Diffusion of Liquid Metals and Alloys
—The study of self-diffusion under microgravity
in liquid Sn in the wide temperature range—

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Abstract

In the MSL–1 mission the self-diffusion coefficient, D, in liquid Sn was investigated at five temperatures in the wide temperature range up to 1622 K. The long capillary (LC) method was adopted with the use of stable isotope ^{124}Sn as a tracer. The concentration profiles of ^{124}Sn were determined by the SIMS analysis. The D was determined by the analytical solution of the Fick's second law combined with the effective time, t_{eff}. In this effective time the effect of diffusion on both the heating and cooling periods was taken into account properly in addition to the keeping time. In the practical application the iteration method was adopted. The obtained self-diffusion coefficients remain to be small enough even at 1622 K contrary to the abrupt increase of the ground data in the literature due to the same LC method. The present data at 1622 K was in good agreement with D obtained by the shear cell technique, which was adopted in the present MSL–1 mission by NASDA. The extrapolation of present data to the low temperature range is in good agreement with the microgravity data of D due to Frohberg et al. The power index in the temperature dependence of D is 1.81 for the present data and 2.04 for the all microgravity data of D though the latter index seems to be much affected by the data due to Frohberg et al. Obtained data was analyzed by the hard sphere model. Agreement between calculations and experiments is qualitatively good though 1.77 was obtained as the power index for the calculated temperature dependence of D. The prediction of the viscosity of some liquid metals was successfully performed by the hard sphere model, in which the present experimental information of D under microgravity is taken into account.

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I. Introduction

The importance of study of atomic transport in liquids with the high melting temperature, T_m has been recognized deeply from fundamental and applied points of view. The former interests are mainly related to the actual important industrial processes and the latter interests are derived from an interesting and complicated features as many body problems. However, on the ground with gravity, the thermal convection is always accompanied in liquid samples even in the process for keeping at a constant temperature in addition to the heating and cooling processes. The study of diffusion of such melts on the ground, in particular, has been seriously spoiled because of the significant effects of convection on the experimental accuracy. The microgravity is the fascinating condition for the study of diffusion of melts with high T_m because of its property, "no convection". This advantage of microgravity circumstance for the diffusion experiments was for the first time made clear in the self-diffusion measurement of liquid Sn in the D1 mission by Frohberg et al[1], though it was limitted to the rather low temperature range. In this study the self-diffusion, D, of liquid Sn under microgravity was planned to be studied in the wide temperature range on the flight chance of space shuttle "Columbia" in the MSL-1 mission. One reason for this selection is that it is easy to confirm the validity of microgravity for the study of diffusion in melts with high T_m because of the presence of excellent reference data[1]. Another reason is that the temperature dependence can be discussed in the extremely wide temperature range based on the "exact diffusion data under microgravity", which can be constructed with the combination of present data with the excellent reference data[1].

Recently one of present authors[2] presented a simple analytic form of hard sphere model, in which the "exact self-diffusion data under microgravity" play an important role for its discussion.

2. Experimental

The self-diffusion coefficient was measured at temperatures, 900, 1191, 1423 and 1622 K. The measurement at 900 K was performed twice (MET1 and MET5) and corresponds to measurements in the temperature range performed by Frohberg et al[2]. MET2 (1191 K), MET3 (1423 K) and MET4 (1622 K) correspond to measurements in the temperature range beyond it.

The D was planned to be measured by the long capillary (LC) method. In **Fig. 1** is shown the construction of sample container. The carbon spring provides the addition of the slight compression to the liquid sample throughout the course of experiments with considerable volume changes due to the thermal expansion, melting, shrinkage and solidification. This mechanism is required to prevent the Marangoni convection in liquids, which appears easily under microgravity if the free surface or void in liquids is present.

The selection of strength and length of carbon spring was performed based on theories of capillary phenomena[3] by taking into account of the precise data about the dimension of sample container and inner lid and the physical properties of samples. For this machanism the material for the sample container must be "non-wetted" by liquid Sn. The graphite
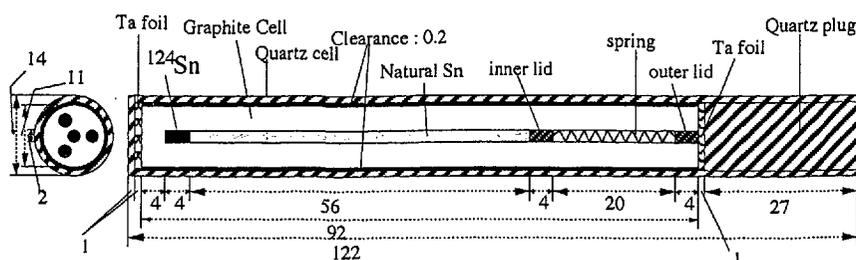

Fig. 1 Constitution of sample container for diffusion coefficient measurement due to the long capillary method.
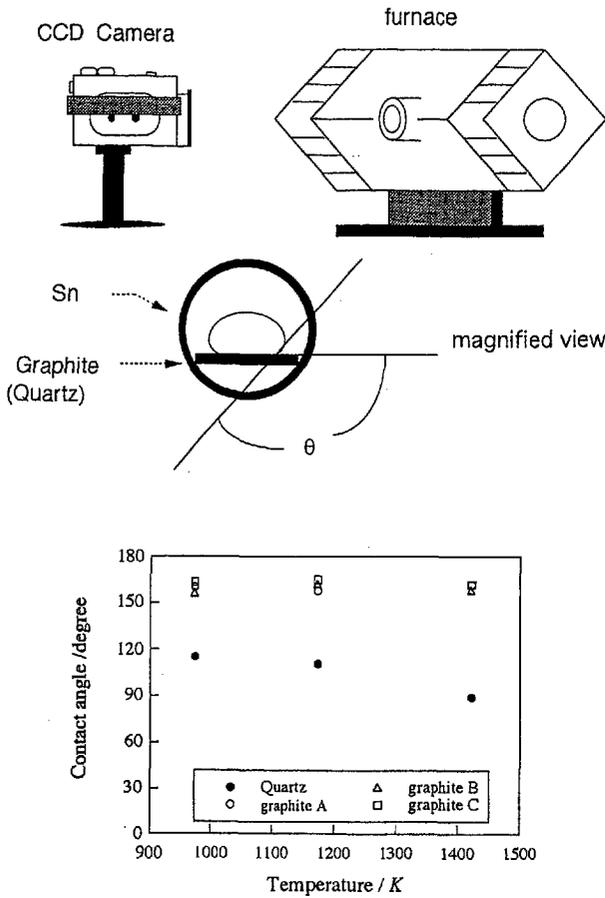
CCD Camera

furnace

Sn

Graphite
(Quartz)

magnified view

θ

Fig. 2 The experimental apparatus and the result of the contact angle θ of liquid Sn against graphite and quartz.

$D_{i,0}$ by using $t_{i,eff}=t_{i,keep}$

$(T_i, D_{i,0}) \rightarrow D_0(T)=A_0 T^{B_0}$

$D_{in}(T)=D_0(T)$

$D_{in}(T)$

$D_{in}(T)=D_{out}(T)$

$D_{in,i}=AT_i^B$

$t_{i,eff}=\frac{1}{D_{in,i}}\int_{T_m}^{T_i}\frac{D_{in}(T)}{dT/dt}dT+t_{i,keep}+\frac{1}{D_{in,i}}\int_{T_i}^{T_m}\frac{D_{in}(T)}{dT/dt}dT$

$D_{i,calc}$ is calculated
in order that $n(x_i, t_{eff})$ may reproduce experimental profile

$n(x, t_{i,eff})=\frac{n_2-n_1}{2}\left[erf(\frac{d+x}{2\sqrt{D_{i,calc}t_{i,eff}}})+erf(\frac{d-x}{2\sqrt{D_{i,calc}t_{i,eff}}})\right]+n_1$

$erf(z)=\frac{2}{\sqrt{\pi}}\int_0^z exp(-\eta^2)d\eta$

$D_{out}(T)=A' T^{B'}$ determined by $(T_i, D_{i,calc})$

$\sigma=\sum_{i=1}^{n}(D_{out}(T_i)-D_{i,calc})^2$ if σ is not the minimum

if σ is the minimum

$D(T)=D_{out}(T)$

Fig. 3 The flow chart of the iteration procedure for the determination of the temperature dependence of diffusion coefficient.

showed such a excellent property, which was confirmed by the observation of almost constant contact angle, 160 degree, between graphite and liquid Sn over 1400 K, which can be seen in **Fig. 2**. Quartz with small contact angles was found to be inappropriate for the present use.

The stable isotope, ^{124}Sn, was employed as the tracer. As shown in Fig. 1, enriched ^{124}Sn (96.96%) was employed as the tracer part and natural Sn of 5N purity (^{124}Sn 5.60%) was employed as the counter part. After the diffusion run the concentration profile of ^{124}Sn in the sample was analyzed by the SIMS analysis.

The self-diffusion coefficient was determined as a function of temperature by using the iteration method, in which the exact solution of the Fick's second law[3] and the effective time[3], t_{eff}, was employed. Explicit expressions for these are as follows:
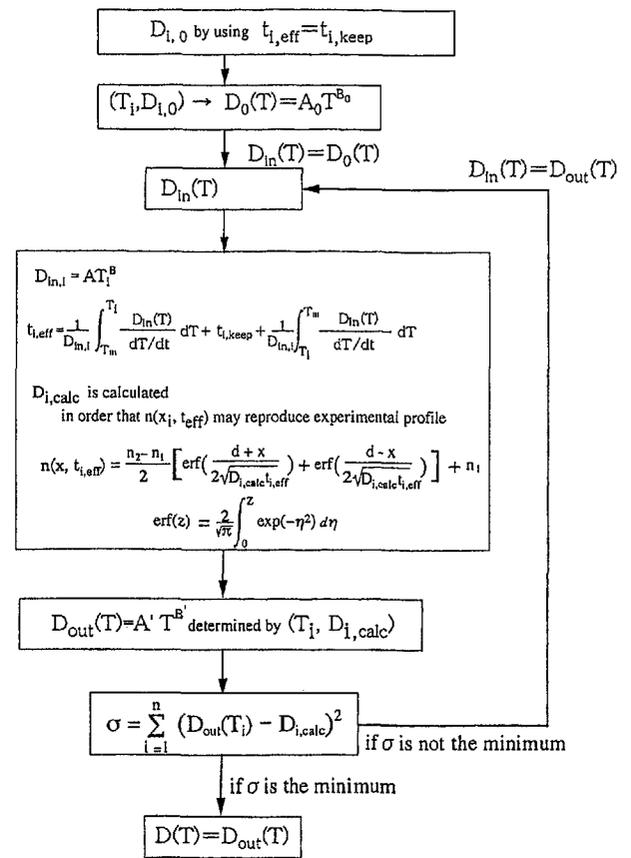
$$n(x, t_{eff})=\frac{n_2-n_1}{2}\left[erf\left(\frac{d+x}{2\sqrt{Dt_{eff}}}\right)\right.$$
$$\left.+erf\left(\frac{d-x}{2\sqrt{Dt_{eff}}}\right)\right]+n_1. \qquad (1)$$

$$t_{eff}=\frac{1}{D_{keep}}\int_{T_m}^{T_{keep}}\frac{D(T)}{dT/dt}+t_{keep}$$

$$+\frac{1}{D_{keep}}\int_{T_{keep}}^{T_m}\frac{D(T)}{dT/dt}dT. \qquad (2)$$

In Equation (1) $n(x, t_{eff})$ is the concentration at the position x and time t_{eff} and n_2 and n_1 respectively represent the initial concentration of tracer in the tracer part (with length d) and that in the counter part. In Equation (2) D_{keep} represents the diffusion coefficient at the keeping temperature T_{keep}; dT/dt is the heating rate and cooling rate respectively. In **Fig. 3** is shown the flow chart of this iteration method. In this iteration method the calculat-
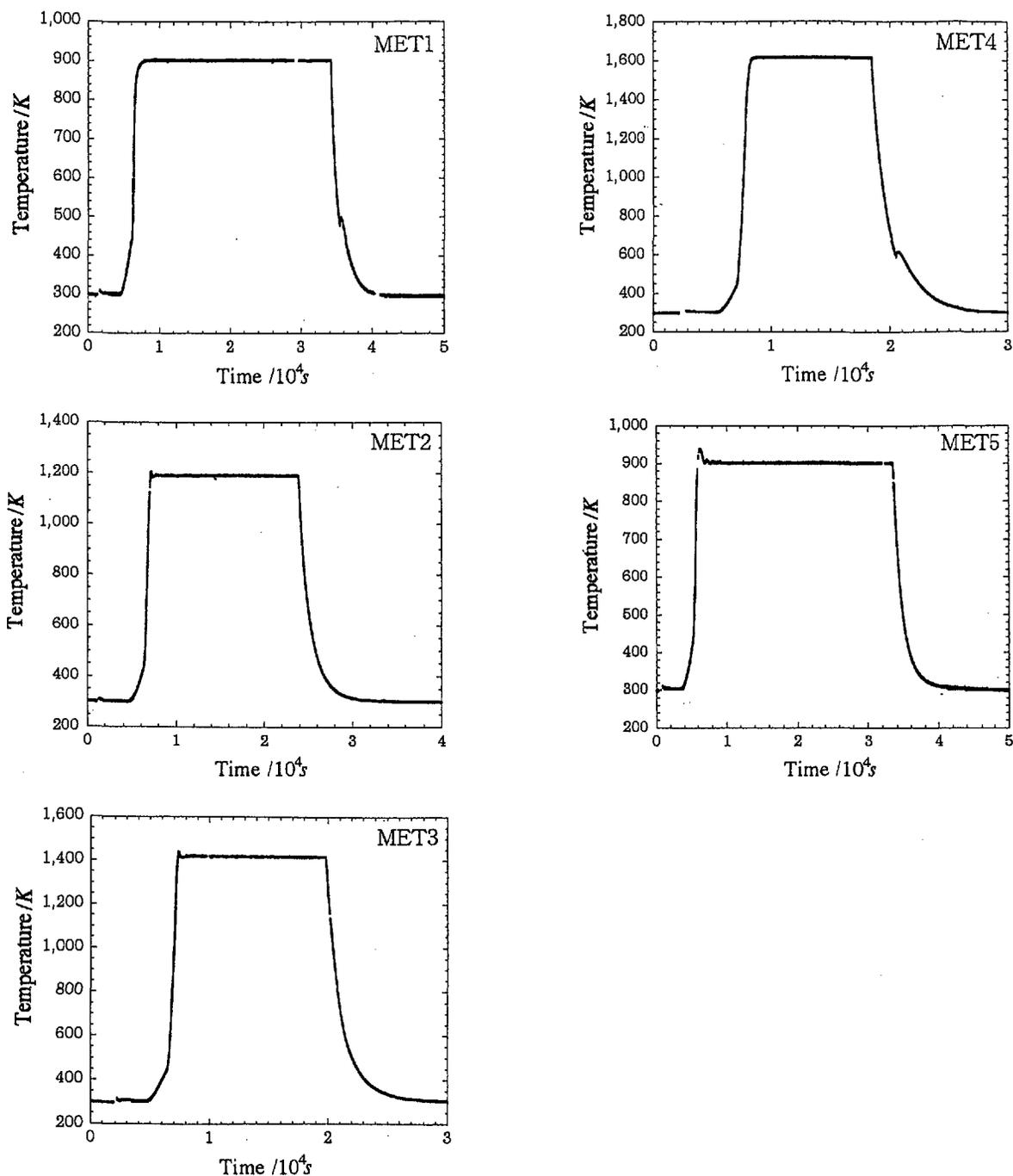
Fig. 4 The temperature variation undr microgravity of the sample in the liquid state for the MSL-mission.

ed concentration profile can reproduce the experimental one with $t = t_{eff}$, in which the diffusion coefficient to be determined is included. The convergency of this iteration is excellent.

3. Results

In **Fig. 4** is shown the temperature variation of samples in the MSL-1 mission. The temperature condition, obtained by the LIF (Large Isothermal Furnace), was good for this present diffusion experiment except for the overheating in some chances and the recalescence in MET1. The former problem was properly taken into account in the analysis of diffusion coefficient due to the iteration method, in which the experimental temperature hysteresis with this overheating was inserted. The latter problem was finally found to be no harm in the analysis because the thermal analysis due to the computer simulation tells us that the

sample of MET1 remained to be in the solid state even after the recalescence.

Measured concentration profiles are shown in **Fig. 5**.

4. Discussions

In Fig. 5 is included also the calculated concentration profiles, which are calculated by this iteration method. In this method a con-siderably good agreement between experiments and calculations was obtained. It is to be noted that all concentration profiles at various temperatures were fitted by using one common temperature dependence of diffusion coefficient.

In **Fig. 6** is shown the temperature, T, dependence of self-diffusion coefficient, D, obtained by the LC method in the present MSL-
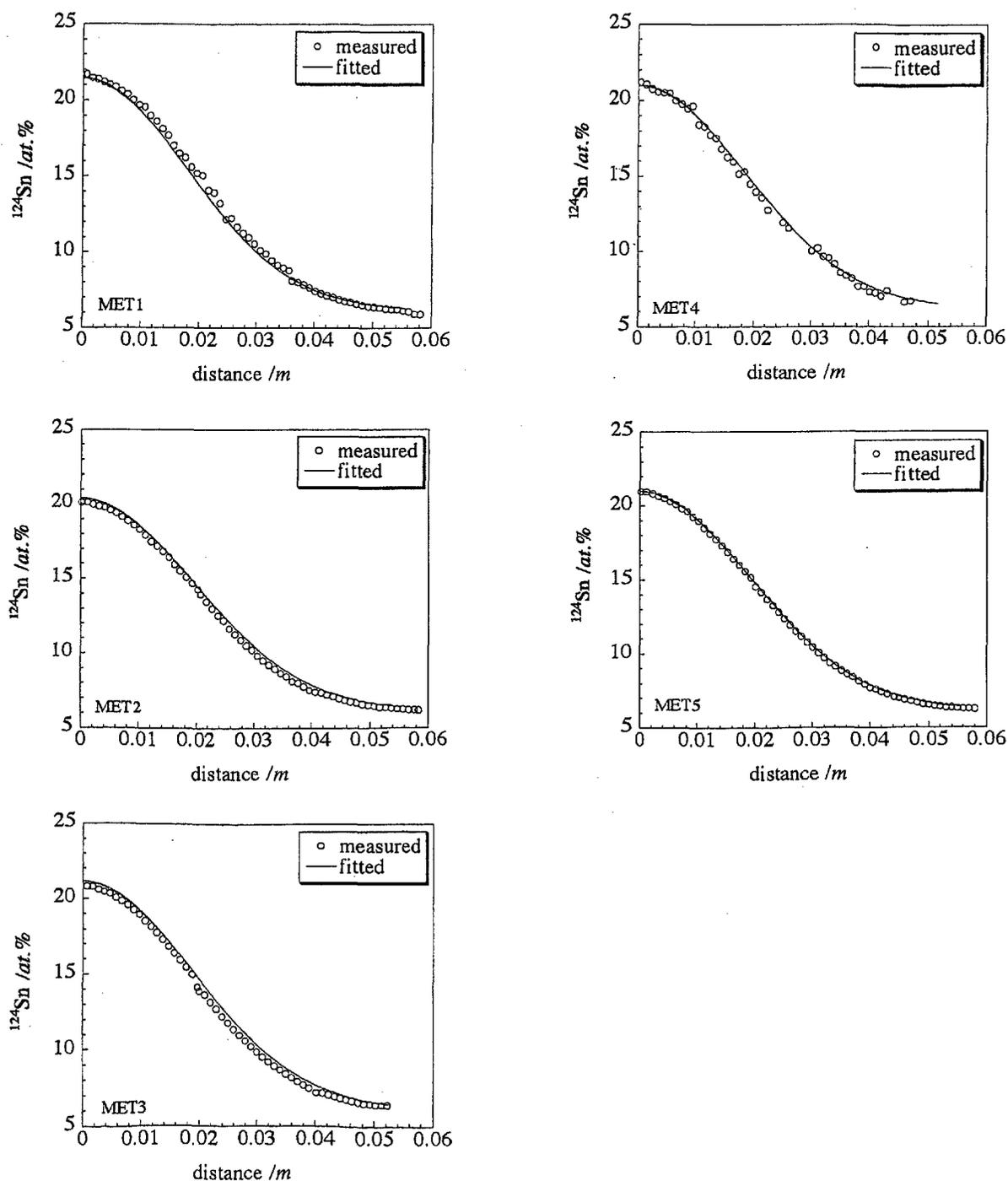

Fig. 5 The comparison of ^{124}Sn in the samples between measured and calculated by the fitting procedure.

1 mission. In the present analysis, this T dependence was summarized by the power law of T, that is $D=AT^B$ and 1.81 was obtained as the power index B.

In **Fig. 7** the present experimental result under microgravity was compared with the data of other data sources. At first, comparisons should be performed between the present microgravity data and the previous data[4] obtained on the ground by the same LC method. It can be known that this ground data shows an abrupt increase in the temperature range over 1100 K. The present data never shows such an abrupt increase even in the temperature range up to 1622 K. The present data are well situated on the extrapolated tendency of data due to Froberg et al[1] under microgravity. In addition the present data at 1622 K well agrees with the data due to the shear cell method performed by NASDA in the present MSL-1 mission. As is well known, the shear cell technique is free from the convection in liquids and the most promizing method for the determination of D for melts with high T_m. The LC method in the present MSL-1 mission can be considered to be performed considerably freely from the effect of convection.

The power index was determined to be 2.02 by using these "all microgravity self-diffusion data for liquid Sn", in which data in lower temperature range due to Frohberg et al[1] seem

to influence this determination significantly.

Following to the previous paper[2] the hard sphere model in an analytic form was employed to explain the behaviour of D obtained under microgravity. The self-diffusion coefficient can be written in the hard sphere model, as follows:

$$D=C_{BS}D_{ENS}. \qquad (3)$$

In this equation, D_{ENS} is the self-diffusion coefficient of dense hard sphere fluid and C_{BS} represents the cage effect in the dense liquids. The explit forms of these are seen in Reference 2).

As can be seen in **Fig. 8**, the calculated values agree with experimental ones particularly in the low temperature range. In this model the hard sphere diameter, σ, plays an essential roles together with the packing fraction, $y(=(\pi n\sigma^3/6$ (n: number density)). The packing fraction, y, is conventionally taken to be $0.46 \sim 0.47$ to represent the structure of liquid metals at the T_m based on the hard sphere model. In this calculation $y=0.464$ was adopted as y at T_m. The empirical equation of Protopapas et al[5],

$$\frac{\sigma(T)}{\sigma(T_m)}=1.123\left\{1-0.112\left(\frac{T}{T_m}\right)^{1/2}\right\}, \qquad (4)$$

was adopted as the T dependence of σ (see the Reference 2). The power index for this calculated curve is 1.77, which is rather closer to
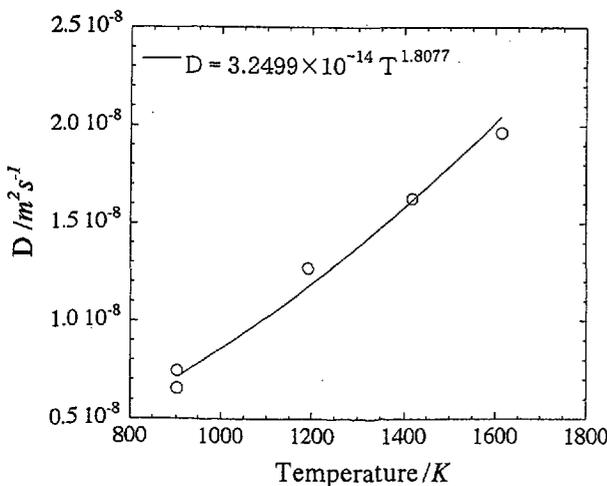

Fig. 6 The temperature dependence of the self-diffusion coefficient in liquid Sn obtained by the long capillary method under the microgravity of MSL-1.
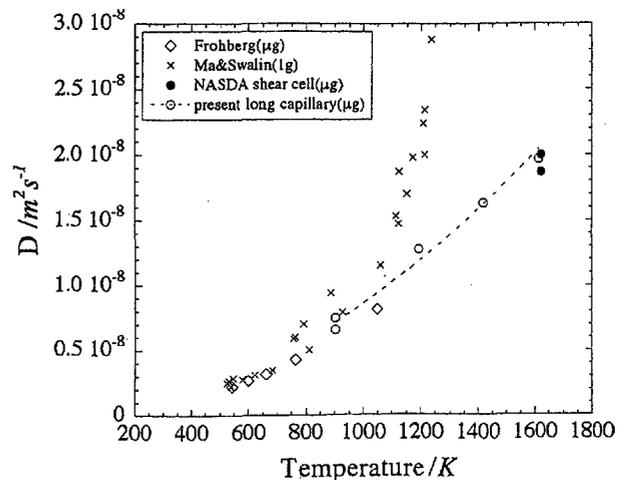

Fig. 7 Comparison of self-diffusion coefficient in liquid Sn with the other data sources.
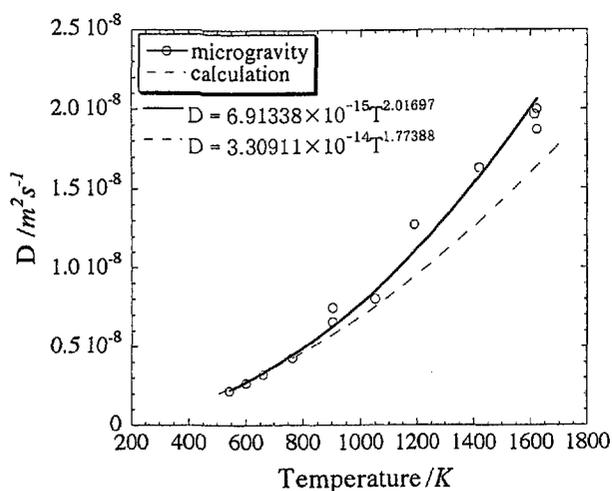
Fig. 8 Comparison of the self-diffusion coefficient of liquid Sn between the present data and calculations based on the hard sphere model.

1.81 determined only by the present data due to the LC method in the MSL-1 mission. In order to determine the exact power index, it may be important to perform the measurement of D in the extremely wide temperature range in one experimental chance.

An "universal" relation was tried to be newly determined for the T denpence of σ. This relation was determined so that the calculated D due to the hard sphere model may reproduce the experimental microgravity, that is "all microgravity self-diffusion data for liquid Sn". Determined relation is in the non-dimensional form as follows:

$$\frac{\sigma(T)}{\sigma(T_m)} = -4.43944 \times 10^{-3} \left(\frac{T}{T_m} - 1 \right)^2$$

$$-5.6447 \times 10^{-2} \left(\frac{T}{T_m} - 1 \right) + 1. \quad (5)$$

Here Equation (5) was tried to be applied to predict the physical properties, which is free from the problem of convection. One such a candidate is the viscosity, which is usually measured under the forced flow. In the case of hard sphere dense liquids it is known that the Stokes-Einstein relation with the slip boundary condition may be established[2]. Therefore, the viscosity can be written as follows:

$$\eta = \frac{k_B T}{2 \pi \sigma D}. \quad (6)$$

In this equation k_B is the Boltzmann constant. The viscosity was calculated for liquid Sn, Pb, In and Sb. The agreement between calculations and experiments is rather good except for liquid Sb, as can be seen in **Fig. 9**. This indicates that the hard sphere model is valid as an universal model for liquid In, Sn and Pb and possibly many liquid simple metals. On the other hand, this model fails to predict successfully the viscosity of liquid Sb. In the case of liquid state of semi-metals, such as liquid Sb, and semiconducting matters, such as liquid Ge[3], the hard sphere model is not valid at least in a straight manner. The effect of covalency in this kinds of liquids may be responsible to this disagreement. In near future these points will be discussed in more detail.

Finally, compared with the case of "previous" equation (4) of Protopapas et al, the prediction of viscosity is better in the case of "present" equation (5) newly determined with the use of microgravity data (see Fig. 9). This indicates that the acquisition of accurate data under microgravity may contribute significantly to the fundamental science at least for the diffusion of melts with the high melting temperature.

5. Conclusions

The self-diffusion coefficient, D, in liquid Sn was measured by the long capillary method under microgravity in the MSL-1 mission. Obtained D remains to be small even at 1622 K contrary to the abrupt increase over 1100 K for ground data in the literature measured by the same long capillary method. The power index for the temperature, T, dependence of D for liquid Sn is 1.81 for the present long capilary data and 2.02 if "all self-diffusion data of liquid Sn under microgravity" are included. The T dependence was reproduced qualitatively by the hard sphere model with the power index 1.77. New equation is proposed for the T dependence of hard sphere diameter, which was determined by using "all self-diffusion data of liquid Sn under microgravity". The adoption of this equation in the hard sphere model was succesful to predict the viscosity of some liquid metals except for liquid Sb. The
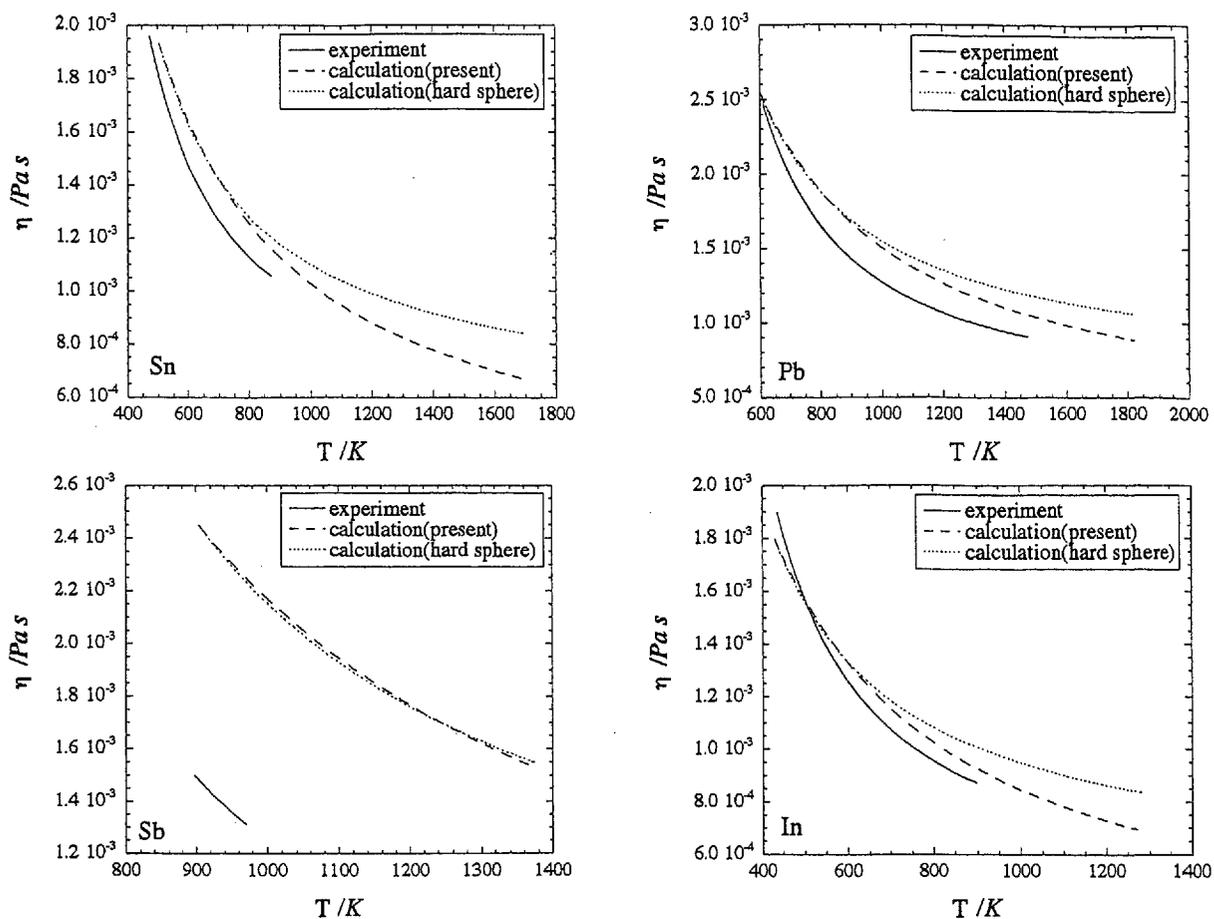
Fig. 9 Comparison between calculated viscosities due to the hard sphere model and experimental ones.

failure in the case of liquid Sb may be related to the particular feature of its liquid structure. In future the atomic transport in melts with the high melting temperature must be intensively studied under microgravity with the relation to the complexity of melts or the structure of melts.

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