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Measurement of the surface tension of liquid Ga, Bi, Sn, In and Pb by the constrained drop method

The effect of the droplet size on the accuracy of surface tension measurement by the sessile drop method is discussed for liquid metals through a simulation by using the Laplace equation. It is found that with increasing size of the droplet, a higher accuracy of the measured value of the surface tension can be obtained. In order to make a large droplet of liquid metals, the constrained drop method with a special crucible shape was applied to measure the surface tension of liquid Ga, Sn, Bi, In, and Pb. The uncertainty of the measured surface tension was within 1 %. The temperature dependences of the surface tension of liquid Ga, Sn, Bi, In, and Pb were obtained in the present experiment as follows:

Ga: $\sigma_{Ga} = 737 - 0.062T$ mN/m $(823 \le T \le 993K)$
Sn: $\sigma_{Sn} = 579 - 0.066T$ mN/m $(723 \le T \le 993K)$
Bi: $\sigma_{Bi} = 417 - 0.070T$ mN/m $(773 \le T \le 873K)$
In: $\sigma_{In} = 600 - 0.082T$ mN/m $(673 \le T \le 993K)$
Pb: $\sigma_{Pb} = 499 - 0.089T$ mN/m $(757 \le T \le 907K)$

Keywords: Large drop method; Sessile drop method; Capillary constant

1. Introduction

The information on the surface tension of liquid metals and alloys is indispensable for various methods of materials processing. The authors have have studied the evaluation of the surface tension of liquid alloys and molten ionic mixtures by using thermodynamic databases, which are usually applied to the calculation of phase diagrams [1–8]. In addition, we have evaluated the phase diagrams of nano-particle binary alloy systems, which are affected largely by the surface tension due to the large ratio of the surface to the unit volume in a small particle [9–10]. Since the precise information on the surface tension is required in the above evaluation, the authors have measured the surface tension of liquid metals and alloys by the sessile drop method [11]. A few % of uncertainties are, however, included in the measured values of the surface tensions obtained by the sessile drop method. These uncertanties have been generally reported in compilations of the value of the surface tension of liquid metals and alloys.

When we try to revise the accuracy of the measured surface tension from the sessile drop method, we have to pay attention to the precise observation of the clear profile of a droplet because the surface tension is determined by the profile via the Laplace equation in this experimental method. Therefore, the final result of the surface tension might be affected by the shape and size of the droplet. Thus, the effect of the size and shape of a droplet on the accuracy of the determination of the surface tension of liquid metals by the sessile drop method is discussed through a simulation by using the Laplace equation in the present work. Then, on the basis of the results of the simulation, a constrained drop method was applied to obtain reliable values of the surface tension of liquid Ga, In, Bi, Sn, and Pb.

2. Effect of the droplet size

The profile of a droplet is given by the following Laplace equation:

$$\Delta P = \sigma\left(\frac{1}{R} + \frac{1}{R'}\right) \tag{1}$$

where ΔP is the pressure difference between the outside and the inside of the droplet. R and R' are the radii of two curvatures in a point on the surface of the droplet. The following

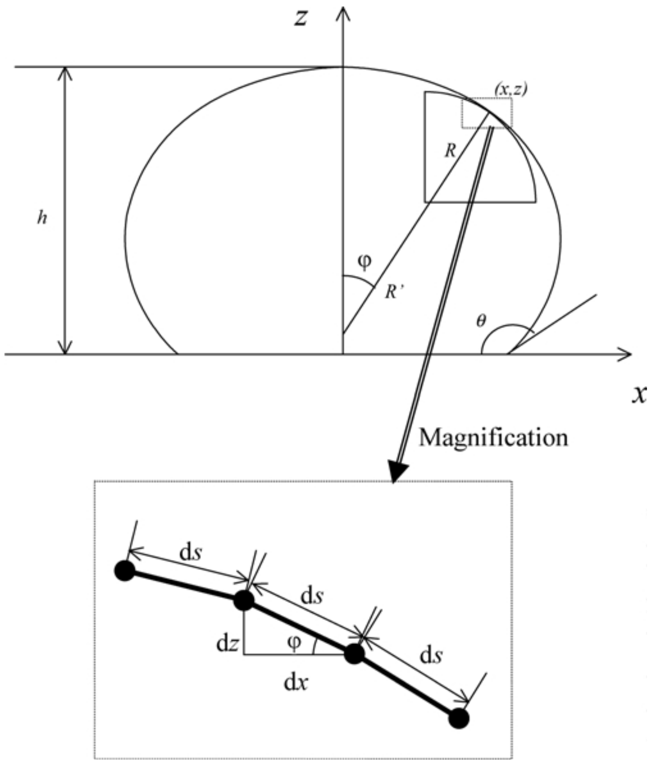

Fig. 1. Definition of the coordinates of a sessile drop.

three equations are given for the profile of the droplet in Fig. 1 on the basis of the above Eq. (1):

$$\frac{dx}{d\varphi} = R \cdot \cos\varphi \tag{2}$$

$$\frac{dz}{d\varphi} = -R \cdot \sin\varphi \tag{3}$$

$$R = \frac{1}{\left\{\dfrac{\Delta\rho g}{\sigma}(h-z) + \dfrac{2}{b} - \dfrac{\sin\varphi}{x}\right\}} \tag{4}$$

$$\Delta\rho = \rho_{\text{metal}} - \rho_{\text{gas}} \approx \rho_{\text{metal}} \quad (\because \rho_{\text{metal}} \geq \rho_{\text{gas}})$$

In the above equations, h is the height of the droplet, b is the radius of the curvature at the vertex of the droplet. σ is the surface tension of the liquid. ρ_{metal} and ρ_{gas} are the densities of liquid metal and gas around the metal. g is the acceleration of the gravity. The above equations can be converted to the following difference equations (6)–(8):

$$x_{i+1} - x_i = R_i \cos\varphi_i(\varphi_{i+1} - \varphi_i) \tag{6}$$

$$z_{i+1} - z_i = -R_i \sin\varphi_i(\varphi_{i+1} - \varphi_i) \tag{7}$$

$$R_i = \frac{1}{\left\{\dfrac{\rho_{\text{metal}} g}{\sigma}(h-z_i) + \dfrac{2}{b} - \dfrac{\sin\varphi}{x_i}\right\}} \tag{8}$$

When the initial conditions $x_0 = 0$, $z_0 = h$, $\varphi_0 = 0$ are given and the value of $\Delta\varphi = \varphi_{i+1} - \varphi_i$ is set to a certain amount, the relationship between x_i and z_i from Eqs. (6)–(8) can be used to draw the profile of the droplet. Conversely, a measured droplet profile obtained experimentally from the sessile drop method is used to determine the surface tension by comparing the observed shape with that of the solution of the Laplace equation with the surface tension as a fitting parameter. We, therefore, need to obtain a droplet profile as precisely as possible by the sessile drop method.

In the present work, the contour of the droplet for some liquid metals has been drawn from Eqs. (6)–(8) at fixed height of the droplet. The solid curves in Fig. 2 show the profile of the droplet of liquid Bi, Sn, and Ga at their melting points for h = 2.6, 3.1, and 3.6 mm when the recommended values σ_{rec} of the surface tension proposed by Keene [12] are inserted into the above Eqs. (6)–(8). The dotted curves and the broken curves in Fig. 2 indicate the profiles obtained from the conditions for $\sigma_{\text{rec}} \times (1 \pm 0.05)$ and $\sigma_{\text{rec}} \times (1 \pm 0.1)$, respectively. These curves correspond to the profiles of the droplet, which are obtained when the value of the surface tension has 5 % or 10 % of the uncertainty from the values of σ_{rec}. The contact angle for these profiles has been set to be 180°. The values of the density for those liquid metals are quoted from Ref. [13]. As can be seen from Fig. 2, the shape for σ_{rec} can be distinguished

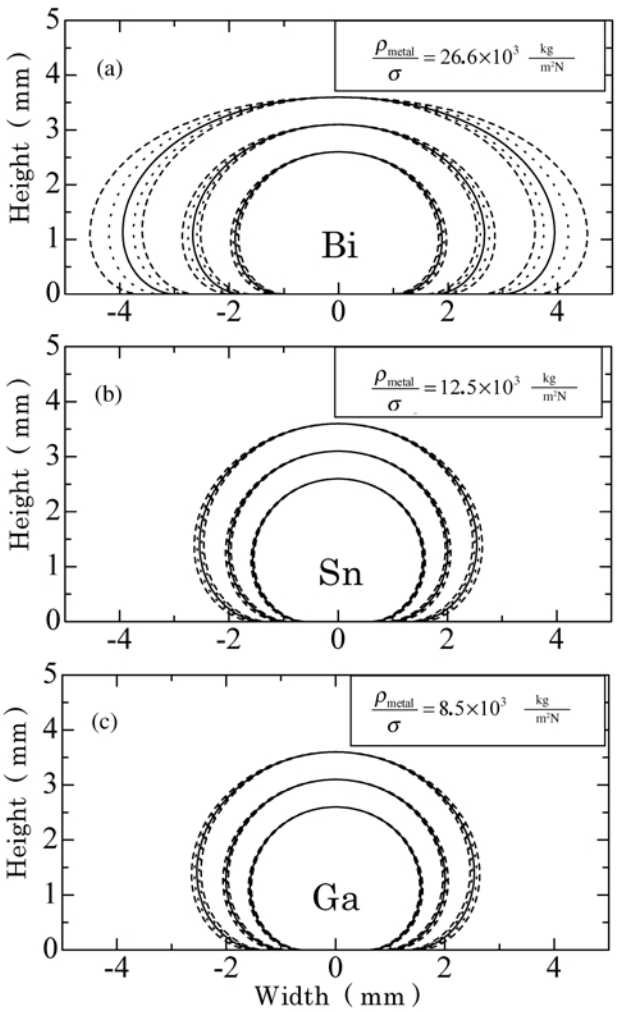

Fig. 2. Drop outline for liquid (a) Bi, (b) Sn, and (c) Ga. Drop heights: 2.6, 3.1, and 3.6 mm.

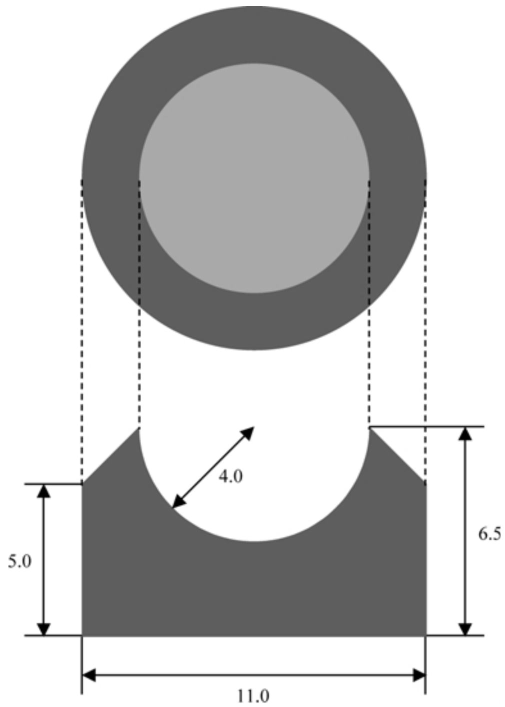

Fig. 3. Shape of a carbon crucible for the courtrained drop method. In unit of mm.

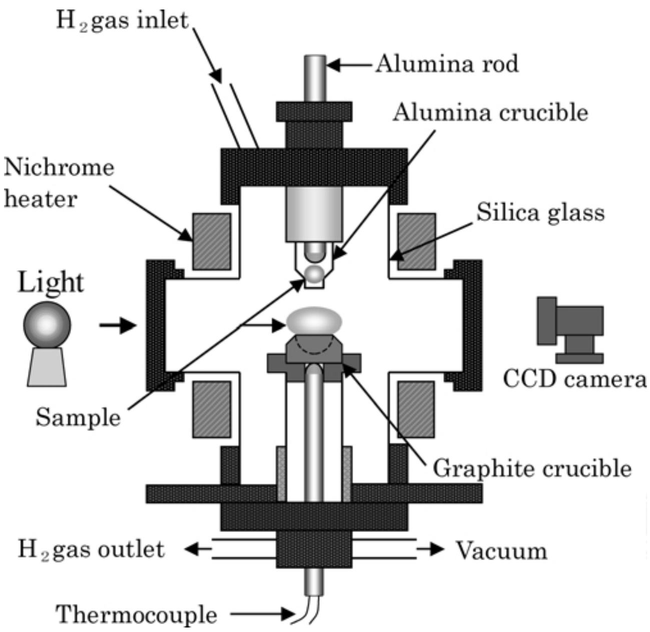

Fig. 4. Schematic diagram of the experimental apparatus.

more clearly from that for $\sigma_{\mathrm{rec}} \times (1 \pm 0.05)$ or $\sigma_{\mathrm{rec}} \times (1 \pm 0.1)$ as the size of the droplet increases. In other words, if a small droplet is investigated, the measured value of the surface tension contains easily 5 % or 10 % uncertainty. In addition, the change in the profile due to the uncertainty of the surface tension depends on the capillary constant, i. e., the ratio of $\rho_{\mathrm{metal}} \cdot g/\sigma$. The values of the ratio $\rho_{\mathrm{metal}}/\sigma$ for each metal are indicated in Fig. 2. If the liquid has a smaller capillary constant, a larger droplet is necessary to obtain high accuracy of the surface tension of liquid metals. Thus, a highly reliable value of the surface tension can be obtained if a large drop can be made as a sessile drop. It is, however, difficult to make a large droplet of liquid metal and to keep it stable on a flat substrate which is not wetted by liquid metals. We have, therefore, used a crucible made of carbon, shown in Fig. 3, to make a large drop on that, as shown in Fig. 4 in the present work.

3. Experimental

Figure 4 shows the experimental apparatus. The furnace is heated by a Ni–Cr resistance wire, and its temperature is controlled within ±1 K by a PID controller. The temperature of the sample is determined with a Pt–Pt13 %Rh thermocouple located beneath the crucible. The crucible was set on the alumina pedestal in a uniform-temperature area and accurately levelled. The reaction tube (5.5 cm outer diameter, 5.0 cm inner diameter, 20.0 cm height) is a quartz tube. The atmosphere in the furnace is hydrogen gas, which is flown into the gas-cleaning unit to remove small contaminations of water and oxygen. The quartz tube was evacuated with a mechanical pump and backfilled with high-purity hydrogen.

The drop shadow profile was taken using a CCD camera fitted with a 70–210 mm zoom allowing magnification. The shape of the drop was determined using image analysis software. Then, this drop profile was used to determine the surface tension by comparing the observed shape with that of the solution of the Laplace equation, with the surface tension as a fitting parameter using the computational method developed by Krylov et al. [14]. The values of the density for the liquid metals are quoted from the Ref. [13].

4. Experimental results and discussions

4.1. Dependence of the droplet size on the accuracy of the measured surface tension

As described in the preceding section, the accuracy of the measured surface tension becomes higher the larger the size of the droplet. However, since the experimental conditions such as the size of the apparatus are limited, the adequate size of the droplet in the present experimental conditions was determined. Then, the surface tension of liquid Sn was measured by using the crucible shown in Fig. 3 with an inner diameter of 6, 8, and 10 mm. Figure 5 shows the experimental results of liquid Sn with experimental error bars. In this figure, the open symbols indicate the average value of the measured surface tension by the constraihed drop method, and the closed symbol shows the average value of the experimental results which have been obtained by a sessile

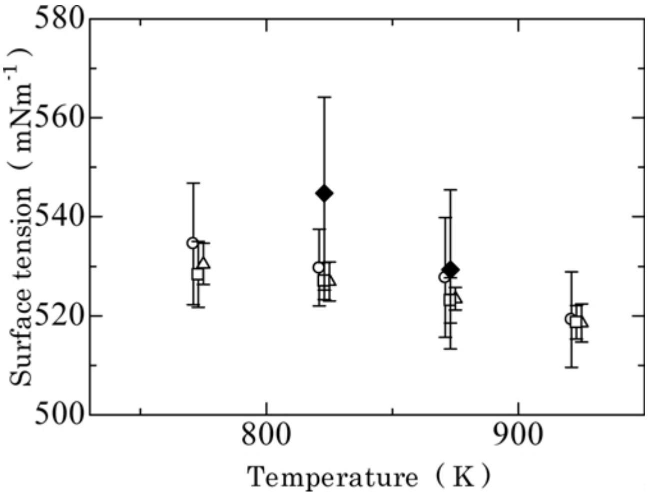

Fig. 5. Surface tension of liquid Sn for various crucible sizes: inner diameters 6 mm (○), 8 mm (□), 10 mm (△).
◆ Data for sessile drop experiment [11].

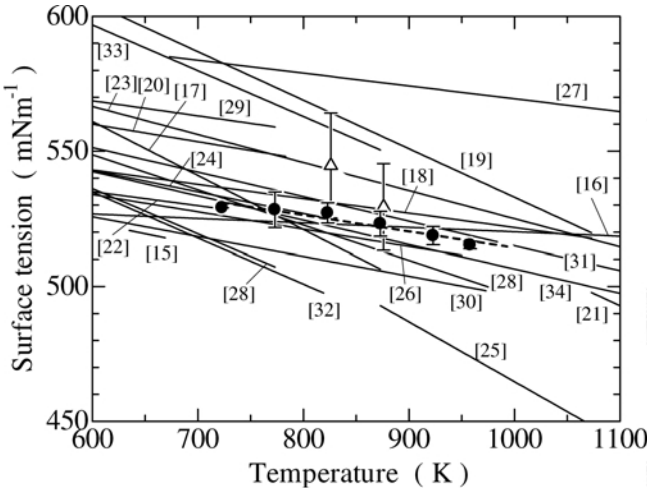

Fig. 6. Surface tension of liquid Sn.
●: Present work, △: Sessile drop [11].

drop method in a previous work [11]. As shown in this figure, the results with the inner diameter of 8 mm indicate higher accuracy than those with 6 mm diameter as well as the results from the sessile drop method. However, by comparing the results with an inner diameter of 8 mm with those with 10 mm, both exhibited almost the same scattering. This is why the ray was not radiated uniformly to the droplet when the 10 mm crucible was used in the present apparatus. Consequently, we have used the crucible with the inner diameter of 8 mm in the present experiments to measure the surface tension of liquid Sn, In, Bi, Pb, and Ga.

4.2. Surface tension of liquid Sn, In, Bi, Pb and Ga

Figures 6–10 show the experimental results of the surface tension of liquid Sn, In, Bi, Pb, and Ga with literature values (Sn: [15–34], In: [20, 26, 32, 35–38], Bi: [15, 17, 28, 32, 37, 39–43], Pb: [15–18, 20, 24, 25, 28, 29, 31, 40, 41, 43–45], Ga: [22, 26, 37, 38, 46–48]). In these figures, the circle and the dotted lines indicate the average value of the measured surface tension at each temperature and its temperature dependence, and the triangle shows the average value of the experimental results, which have been obtained by a sessile drop method in a previous work [11]. As can be seen in Figs. 6–10, the uncertainties of the present results on the surface tension are within 1 %, which is better than in a sessile drop measurement in a previous study [11]. The temperature dependences of the surface tension of liquid Ga, Sn, Bi, In, and Pb are obtained in the present experiment as follows:

Ga: $\sigma_{Ga} = 737 - 0.062T$ mN/m $(823 \leq T \leq 993K)$
Sn: $\sigma_{Sn} = 579 - 0.066T$ mN/m $(723 \leq T \leq 993K)$-
Bi: $\sigma_{Bi} = 417 - 0.070T$ mN/m $(773 \leq T \leq 873K)$
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Pb: $\sigma_{Pb} = 499 - 0.089T$ mN/m $(757 \leq T \leq 907K)$

The large drop method has been applied so far by many researchers [13], but we can elucidate the reason why a large drop should be made to determine the surface tension of liquid metals with high accuracy as described above.

5. Concluding Remarks

(1) The effect of the size of a droplet on the accuracy of the determination of the surface tension is discussed by using the Laplace equation. As the size of the droplet increases, a higher accuracy of the measured surface tension can be

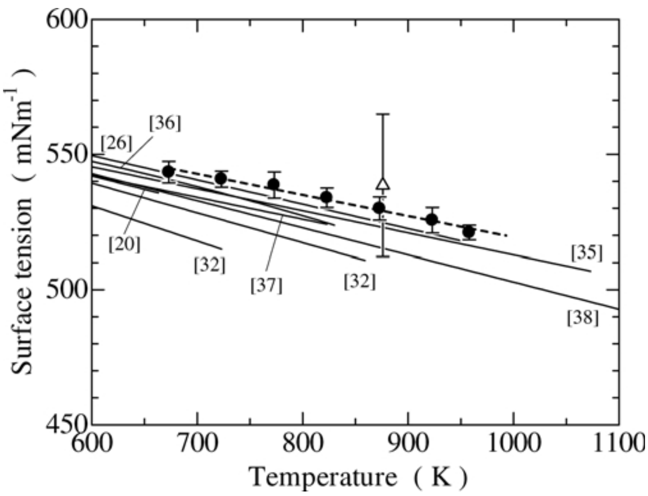

Fig. 7. Surface tension of liquid In.
●: Present work, △: Sessile drop [11].

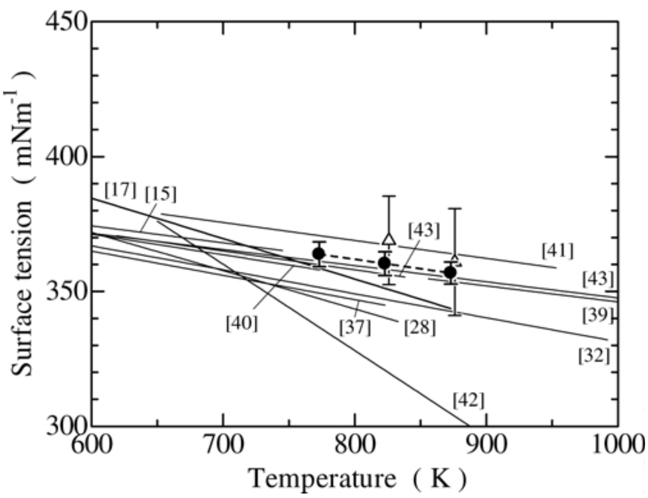

Fig. 8. Surface tension of liquid Bi.
●: Present work, △: Sessile drop [11].

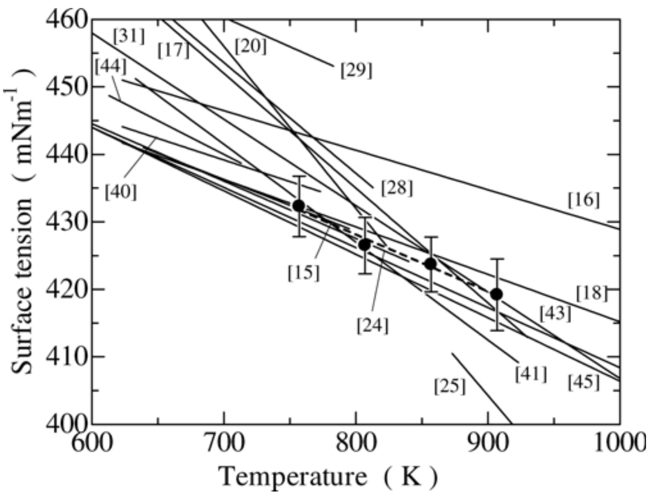

Fig. 9. Surface tension of liquid Pb.
●: Present work.

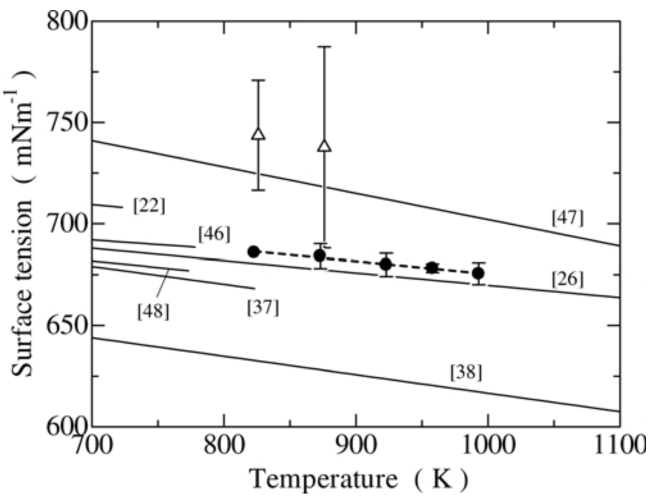

Fig. 10. Surface tension of liquid Ga.
●: Present work, △: Sessile drop [11]

obtained. The effect of the droplet size on the accuracy of the determination of the surface tension depends on the capillary constant of liquid metals, and as the capillary constant becomes larger, the profile of the droplet is identified more clearly for a given value of the surface tension.

(2) The constrained drop method with a special shape crucible was applied to measure the surface tension of liquid Ga, Sn, Bi, In, and Pb. The uncertainty of the measured surface tension was within 1 %.

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