

Research Article

Theoretical Study of a Thermophysical Property of Molten Semiconductors

Fathi Aqra and Ahmed Ayyad

Department of Chemistry, Faculty of Science and Technology Hebron University, P.O. Box 40, Hebron, West Bank, Palestine

Correspondence should be addressed to Fathi Aqra, fathiaqra2009@hotmail.com

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This paper deals with theoretical approach to surface tension of molten silicon and germanium, and contributes to this field, which is very important. A theoretical calculation for determining the surface tension of high-temperature semiconductor melts, such as molten silicon and germanium, in the temperature range 1687–1825 K and 1211–1400 K, respectively, is described. The calculated temperature-dependence surface tension data for both Si and Ge are expressed as $\gamma = 876 - 0.32 (T - T_m)$ and $\gamma = 571 - 0.074 (T - T_m)$ (mJ m^{-2}), respectively. These values are in consistence with the reported experimental data (720–875 for Si and 560–632 mJ m^{-2} for Ge). The calculated surface tension for both elements decreases linearly with temperature.

1. Introduction

High-temperature melts are substances that are solids at room temperature and liquids at the temperature of interest, namely, at high temperatures. They include liquid metals, molten salts, and recently also molten semiconductor materials. Information on the thermophysical properties of these substances is needed not only because of their scientifically interesting behavior but also because of rising interest in modern industrial applications. Data are needed on semiconductor materials for the production of new materials in microgravity. Accurate thermophysical properties of molten semiconductors (silicon and germanium) are important ingredients and are needed for understanding liquid structures, the solidification process, and the numerical modeling of crystal growth processes. However, the measurement of thermophysical properties at high temperatures, such as high-temperature melts of liquid metals is a necessary, but difficult, task.

Although solid silicon and germanium have been extensively investigated, results on the properties of molten Si and Ge are scarce and there are substantial differences between them. The surface tension is sensitive to even minute surface

contamination. However, it has been measured for molten silicon and germanium at the melting points [1–7] and at different temperatures [8–12]. The surface tension of high-temperature melts is the most needed and the most poorly established property. It is needed in the study of droplet or surface behavior, in the prediction of Marangoni convection, and it has significant importance in science and recent engineering applications. Control of surface behavior is the key to obtain high-quality single crystals of silicon and germanium from the melt. A study of direct contact heat transfer requires surface tension data in order to predict the behavior of droplets or bubbles. The surface tension of liquid elements is essential from the scientific point of view of validating theories of the liquid state, as well as for practical applications in processing by chemical and metallurgical industries [13] such as casting, molding, refining, sintering, and crystal growth operations [14].

In extension to the earlier work [15–17], this paper presents a theoretical calculation of the temperature dependence surface tension of molten silicon (1687–1825 K) and germanium (1211–1400 K). The model-calculated results showed reasonable consistency with the reported experiment measured.

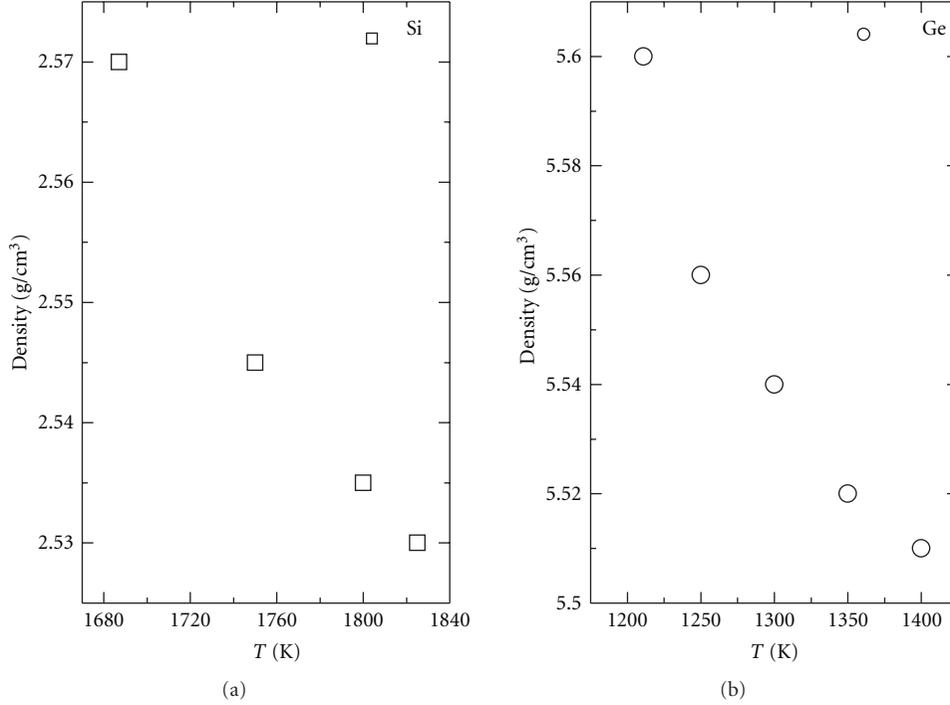


FIGURE 1: Density as a function of temperature for molten Si and Ge (data taken from [10] for Si and from [11, 22] for Ge).

2. Theory and Model

The theoretical consideration is based on classical statistical thermodynamics formulation of Eyring and coworkers [18–20]. Their theory is focused on the assumption that the metal upon melting acquires vacancies that are moving freely through the melt, and there is short-range order in the liquid. The thermodynamic properties of the liquid metal may be calculated from the relationship between the Helmholtz free energy and the partition functions. Eyring has shown that this approach can predict the thermodynamic properties of a large number of liquids and pure liquid metals. The Eyring’s approach in calculating the surface tension of a liquid metal was made by Schoutens [21], who calculated the surface tension of pure liquid Al.

Recently, an equation was derived for calculating the surface tension of pure liquid metals [15–17]. This equation may be applied for surface tension calculations of a nonmetal and a metalloid such as molten silicon and germanium. The equation has the following form:

$$\gamma = \varphi^{-1} \left(\frac{V_s}{V} \right)^2 kT \left[\frac{E_s}{RT} (1 - 3f) + \frac{3}{2} \ln \frac{3}{4} (1 + f) \right], \quad (1)$$

where γ is surface tension (mJ m^{-2}), φ is the area occupied by one atom ($\text{cm}^2 \text{atom}^{-1}$) given by $\varphi = (\sqrt{3}/2)(\sqrt{2}V_s/N)^{2/3}$, where N is Avogadro number ($6.02 \cdot 10^{23}$ atoms/mol), V and V_s are molar volumes ($\text{cm}^3 \text{mol}^{-1}$) at any temperature and at the melting point, respectively, that are given by V or $V_s = M/\rho(T)$, where M is the atomic weight and $\rho(T)$ is the density as a function of temperature, k is the Boltzmann

TABLE 1: Parameters needed for calculations of the surface tension of molten Si and Ge (T_m , density, and E_s values were taken from [23], while V_s , f , and φ were determined as given in the text).

Parameter	Si	Ge
T_m (K)	1687	1211
Density at m.p. (g/cm^3)	2.57	5.60
E_s (kJ/mol)	456	377
V_s (cm^3/mol)	10.92	12.96
f	0.297	0.297
φ ($\times 10^{-16}$)	7.53	8.44

constant ($1.38 \cdot 10^{-23} \text{ J K}^{-1}$), T is the absolute temperature (1687–1825 K for Si and 1211–1400 K for Ge), E_s is the sublimation energy (J mol^{-1}), and R is the universal gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$). The f term is a dimensionless constant parameter that describes the fraction of broken bonds (equal to 0.297 for Si and Ge). This value is a positive fractional number and is fixed by the best fit of the results with the experimental measurements for many metals. It has been determined by taking experimental surface tension values of 10 metals at their melting points and its value was varied until the calculated surface tension matches that of the experimental one. Therefore, the main equation calculating surface tension contains a parameter f , and the value of f was determined through fitting the equation to the experimental results measured at the melting point.

TABLE 2: Density and surface tension data for molten Si and Ge.

Element	Temperature (K)	Density (g/cm ³) [10, 11]	Exp. γ (mJ m ⁻²) [10, 11]	Exp. γ (mJ m ⁻²) [8, 9]	Cal. γ (mJ m ⁻²)
Si	1687	2.57	875	820	876
	1750	2.545	851	801	855
	1800	2.535	808	786	839
	1825	2.530	779	778	831
Ge	1211	5.60	583	591	572
	1250	5.56	579	587	568
	1300	5.54	576	583	562
	1350	5.52	571	579	558
	1400	5.51	568	575	556

Density and measured surface tension data were taken from [8–11]. Note that $\text{mJ m}^{-2} = \text{dynes cm}^{-1} = \text{mN m}^{-1}$.

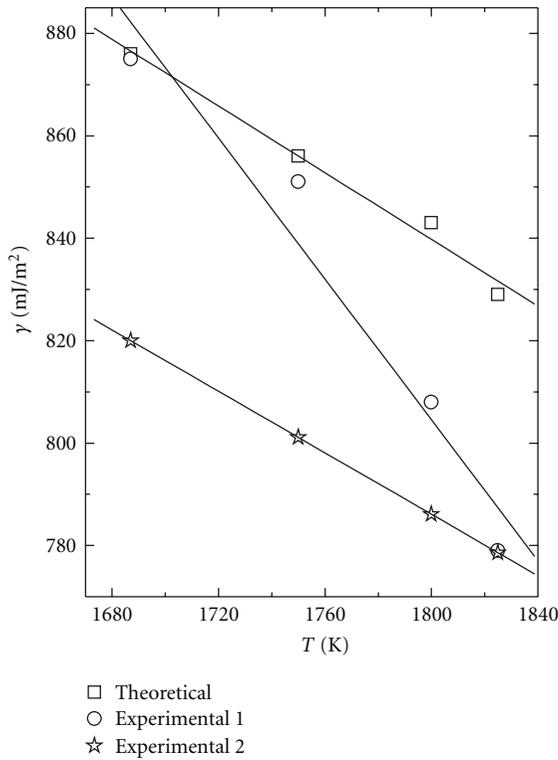


FIGURE 2: The calculated and the measured temperature-dependence of the surface tension of molten Si (open squares are our results, open circles are reported experimental data 1 taken from [10] and stars are reported experimental data 2 taken from [8]). $\gamma = 876 - 0.32 (T - T_m)$ (mJ m⁻²) (our data, theoretical), $\gamma = 875 - 0.68 (T - T_m)$ (mJ m⁻²) (experimental 1 [10]) and $\gamma = 820 - 0.3 (T - T_m)$ (mJ m⁻²) (experimental 2 [8]).

3. Calculations and Discussion

The sublimation energy, molar volume and other parameters needed to calculate the surface tension are illustrated in Table 1 [23]. The molar volumes, V , were calculated using the reported experimental temperature-dependence density data of molten Si and Ge [10, 11]. The data in these references are shown in Figure 1 and in Table 2. It is clear that the density is monotonically decreasing and almost

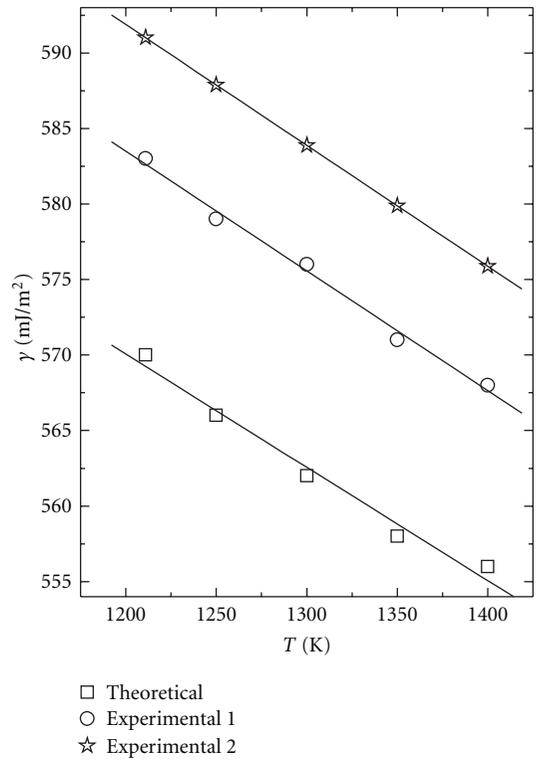


FIGURE 3: The calculated and the measured temperature-dependence of the surface tension of molten Ge (open squares are our results, open circles are reported experimental data 1 taken from [11] and stars are reported experimental data 2 taken from [9, 22]). $\gamma = 571 - 0.074 (T - T_m)$ (mJ m⁻²) (our data, theoretical), $\gamma = 583 - 0.079 (T - T_m)$ (mJ m⁻²) (experimental 1 [11]) and $\gamma = 591 - 0.08 (T - T_m)$ (mJ m⁻²) (experimental 2 [9]).

a linear function with the temperature. Table 2 shows the density as well as calculated and reported experimental surface tension data as a function of temperature for both of the molten elements. According to our calculations, the resulting theoretical function showed a decreasing function in the temperature range 1687–1825 K and 1211–1400 K for molten Si (Figure 2) and Ge (Figure 3), respectively. However, Figures 2 and 3, and Table 2 show a comparison between the experimental values of the surface tension for

molten Si and Ge [8–11] and the calculated ones as a function of temperature. The solid lines present the best linear least square fitting. It is observed that there is a similar decrease of the surface tension as a function of temperature both theoretically and experimentally. As reported, the recommended surface tension at different temperature for Si [8] is $\gamma = 820 - 0.3(T - T_m)$ (mJ m^{-2}), while for Ge [9], $\gamma = 591 - 0.08(T - T_m)$ (mJ m^{-2}). Also, Rhim and Ishikawa fitted their surface tension data for molten Ge [11] as: $\gamma = 583 - 0.08(T - T_m)$ (mJ m^{-2}), and for molten Si [10, 24] as: $\gamma = 875 - 0.22(T - T_m)$ (mJ m^{-2}) and $\gamma = 765 - 0.016(T - T_m)$ (mJ m^{-2}). The calculated surface tension data show good agreement and are expressed as:

$$(i) \text{ for molten silicon, } \gamma = 876 - 0.32(T - T_m) \text{ (mJ m}^{-2}\text{),}$$

$$(ii) \text{ for molten germanium, } \gamma = 571 - 0.074(T - T_m) \text{ (mJ m}^{-2}\text{).}$$

Figures 2 and 3 reveal that there is about 6% and 4% difference between the calculated and the experimental results for Si and Ge, respectively. This may be attributed to the fact that the surface tension of molten silicon and germanium is difficult to measure accurately, and consequently, the available experimental data for the surface tension of molten silicon [1–5] and molten germanium [5–7] is currently widely scattered, not only their absolute values but also their temperature dependence, and agreement between the existing experimental data is quite poor (for Si, γ ranges from 720 to 875 mJ/m^2 , whereas the range is 560–632 mJ/m^2 for Ge). The data reported in the literature suffer from experimental problems and the presence of impurities. Most often, the surface tension is strongly affected by surface active impurities such as oxygen, and so strongly dependent on the oxygen concentration in the liquid phase. The experimental measurements of this property is extremely difficult at high temperatures because surface tension is very sensitive to physical and chemical interactions. The difficulties are due to strong reactivity of the sample with container walls, rapid degradation of the samples, effect of electrical conductivity on sensors, sensitive impurity effects, and occurrence of supercooling and non Newtonian behavior near the melting temperature. The theoretical prediction of the surface tension of silicon is higher than the experimental values and lower for germanium because Si is a nonmetal, and thus, it is less sensitive than Ge to environmental effects.

The calculated surface excess entropy ($-dy/dT$) from the slope of the theoretical graphs (0.32 and 0.074 $\text{mJ m}^{-2} \text{K}^{-1}$ for Si and Ge, resp.) is close to the reported experimental values (for Si; 0.22 [10], 0.28 [25], 0.308 [26] and 0.65 [27], and 0.08 $\text{mJ m}^{-2} \text{K}^{-1}$ for Ge [11]). However, our results may be strictly compared with experimental surface tension data, as a function of temperature for molten Si and Ge, reported by others [22, 28–32]. Therefore, the model looks acceptable and predicts the same order of magnitude values for the temperature dependence of the surface tension of metals (Ga), metalloids (Ge), and nonmetals (Si).

4. Conclusion

This paper applies a previously developed equation to theoretically predict the surface tension of liquid silicon and germanium. The predictions are in satisfactory agreement with available experimental data and the theoretical calculation greatly supports the experimental observations. The result is very important and can provide additional insight for the understanding of the physical and chemical properties of silicon and germanium.

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