercooling in this work is 611 K for pure Ge. For all the  $\text{Si}_{100-x}\text{Ge}_x$  ( $x = 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100$ ) alloys, the densities exhibit quadratic relationship with temperature. The density of Si at the melting temperature is  $2.59 \text{ g}\cdot\text{cm}^{-3}$ , existing a slight deviation of 0.39% compared with the experiential data. For liquid Ge, the density at the melting temperature is  $5.62 \text{ g}\cdot\text{cm}^{-3}$ , nearly identical with the reported values. In all the cases, the densities of Si-Ge alloys with different compositions are larger than those of ideal solution. Therefore, liquid Si-Ge alloys display negative excess volume, which reaches the minimum at 40% Ge content. The specific heat was obtained by thermodynamic function and energy fluctuation approaches, respectively. Both of the results are in good agreement with experimental data around the liquidus temperatures. Furthermore, the diffusion coefficients were obtained by calculating the mean square displacement. The pair distribution function was applied to analyze the liquid structure. It is found that the peaks occur around the liquidus temperatures, which implies the structure change between normal and undercooled liquid alloys.

## 1. Introduction

The development of phase change materials (PCMs), whose optical and electrical properties change drastically during the transition from the amorphous to crystalline state, has triggered extensive innovations for rewritable data storage devices [1–3]. Liquid state, especially metastable liquid state is a necessary process when PCMs transform from crystal to amorphous phase. Meanwhile, germanium, silicon and their alloys, which have attract considerable attentions due to the excellent electronic and optical properties, are widely utilized in phase change memory, directly composing some of the PCMs [4–6]. Despite the Si-Ge system is of great industrial and technological importance, the data of its thermophysical properties, in particular for liquid state is still incomplete. Furthermore, the solution of elemental separation during repeated melting, which reduces the cyclability of phase change

memory devices, requires in-depth knowledge of liquid structure [7,8]. Therefore, in order to improve the performance of phase change memory devices, the thermophysical properties and the atomic structure of liquid Si-Ge alloys have become a crucial subject.

However, the molten Si is so chemically active that it reacts with almost every material of containers [9]. The strong reactivity at high temperature makes it extremely difficult to determinate thermophysical properties or the liquid structure. Indeed, there are still a few experimental data about thermophysical properties of liquid Si-Ge alloy. Chathoth et al. [10] measured the densities, thermal expansion coefficients and surface tensions of liquid Si-Ge alloys under microgravity conditions. Mizuno et al. [11] reported the densities and molar volumes of molten Si-Ge alloys by electromagnetic levitation coupled with a static magnetic field. Ricci et al. [12] determined the surface tension and densities of liquid Si-Ge alloys by the pendant drop method.

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Nonetheless, the experimental data in these literature exhibits a significant scatter. For instance, the density of Si<sub>50</sub>Ge<sub>50</sub> measured by Chathoth et al. [10] and Mizuno et al. [11] displays a maximum difference of 41.55%.

As an alternative approach, molecular dynamic (MD) simulations can easily obtain normal and metastable liquid alloys [13]. Besides, it also gives the precise atomic coordinate during simulated process, which is the critical information to analyze the liquid structure. As a result, there are a number of reported literature studying Si-Ge alloys by molecular dynamics. Hahn et al. [14] determined the thermal conductivity of SiGe-based materials by the chemical composition via approach-to-equilibrium molecular dynamics. Skye et al. [15] calculated thermal resistivity of Si-Ge alloys using Stillinger-Weber potential. Ishimaru et al. [16] explored structural and dynamical properties of amorphous Si-Ge alloy using the Tersoff interatomic potential. Thus, molecular dynamic simulations seem to be a good choice to obtain thermophysical properties and explore liquid structure.

Above researchers investigated thermophysical properties, dynamic properties and structure of Si-Ge alloys in crystalline and amorphous state, except for liquid state. Besides, current literature focus on a few types of thermophysical properties for specific compositions. There isn't a comprehensive study of thermophysical properties and microstructure of liquid Si-Ge system yet. The objective of this paper is to perform MD calculations on the thermophysical properties, including density, excess volume, specific heat and diffusion coefficient of liquid Si-Ge alloys by using a reasonable potential model over a much broader temperature range. In addition, the pair distribution function was employed to explore the atomic structure of normal and undercooled liquid state.

## 2. Method

The accuracy of calculated result depends on whether the potential model describes the interaction between atoms in perspective. Therefore, it is crucial to select an appropriate potential model. Although there are abundant of potential models studying Si-Ge alloy, the empirical Stillinger-Weber (SW) potential is still one of the most successful potentials for Si and Ge [17–20]. Generated to describe the interaction of semiconductor element Si, the original SW potential [17] takes the following form:

$$E_{tot} = \sum_i \sum_{i < j} \varphi_2(r_{ij}) + \sum_i \sum_{i \neq j} \sum_{j < k} \varphi_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad (2.1)$$

where  $r_{ij}$  is the distance between atom  $i$  and  $j$ ,  $\theta_{ijk}$  the angle subtended by  $r_{ij}$  and  $r_{ik}$ .  $\varphi_2$  is the two-body pair interaction and  $\varphi_3$ , the three-body interaction term. The two-body term describes the formation of chemical bonds between atoms and can be written as [17]

$$\varphi_2(r_{ij}) = \begin{cases} \varepsilon A \left( B \left( \frac{r_{ij}}{\sigma} \right)^{-4} - 1 \right) \exp \left[ \left( \frac{r_{ij}}{\sigma} - a \right)^{-1} \right] & \text{for } \frac{r_{ij}}{\sigma} < a \\ 0 & \text{for } \frac{r_{ij}}{\sigma} > a \end{cases}, \quad (2.2)$$

where  $\varepsilon$  is an energy scale and  $\sigma$ , a length scale.  $A$  and  $B$  are positive constants defined in literature [17]. Parameter  $a$  refers to cutoff radius and equals to 1.80. The three-body part is taken to be [17]

$$\varphi_3(r_i, r_j, r_k) = \varepsilon \left[ h \left( \frac{r_{ij}}{\sigma}, \frac{r_{ik}}{\sigma}, \theta_{ijk} \right) + h \left( \frac{r_{ji}}{\sigma}, \frac{r_{jk}}{\sigma}, \theta_{ijk} \right) + h \left( \frac{r_{ki}}{\sigma}, \frac{r_{kj}}{\sigma}, \theta_{ikj} \right) \right]. \quad (2.3)$$

The function  $h$  has the following form: [17]

$$h(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda \exp [\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \left( \cos \theta_{ijk} + \frac{1}{3} \right)^2 \quad (2.4)$$

**Table 1**

The SW potential parameters for Si [23] and Ge [25].

Element	$\varepsilon$ (eV)	$\sigma$ (Å)	$\lambda$
Si	2.1683	2.0618	21.0
Ge	1.7400	2.2150	19.5

where  $\gamma$  is equal to 1.20, regardless of the atom type.  $\lambda$  measures the relative strengths of the three- and two-body potentials.

The originally proposed SW potential models crystalline Si accurately [21,22]. Nonetheless, some fundamental properties for liquid state, such as density, deviate from experiments. Kadiri et al. [23] modified the SW potential and got a good description of liquid Si. Ge has the same crystal structure and quite similar physical properties to Si. Thus, a number of SW potentials were developed for Ge [24–26]. Here, a set of SW potential parameters for liquid Ge proposed by Yu et al. [25] are chosen. The parameters  $\varepsilon$ ,  $\sigma$  and  $\lambda$  for Si and Ge applied in this work are presented in Table 1. The rest of parameters are the same to initial version of SW potential.

In order to describe interactions between Si and Ge atoms, the divers-species parameters  $\sigma_{ij}$ ,  $\varepsilon_{ij}$ ,  $\lambda_{ij}$  and the mixed-species parameters  $\varepsilon_{jik}$ ,  $\lambda_{jik}$  are needed. Considering the geometric mean for the energy parameter and the arithmetic mean for the length parameter,  $\sigma_{ij}$  and  $\varepsilon_{ij}$  take the form of  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$  and  $\varepsilon_{ij} = (\varepsilon_i \cdot \varepsilon_j)^{1/2}$ . The parameter  $\lambda_{ij}$  is similar to  $\varepsilon_{ij}$  and assumed to be  $\lambda_{ij} = (\lambda_i \cdot \lambda_j)^{1/2}$  [26]. The approximation proposed by Grabow and Gilmer in Ref. [27] was iterated to construct mixed-species parameters, in which

$$\varepsilon_{jik} = \sqrt{\varepsilon_{ij} \varepsilon_{ik}} = \varepsilon_j^{\frac{1}{4}} \varepsilon_i^{\frac{1}{2}} \varepsilon_k^{\frac{1}{4}} \quad (2.5)$$

and

$$\lambda_{jik} = \sqrt{\lambda_{ij} \lambda_{ik}} = \lambda_j^{\frac{1}{4}} \lambda_i^{\frac{1}{2}} \lambda_k^{\frac{1}{4}} \quad (2.6)$$

The above two sets of SW parameters combining with Grabow and Gilmer's approximation were employed to simulate liquid Si-Ge alloys in different compositions using large-scale atomic/molecular massively parallel simulator (LAMMPS) packages [28]. At the beginning of each simulation, 8000 Ge atoms were arranged as the style of diamond structure in a cubic box. The system was subjected to periodic boundary condition in three dimensions under isothermal-isobaric (NPT) ensemble. The Si atoms replaced Ge atoms randomly according to the simulated compositions. The pressure and time step were set to  $10^5$  Pa and 1 fs respectively. In order to get the equilibrium liquid state, the system started at 2500 K, which is far above the liquidus temperatures, and run for  $2.5 \times 10^5$  fs. A cooling process with a cooling rate of  $1.33 \times 10^{14}$  Ks<sup>-1</sup> was performed to calculate the thermophysical properties at 100 K temperature interval. At each temperature,  $5 \times 10^5$  fs were carried out for equilibrium.

## 3. Results and discussion

### 3.1. Density

Density is one of the most fundamental thermophysical properties and often used in numerical model and materials design. A total of 11 Si-Ge alloys with different compositions were investigated in this work. Their liquidus temperatures,  $T_L$ , are listed in Table 2. The predicted density,  $\rho$ , displays quadratic function of temperature  $T$ :

$$\rho = \rho_L + b(T - T_L) + c(T - T_L)^2 \quad (3.1)$$

where  $\rho_L$  is the density at liquidus temperature.  $b$  and  $c$  serve as temperature coefficients and are also presented in Table 2.

The last column in Table 2 represents the temperature range of simulated liquid Si-Ge alloy. The melting temperature of Ge is far smaller than that of Si. Besides, Si-Ge system shows a complete solubility in

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