Molecular dynamics calculation of thermophysical properties for a highly reactive liquid

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In order to further understand the physical characteristics of liquid silicon, the thermophysical properties are required over a broad temperature range. However, its high reactivity brings about great difficulties in the experimental measurement. Here we report the thermophysical properties by molecular dynamics calculation, including density, specific heat, diffusion coefficient, and surface tension. The calculation is performed with a system consisting of 64 000 atoms, and employing the Stillinger-Weber (SW) potential model and the modified embedded atom method (MEAM) potential model. The results show that the density increases as a quadratic function of undercooling, and the value calculated by SW potential model is only 2–4 % smaller than the reported experimental data. The specific heat is obtained to be 30.95 J mol^{-1} K^{-1} by SW potential model and 32.50 J mol^{-1} K^{-1} by MEAM potential model, both of which are constants in the corresponding ranges of temperature. The self-diffusion coefficient is exponentially dependent on the temperature and consistent with the Arrhenius equation. The surface tension increases linearly with the rise of undercooling and agrees well with the reported experimental results. This work provides reasonable data in much wider temperature range, especially for the undercooled metastable state.

I. INTRODUCTION

The thermophysical properties of metastable undercooled liquids, such as density, specific heat, diffusion coefficient, and surface tension are of both fundamental and practical importance [1–5]. These parameters can also give some information on the local liquid structure. Due to the thermodynamic metastable state, these data are rather rare. Therefore, the thermophysical properties of undercooled liquids have aroused great scientific research interest over the last twenty years [5–10]. There are two main approaches to obtain these data: direct experimental determination and computer simulation. Experimental measurement methods are usually based on containerless processing techniques, for example, electromagnetic levitation (EML) and electrostatic levitation (ESL). Computer simulations mainly include first principle (FP), Monte Carlo (MC), and molecular dynamics (MD) methods. The noncontact measurement is an effective experimental method, such as drop calorimetry with electromagnetic levitation technique [9,10]. Due to the great difficulty in achieving large undercooling, these parameters are hard to measure directly, especially for high-temperature materials and highly reactive liquids. The experimental investigation also requires much time and financial cost. This computer experiment is an approach to perform this kind of research [11–16]. Its advantage lies in easily achieving large undercooling for the studies on thermophysical properties.

For silicon, the requirement for thermophysical property research has been increasing due to its wide application in integrated circuits and many industrial alloys. In order to further understand the physical characteristics of this semiconductor, the thermophysical properties are required over a broad temperature range. However, liquid Si is highly reactive with most crucibles. This brings about great difficulties

in the experimental measurement. In recent twenty years, researchers have reported some thermophysical properties of liquid Si. Morishita [1] reported the calculated density under the supercooled state. Watanabe *et al.* [2] measured and calculated the density by an electromagnetic levitation technique and first-principles molecular dynamics simulation. Rhim *et al.* [3] determined the density, specific heat, and surface tension. Langen *et al.* [4] measured the density. Sung *et al.* [5] determined the specific heat. Lu *et al.* [7] gave the prediction of surface tension and self-diffusion coefficient by thermodynamic calculation. Yu *et al.* [17] calculated the self-diffusion coefficient above the melting point by MD method. However, there also exist differences among their reported results. Though there are some reported results of liquid Si, the properties are still lack and the temperature range is still small. Especially, the numerical calculation on liquid Si is limited. Therefore, it is essential to further investigate its thermophysical properties.

The objective of this paper is to perform MD calculations on the thermophysical properties of undercooled Si by using the Stillinger-Weber (SW) potential model and modified embedded atom method (MEAM) potential model, including density, specific heat, diffusion coefficient and surface tension. The experimental data available in literature are used to evaluate the present calculated thermophysical properties.

II. SIMULATION METHOD

Among the many empirical potential models for Si, SW can successfully describe both crystalline and liquid Si. It takes the following form [18]:

$$E_{\text{tot}} = \sum_i \sum_{i<j} \phi_2(r_{ij}) + \sum_i \sum_{i \neq j} \sum_{j<k} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}), \quad (1)$$

where ϕ_2 is the two-body pair interaction term and ϕ_3 the three-body interaction term. The expressions of ϕ_2 and ϕ_3 are described by Stillinger and Weber [18] in more details. i,

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j, and k the atom number, r the distance, and θ the angle between two direction.

Moreover, the embedded atom method (EAM) potential model, proposed by Daw and Baskes [19,20] based on the density function theory, is a powerful model for atomic interactions in a bulk metal. Modifications can be made to be more universal. Baskes [21] developed this potential model to the MEAM model. It can be applied to the calculation of the semiconductor materials. According to this model, the total energy is a sum of direct contributions from all atoms [21]

$$E_{\text{tot}} = \sum_i \left[F_i(\rho_i) + \frac{1}{2} \sum_{i,j(i \neq j)} \phi_{ij}(r_{ij}) \right], \qquad (2)$$

where F_i is the energy of embedding atom i in an electron density ρ_i, $\phi_{i,j}$ a pair potential interaction between atoms i and j, which is summed over all neighbors j of atom i within the cutoff distance. The details are described by Baskes [21].

The above two potential models are employed respectively to simulate the thermophysical properties of liquid Si. 64 000 atoms are arranged in a cubic box as the style of diamond structure. The system is subjected to periodic boundary conditions in three dimensions under constant-pressure and constant-temperature (NPT). The pressure is set to 1 bar. The time step is 1 fs. The temperature is adjusted every 50 steps. In order to get the equilibrium liquid state, the system starts at 3000 K, which is far above its melting point. The initial temperature is kept constant for 200 000 steps. The cooling process with a cooling rate of 10^{13} K s^{-1} is performed to calculate the thermophysical properties at 100 K temperature interval. At each temperature, 100 000 steps are carried out for equilibrium. The last 50 000 steps are applied to calculate the final results. During the calculations, the systems of Si still kept liquid state. The calculated temperature is in the range of 1400–2200 K, including a maximum undercooling of 285 K. All of codes run in the Lenovo 1800 Cluster system. This cluster system has 32 nodes for calculations and the computational performance is 768 GFlops.

III. RESULTS AND DISCUSSION

A. Density

The density is one of the most fundamental properties. It is applied in most numerical model and materials design. Figure 1 gives the calculated density of liquid Si. It can be seen that the density ρ exhibits a nonlinear dependence on the temperature T. Figure 1(a) is the results by SW potential model

$$\rho = 2.47 - 4.84 \times 10^{-5}(T - T_m)$$
$$- 3.57 \times 10^{-8}(T - T_m)^2 \text{ g cm}^{-3} \qquad (3)$$

and Fig. 1(b) is the result by MEAM potential model

$$\rho = 2.32 - 1.12 \times 10^{-4}(T - T_m)$$
$$- 5.89 \times 10^{-8}(T - T_m)^2 \text{ g cm}^{-3}, \qquad (4)$$

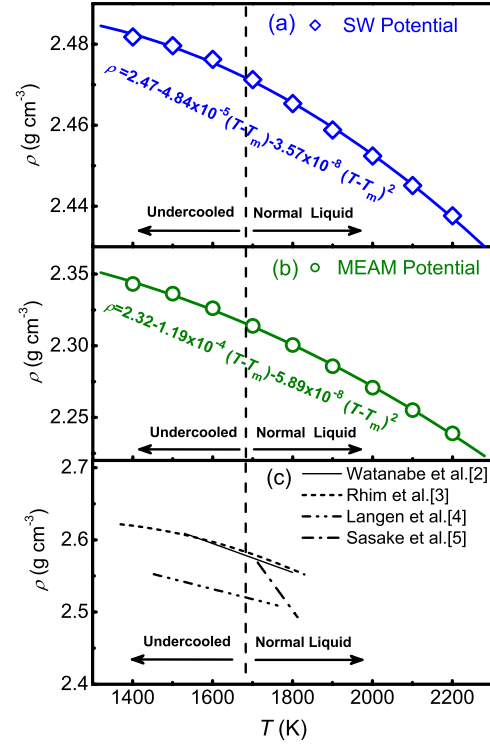where the melting point T_m is equal to 1685 K. Figure 1(c)

FIG. 1. (Color online) The density of stable and metastable liquid Si as a function of temperature.

gives the reported experimental results. Watanabe *et al.* [2] measured the density by an EML method and derived the following correlation:

$$\rho = 2.578 - 2.0 \times 10^{-4}(T - T_m) \text{ g cm}^{-3}. \qquad (5)$$

Rhim *et al.* [3] determined the density by an ESL method and obtained the following expression:

$$\rho = 2.583 - 1.851 \times 10^{-4}(T - T_m)$$
$$- 1.984 \times 10^{-7}(T - T_m)^2 \text{ g cm}^{-3}. \qquad (6)$$

Langen *et al.* [4] measured the density by an EML method and obtained the following linear relationship:

$$\rho = 2.52 - 1.49 \times 10^{-4}(T - T_m) \text{ g cm}^{-3}. \qquad (7)$$

Sasaki *et al.* [5] determined the density by an Archimedean method and reported the following relationship:

$$\rho = 2.59 - 7.6 \times 10^{-4}(T - T_m) \text{ g cm}^{-3}. \qquad (8)$$

The results by Rhim [3] and Langen [4] include the data at undercooled state. Sasaki [5] only obtained the density data in the range of about 100 K superheating. Among the reported data, there exists about 3% difference. Compared the experimental result with the calculated results in this work, the result by SW potential model is only 2% smaller Langen's results [4], and 4% smaller than Rhim's results [3] and Watanabe's reports [2]. The result by MEAM potential model is 8% smaller than Langen's results and 10% smaller than Rhim's results and Watanabe's data. For numerical cal-
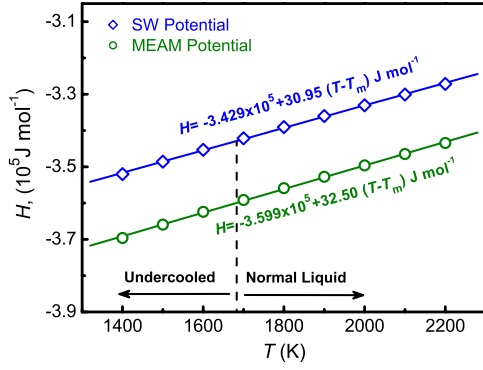
FIG. 2. (Color online) Calculated enthalpy of stable and meta-stable liquid Si as a function of temperature.

culation, so small difference can be quite acceptable. Especially for the SW potential model, the calculated results are in good agreement with the experiments.

B. Specific heat

The enthalpy dependent on the temperature was calculated by the SW potential and MEAM potential models. The result is illustrated in Fig. 2. Obviously, linear relationships exist between the enthalpies and the temperature. The calculated enthalpy H by SW potential model is written by

$$H = -3.429 \times 10^5 + 30.95(T - T_m) \text{ J mol}^{-1}. \quad (9)$$

The result by MEAM potential model is expressed by

$$H = -3.599 \times 10^5 + 32.50(T - T_m) \text{ J mol}^{-1}. \quad (10)$$

According to the definition of specific heat

$$C_{PL} = \frac{dH(T)}{dT}. \quad (11)$$

It can be deduced that the specific heat keeps constant in the calculated temperature regime. The results by SW potential and MEAM potential are equal to 30.95 and 32.50 J mol^{-1} K^{-1}, respectively. There exists about 5% difference between the two calculated values. In order to evaluate the present calculated results, a comparison is performed between the calculated values and available experimental values. Sung *et al.* [12] gave an experimental result which is

$$C_{PL} = 24.93 + 4.8 \times 10^{-4}T + 4.157 \times 10^5 T^{-2}$$
$$- 1.002 \times 10^{-7} T^2. \quad (12)$$

Rhim *et al.* [3] reported the experimental results as follows:

$$C_{PL} = 25.553 + 6.3868 \times 10^{-3}(T - T_m)$$
$$+ 1.368 \times 10^{-5}(T - T_m)^2 - 2.0243 \times 10^{-8}(T - T_m)^3$$
$$+ 2.7945 \times 10^{-10}(T - T_m)^4. \quad (13)$$

The calculated results and the reported values are illustrated in Fig. 3 together. Though Sung *et al.* [12] gave the specific heat dependent on the temperature, the value actually changes very little with the temperature and is about 26 J/mol/K. Rhim's result [3] decreases apparently with the
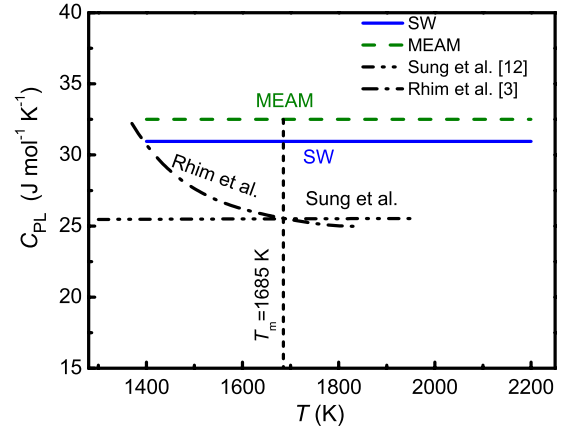

FIG. 3. (Color online) Specific heat of liquid Si versus temperature.

temperature. The measured values drop from 32 to 25 J mol^{-1} K^{-1} in the experimental temperature region. Comparing the experimental and calculated specific heat of liquid Si, both of the calculated specific heat are a little larger than Sung's [12] and Rhim's results [13]. The tendency dependent on temperature is similar to Sung's result [12]. There exists a difference of approximately 5 J mol^{-1} K^{-1}. With the increase of undercooling, the difference between the calculated values and Rhim's results [13] becomes smaller and smaller. The result by SW model is much closer to the reported experimental value. For simulation research, this case is quite good. Moreover, the calculation provides much wider temperature range for the specific heat, especially for the undercooled state. This can be applied in the theoretical analysis of rapid solidification and metastable liquid structure. The factors of creating discrepancy might be the following (1) Different experiment reports have their experimental errors, for example, the maximum difference between Sung's and Rhim's is about 6 J mol^{-1} K^{-1}. (2) For the MEAM and SW potential models adopted in this work, the negligence of quantum effects may produce a discrepancy. (3) The limited atom numbers is another reason influencing the calculated results.

C. Self-diffusion coefficient

The diffusion coefficient is a very important thermophysical parameter. However, it is hard to determine, especially for the semiconductor materials and undercooled liquid state. MD calculation is an effective approach to obtain the diffusion coefficient by computing the mean square displacement X_{MSD} (MSD), which is closely related to the diffusion process. It can be written as

$$X_{MSD} = \frac{1}{N} \left\langle \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2 \right\rangle, \quad (14)$$

where N is the total atom number in the system, $r_i(0)$ the initial position of the ith particle, and $r_i(t)$ the position of the ith particle at some later time t. The diffusion coefficient can be obtained from MSD by
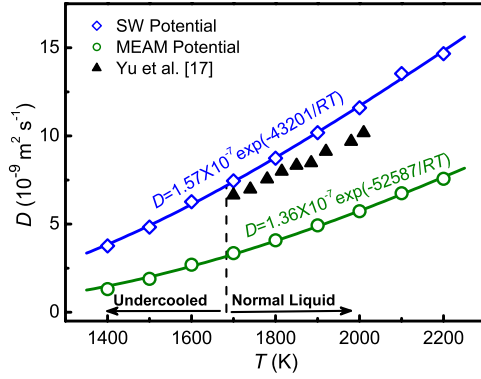
FIG. 4. (Color online) Diffusion coefficient of superheated and undercooled liquid Si versus temperature.

$$D = \frac{1}{6}\frac{\partial}{\partial t}X_{\mathrm{MSD}} \qquad (15)$$

Usually, the MSD is calculated at first, and then the derivative is obtained.

According to Eqs. (14) and (15), the MSD value of pure Si is a linear relationship of calculated time at a certain temperature, i.e., the self-diffusion coefficients can be directly computed from the first derivative of MSD versus time. Figure 4 presents the calculated result versus temperature. In general, the relationship between the diffusion coefficient and the temperature for liquid metals is described by the Arrhenius equation. The calculated diffusion coefficient by SW model is

$$D = 1.57 \times 10^{-7} \exp\left(-\frac{43201}{RT}\right) \mathrm{m^2\,s^{-1}} \qquad (16)$$

and the result by MEAM model is

$$D = 1.36 \times 10^{-7} \exp\left(-\frac{52587}{RT}\right) \mathrm{m^2\,s^{-1}}. \qquad (17)$$

From Fig. 4, it can be seen that the calculated result by SW potential model is larger than that by MEAM model. Figure 4 also gives the calculated results by Yu *et al.* [17], who obtained the data at superheated state of 300 K. The difference lies in that the ensemble selected by Yu is constant volume and constant energy and only 4092 atoms were calculated, whereas *NPT* ensemble is applied in this work. This leads to a little variation between the two calculated results. In addition, Lu *et al.* [7] report the calculated self-diffusion coefficient by a thermodynamic model, and the results are larger than both the present results and the values of Yu *et al.* Owing to the lack of experimental data of liquid Si, a comparison of the present study with other investigations is limited.

D. Surface tension

As one of the most important thermophysical properties, the surface tension is of particular scientific and technological importance in analyzing and understanding many physical processes in outer space. The surface tension value and
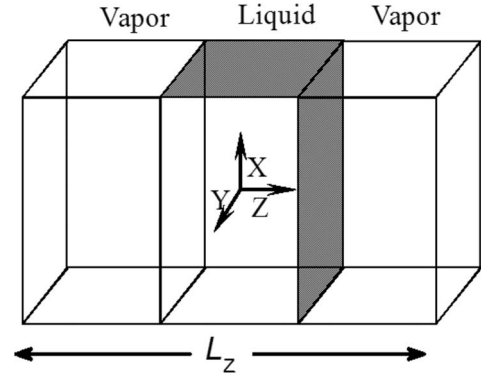

FIG. 5. A rectangular simulated cell with liquid in the middle and vapor in both sides, $L_z = 300$ Å.

its temperature dependence are essential for describing surface-tension-driven flow on the liquid surface. The surface tension can be obtained by calculating the pressure tensor of simulated cell [16].

$$\sigma = \frac{V}{2A}\left\langle P_{zz} - \frac{1}{2}(P_{xx} + P_{yy}) \right\rangle, \qquad (18)$$

where V is the volume, $A = L_x L_y$ the surface area, and P_{xx}, P_{yy}, P_{zz} the components of pressure tensor in x, y, and z directions, as shown in Fig. 5.

During the calculation, the system including 64 000 atoms first runs with the *NPT* algorithm. After equilibrium, the size of L_z is enlarged to 300 Å so as to form two liquid-gas interfaces, as shown in Fig. 5. Then, the cell runs with the constant-volume and constant-temperature (*NVT*) algorithm for equilibrium and the pressure tensor is computed in the following steps.

The temperature dependence of surface tension was calculated by SW potential and MEAM potential models. The results are illustrated in Fig. 6. Obviously, there exist linear relationships between the surface tension and the temperature. The calculated surface tension σ by SW potential model is

$$\sigma = 0.853 - 1.13 \times 10^{-4}(T - T_m) \mathrm{Nm^{-1}} \qquad (19)$$
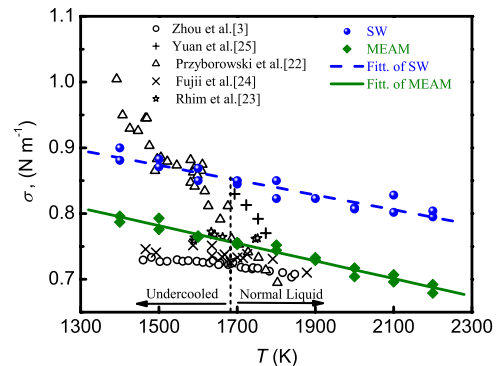
and the result by MEAM model is

FIG. 6. (Color online) Surface tension of superheated and undercooled liquid Si versus temperature.

TABLE I. Surface tension of liquid silicon obtained by different researchers.

$\sigma(T_m)$ (N m^{-1})	$d\sigma(T)/dT$ (10^{-3} N m^{-1} K^{-1})	Temperature range (K)	Reference	Method
0.784	−0.65	1390–1810	Przyborowski [22]	EML
0.765	−0.016	1580–1760	Rhim [23]	ESL
0.735	−0.074	1460–1890	Fujii [24]	EML
0.835	−0.74	1690–1780	Yuan [25]	Sessile Drop
0.721	−0.0615	1460–1850	Zhou [3]	ESL
0.764	−0.175		Lu [7]	Thermodynamics
0.759	−0.134	1400–2200	This work	MD
0.853	−0.113	1400–2200	This work	MD

$$\sigma = 0.759 - 1.34 \times 10^{-4}(T - T_m) \text{ Nm}^{-1}. \qquad (20)$$

The results calculated by SW potential model and MEAM potential model are equal to 0.853 and 0.759 N m^{-1} at the melting point, and temperature coefficients are equal to −0.113 and −0.134 mN m^{-1} K^{-1}, respectively. It can be seen that the calculated results by SW potential model are 11% larger than those by MEAM model.

In order to evaluate the present calculated results, a comparison is performed between the calculated and available experimental values. They are presented in Fig. 6 together. Obviously, these values exhibit large difference for different measurement methods and researchers. Yuan's [25] surface tension and temperature coefficient are the maximum, and the minimum values among these results are Zhou's [3] and Rhim's [23], respectively. In order to compare these results clearly and systematically, the related literature values and our calculation results are listed in Table I. For the results obtained by SW potential model, the difference range is from 2 to 15 % at the melting temperature, and is larger than MEAM potential model. The calculated results are located between the values of Zhou [3] and Yuan [25] and the maximum difference is only 15%. The present surface tension values obtained by MEAM potential model are 3–9 % smaller than the studies of Przyborowski [22] and Yuan [25] at the melting temperature, and are 3–5 % larger than Zhou's [3] and Fujii's [24]. Rhim's [23] values are in good agreement with our calculated results, and the total difference involved in the final surface tension values are estimated to be within ±0.9%. In addition to the experimental reports, Lu *et al.* [7] gave the calculated surface tensions by a thermodynamics model, which are close to the present calculated results by MEAM model. From above, it can be seen that the

calculated results is rather accurate and can be applied in the reality.

IV. CONCLUSIONS

The density, specific heat, self-diffusion coefficient, and surface tension of liquid Si and their dependence on the temperature are investigated by MD method. The temperature range includes both superheated and undercooled states, and the maximum undercooling attains 285 K ($0.17T_m$). The density of liquid Si increases as a quadratic function of undercooling and no break occurs at the melting point of 1685 K. The density obtained by SW potential model is only 2–4 % smaller than the reported experimental data. The specific heats by both SW and MEAM potential models keep constants in the investigated temperature range: 30.95 and 32.50 J mol^{-1} K^{-1}, where the former is much closer to the reported value. The calculated self-diffusion coefficient can be well described by the Arrhenius equation. The surface tension increases linearly with the rise of undercooling and agrees well with the reported experimental results. Due to the great difficulties in the experimental measurement of the thermophysical properties of liquid Si, this work provides reasonable data in much wider temperature range, especially for the metastable state.

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