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Quantitative analysis of excess entropy and viscosity for understanding structural transition in liquid bismuth

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In this article, excess entropy (S) and viscosity (η) of liquid Bi were calculated based on pair distribution functions. A sudden increase of excess entropy in S–T curve, consistent with the endothermic peak in differential thermal analysis (DTA) curve, was found. There are two abrupt changes of calculated viscosity in η–T curve, coincident with experimental viscosity. These phenomena demonstrate that structural transition in liquid bismuth is entropy driven and atomic bonds vary twice in liquid bismuth.

Keywords: liquid Bi; excess entropy; viscosity; liquid structural transition

1. Introduction

The nature of viscous liquids is recognized as an important but unsolved problem in condensed state physics [1,2]. The conventional view considers that liquid structure varies smoothly from melting to critical point [3]. Together with pressure-induced liquid change [4], temperature-induced liquid change [5–9] suggests that the conventional view on liquids must be revised. Liquid structure changes discontinuously at hundreds of degrees above liquidus, as a function of temperature at constant pressure in liquid metals and alloys.

Group-V elements are potentially the most interesting in this research field. They exhibit an anomalous temperature dependence of thermo-physical properties above their melting point. Bismuth displays a large number of allotropic forms as a function of temperature and pressure [10]. Recently, liquid bismuth structure has been observed to change abruptly when temperature increases. Using neutron diffraction measurement [6,7] and thermal analysis [6], Greenberg et al. observed that coordination number decreases abruptly at 740°C, and its endothermal nature is revealed at the same temperature. Wang et al. [11] presented the discontinuous point of liquid bismuth viscosity, which occurs at 480°C. Greenberg et al. [12] used sound velocity (SV) measurement to reveal that SV value remains a constant from 271°C to 330°C, and that the SV–T curve deviates from linearity at about 700°C. These experimental results indicate that the liquid bismuth structure may vary twice with increase in temperature. However, prior results had not presented this viewpoint.

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In order to gain an insight into the structural properties and the above-mentioned anomalous behaviour of liquid Bi, we calculated excess entropy and viscosity based on pair distribution functions to obtain an understanding of its structural changes. Note that the results of calculated relative-viscosity and experimental viscosity exhibit similar features, and a sudden increase of excess entropy in S–T curve is consistent with the endothermic peak in DTA curve.

2. Calculation of excess entropy and viscosity

Pair distribution function $g(r)$ is directly measurable and provides quantitative spatial structural information of the liquid systems, and various properties of liquid materials can, in principle, be evaluated when coupled with an appropriate theory. The function $g(r)$ approaches 1 for large r and is always 1 for a random spatial distribution of particles. The total pair correlation function, $h(r) = g(r) - 1$, represents deviations from randomness.

Excess entropy S, i.e. the difference between system thermodynamic entropy and that of the equivalent ideal gas, is a measure of the number of accessible configurations of the system and can be given as $S = S_2 + S_3 + \cdots$, where S_2 is the pair correlation entropy, S_3 is the triplet correlation entropy, and so on. The two-particle entropy [13] is defined by

$$S_2 = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)] - g(r) + 1\}r^2 \mathrm{d}r. \tag{1}$$

Baranyai and Evans [14,15] found that two-body entropy contributes at least 85% of excess entropy at liquid densities. The difference between actual excess entropy and two-body entropy is nearly constant over a wide range of densities. The constant offset merely translates into a constant shift of data on the figures of excess entropy. In the present work, excess entropy is approximated and discussed by two-body approximation. For convenience of the following analysis, we define

$$S(1) = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)]\}r^2 \mathrm{d}r, \tag{2}$$

$$S(2) = 2\pi\rho \int_0^\infty h(r)r^2 \mathrm{d}r. \tag{3}$$

Excess entropy is the sum of $S(1)$ and $S(2)$. Pair potential of mean forces [16], $\omega_2(r)$, is defined in terms of pair correlation functions by

$$\omega_2(r) = -\kappa_\mathrm{B} T \ln g(r). \tag{4}$$

A fundamental relation between structure and thermodynamics is given by

$$\kappa_\mathrm{B} T\rho K_T = 1 + 4\pi\rho \int h(r)r^2 \mathrm{d}r, \tag{5}$$

where ρ is the number density, $K_T \ (=(\partial\rho/\partial P)_T/\rho)$ is the isothermal compressibility, P is the pressure, and κ_B is the Boltzmann constant. According to Equations (2)–(5), $S(1)$ and $S(2)$ are related to total potential and isothermal compressibility, respectively.

Iida and Guthrie [3] proposed an expression for viscosity of liquid metals in terms of pair distribution function and average interatomic frequency

$$\eta = (8\pi/9)v_0 P(T)m\rho^2 \int_0^a g(r)r^4 \mathrm{d}r, \tag{6}$$

where v_0 is a constant that corresponds to the oscillation frequency when there is no net displacement, $P(T)$ is the probability that the atom will stay in a state of oscillation around a fixed coordinate position, and a is the distance over which transfer of momentum takes place. It can be assumed that momentum interactions occur between neighbouring atoms. In Iida and Guthrie [3], the nearest-neighbour distance is estimated to be the minimum between the first and second peaks in the $g(r)$ curve, and this distance is used as the upper limit a of the integral in Equation (6). According to the well-known Enskog theory [17] of atomic transport, the collision frequency Γ is given by $\Gamma = 4\sigma^2 g(\sigma)\rho\sqrt{\pi\kappa_{\mathrm{B}}T/m}$, where m is the atomic mass and σ is the first peak position of $g(r)$. Assuming that $P(T)$ is inversely proportional to Γ because the atom will move to another position once the collision occurs, Equation (6) can be written as

$$\eta \sim \frac{1}{\sigma^2 g(\sigma)\sqrt{T}}\rho \int_0^a g(r)r^4 \mathrm{d}r. \tag{7}$$

Note that, prior investigations on liquid In–Sn alloys [18,19] and pure Sn [20] have indicated that the behaviours of experimental viscosity and calculated relative-viscosity with temperature rising are coincident with each other. These results can be helpful to assess the reliability of our conclusions.

3. Results and discussion

The calculated relative-viscosity and excess entropy are illustrated in Figures 1 and 2 (the data of $g(r)$ are taken from Reference [21]), respectively. As shown in Figure 1, in the low-temperature region the relative-viscosity decreases with temperature and obeys the Arrhenius equation. At about 462°C and 700°C, there is an anomalous change. The relative-viscosity within the range 762–900°C is also considered to obey the Arrhenius equation. Experimental viscosity [11] and relative viscosity calculated from Equation (7)
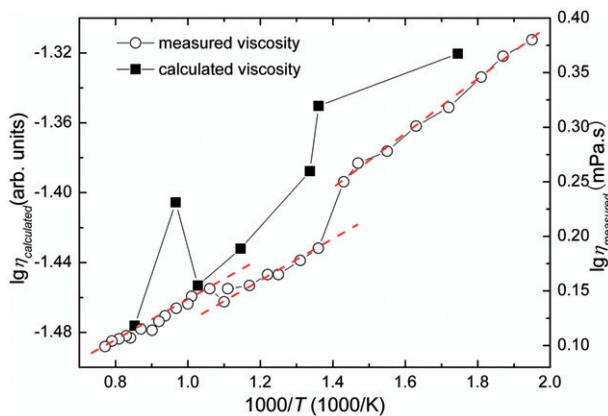

Figure 1. Arrhenius plot lg $\eta \sim 1000/T$. The measured viscosity is obtained from Reference [11]. The dashed line is a guide to the eyes.
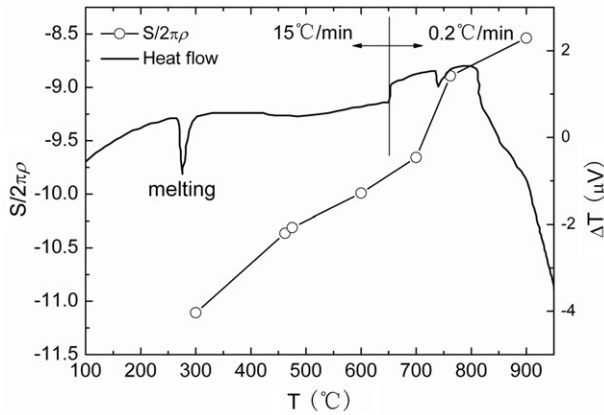
Figure 2. Results of differential thermal analysis (DTA) and the calculated excess entropy (in unit of k_B). The DTA is obtained from Reference [6].
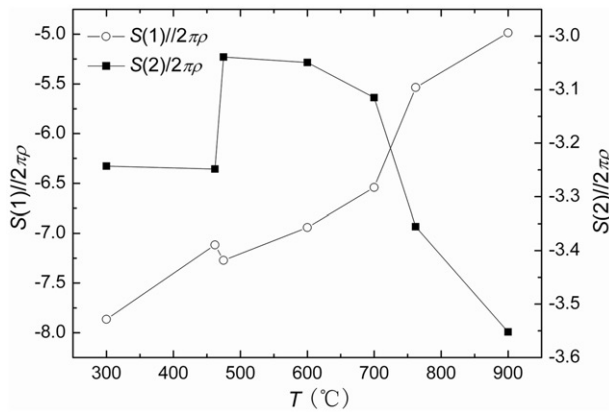

Figure 3. Two parts $S(1)$ and $S(2)$ of excess entropy (in unit of k_B) vs. temperature.

in Figure 1 are presented to make a sharp comparison. Note that experimental viscosity is macroscopically measured, and relative viscosity is obtained from the diffraction-experiment result $g(r)$. As shown in Figure 1, there is a step-down and a step-up for measured viscosity at 426°C and 636°C, respectively. It is obvious that there are two abrupt changes of calculated viscosity in the η–T curve, coincident with experimental viscosity.

Based on the above macroscopic and microscopic results, structure transition takes place. The DTA curve obtained at a heating rate of 0.2°C min^{-1} [6] and the excess entropy curve calculated from diffraction experiment results are both shown in Figure 2. Based on thermodynamics of phase transitions, the appearance of an endothermic peak at 740°C suggests that it is a first-order liquid–liquid transformation peak. Note that the endothermic peak piles up the high endothermic background.

Corresponding to the endothermic peak in DTA curve, a remarkable S-shaped change appears in the S–T curve at the same temperature range, namely, entropy increases abruptly with rising temperature. This phenomenon demonstrates that phase transition is entropy driven. The temperature range of the S-shaped change is in agreement with the

endothermic peak. For thermodynamics, the entropy of the high-temperature phase must be larger than the low-temperature phase at transition temperature. However, the entropy shown in Figure 2 suddenly increases at around 700°C, accompanied by an endothermic peak in DTA measurement. Therefore, it is likely that a metastable structure in liquid bismuth can change to a stable phase with larger entropy and a temperature of around 700°C.

Further work is needed to explore this matter and the concrete change of structure in the whole transition process. The calculated $S(1)$ and $S(2)$ are illustrated in Figure 3 to better understand the mechanism of liquid–liquid transformation. As shown in Figure 3, there is a step-up for $S(1)$ at 700–762°C and a step-up for $S(2)$ at 462–475°C. These results lead to a net S-shaped change in the S–T curve.

According to Equations (2)–(5), the behaviour of $S(1)$ indicates that the total pair potential energies of mean force go up sharply at 700–762°C, namely, the sudden increase in potential energies appears and results in the appearance of the endothermic peak. The behaviour of $S(2)$ indicates that a compressibility maximum occurs, where the isothermal compressibility first goes up suddenly and then goes down. Thus, the behaviour of $S(1)$ and $S(2)$ reveals that atomic bonds vary twice as the temperature rises; the microstructures transform twice in liquid bismuth.

Based on these phenomenological observations, we propose the existence of correlations between temperature dependence of viscosity and structure in liquid bismuth. These correlations can be interpreted qualitatively as arising from relations between viscosity and compressibility. Thus, the existence of strong bonds in Bi causes the structure to retain relative rigidity, namely, low compressibility. As the temperature increases, the value of $S(2)$ goes up abruptly at 462–475°C accompanied by variation in atomic bonds. In parallel, the viscosity of liquid Bi does not obey the Arrhenius equation at 462–475°C. The value of $S(1)$ continuously increases with temperature at 462–475°C, and no anomalous change occurs in the $S(1)$ curve. This finding indicates that changes in viscosity are related to compressibility.

This phenomenological correlation between the endothermic peak in the DTA curve and the temperature dependence of the structure are also exhibited. In thermodynamic theories, the occurrence of an endothermic peak is due to an increase in entropy. As shown in Figures 2 and 3, the variation of S is the same as that of $S(1)$ at 700–900°C and different from that of $S(2)$. The abrupt increase of $S(1)$ brings out the endothermic peak in the DTA curve at around 740°C.

4. Conclusions

The quantitative analysis based on pair distribution functions produces two abrupt changes of viscosity and a sudden increase of excess entropy. The change in calculated viscosity concurs with that in measured viscosity, and the change in entropy is consistent with the appearance of an endothermic peak in the DTA curve. S is decomposed into two parts, $S(1)$ and $S(2)$, and they are related to the total potential and isothermal compressibility, respectively. The behaviour of $S(1)$ and $S(2)$ clearly indicates that atomic bonds vary twice and microstructures transform twice in liquid bismuth. The discontinuous change of excess entropy in liquid bismuth suggests that the natures of these two changes are different. One change is due to the change in isothermal compressibility, which is accompanied by abrupt changes of viscosity. The other is due to the change in total potential, which is accompanied by the appearance of an endothermic peak in the DTA curve.

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