

3. The Experimental Plan for the First IAO (International Announcement of Opportunity) in the ISS (International Space Station)

Toshio Itami¹

¹Japan Aerospace Exploration Agency, 2-1-1 Sengen, Tsukuba, Ibaraki, 305-8505 Japan

1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation $f(x) = \int_0^x f(t) dt$. It is shown that $f(x)$ is a constant function, and its value is determined by the initial condition $f(0) = 1$.

Outline of proposal

Based on the activities in 1999 and 2000, a proposal of the experimental plan for the first international competition in the international space station was performed in January in 2001. The title of the proposal is

“Roles of the short range order on the self- and impurity diffusion of liquid group 14(IVB) elements with a different degree of complexity”.

In this proposal a microgravity experiment for the self- and impurity diffusion coefficients in liquid germanium is proposed. Based on the analysis of the hard sphere model, group IVB liquids are classified into two groups; one is the densely packed liquids of heavier elements, Sn and Pb; the other is the loosely packed liquids of lighter elements, Si and Ge, which are semiconductors in the solid state and whose structures of liquids are known to be “complex”. As for the self-diffusion in liquid germanium, the hard sphere model predicts rather an universal diffusion law among group IVB liquids in spite of the presence of the difference in the packing. On the other hand, molecular dynamics simulations predict different diffusion laws each other among group IVB liquids. The first purpose of the present proposal is to conclude which is correct between these two predictions. Together with the self-diffusion coefficient, the impurity diffusion coefficients for Si and Sn impurities respectively are also measured under microgravity. The Sn impurity tends to be excluded from the host Ge circumstance due to the intrinsic phase separation tendency. On the other hand, the Si impurity tends to be incorporated in the host Ge circumstance. We can investigate the possibility of the existence of covalent bond in liquid Ge by performing the comparison of impurity diffusion coefficients between Si impurity and the Sn impurity. The microgravity experiments from the melting temperature up to 1800K are to be performed based on the shear cell technique, in which the alignment of liquid column of diffusion sample is in-situ confirmed by the X-ray observation system installed in the Advanced Furnace for Microgravity Experiments with X-ray Radiography(AFEX).

The self- and impurity diffusion coefficients obtained in the present proposal provides the exact and important information for the advance of atomic transport theory of liquids, for which up to date we have obtained no rigorous standard theories due to the absence of reliable experimental data. In addition, they are to be utilized for the estimation of diffusion coefficient in melts of semiconductor materials; such information is required for the optimum control of crystal growth processes of semiconductors. The detailed description of the proposal is described in the next part.

A. OBJECTIVES

The main objectives of our “diffusion project” are to clarify the diffusion mechanism and to establish a diffusion model for simple molten metals and complex semiconductor melts such as Si and GaAs by means of highly precise diffusion measurements. Through this “diffusion project” we plan to investigate the relationship between the liquid diffusion and the microscopic liquid structure. We hope to answer which particular features of liquid structures crucially influences the diffusion mechanism in complex liquids. The research activities contained in this proposal consist of the diffusion measurements supported by the numerical simulations of fluid dynamics, the theoretical analysis using the hard sphere model, the classical and *ab initio* molecular dynamics and mode coupling theory, and liquid structure measurements by X-ray scattering and neutron scattering. Especially we have been fascinated with the relationship between the diffusion in liquids and the structure of liquids.

Our target in this proposal is to study the diffusion mechanism in liquid Ge in the systematic trend of the IVB group (Si, Ge, Sn, and Pb). Solid state Si and Ge with lighter atomic masses have the diamond type covalent bonds and show the semiconductive character. On the other hand Pb element with heavier atomic mass has the metallic character. The solid state Sn is intermediate between the metallic and the semiconductive character. It is metallic at the high temperatures while it is semiconducting with a diamond structure at the low temperatures. The structure of liquid group IVB elements reflects this systematic variation of the chemical bond in the solid states. Figure 1 shows the systematic trends of static structure factors, $S(Q)$'s, in the liquid state [1]. In the case of liquid Si, a distinct shoulder is present in the high Q side of the first peak of $S(Q)$. This trend is clear also for liquid Ge. In the case of liquid Sn, this shoulder is small but still present. On the other hand no such a shoulder can be seen in the typical metallic liquid Pb. Therefore, systematic investigation of diffusion in liquid group IVB elements corresponds to the study of diffusion with systematic variation of complexity.

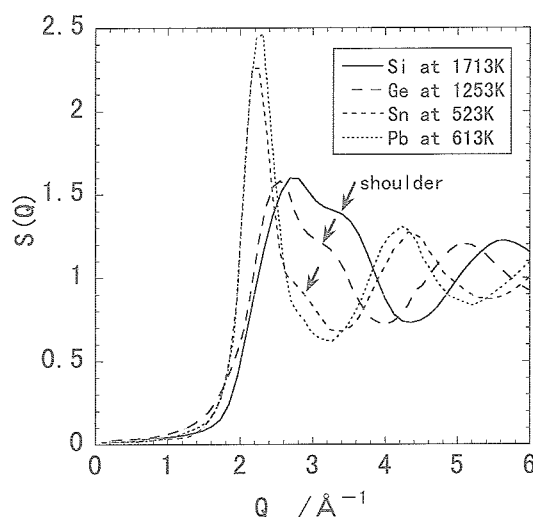


Figure 1. Structure factor of liquid IVB elements near the melting point.

Several excellent self-diffusion experiments have been performed under microgravity in rather simple liquids, the liquid Pb [2] and the liquid Sn [3,4,5]. Present proposal will start with the study of self-diffusion and the impurity diffusion in liquid Ge, and it will be expanded to include more complex liquids such as the liquid Si and the melts of compound semiconductor GaAs.

B. SPECIFIC AIMS

In order to clarify the role played by the complexity in the liquid structure on the diffusion in liquid Ge, the following two specific aims are presented.

- (1) Two hypotheses can be derived from the hard sphere model and the molecular dynamics study to find out whether the complexity in the liquid structure, such as the shoulder of the first peak in the static structure factors, $S(Q)$, will have any effects on the diffusion phenomena. The hard sphere model, which stresses the importance of packing of atoms but doesn't reproduce the shoulder in $S(Q)$, predicts the existence of a common law among the temperature dependence of self-diffusion coefficients of the group IVB elements (Hypothesis A). On the other hand, the molecular dynamics study predicts that the diffusion phenomena

in liquid Ge are different from those in liquid Sn due to the different degree of the complexity or due to the different degree of the existence of the shoulders (Hypothesis B). The first aim is to identify the correct prediction between these two predictions, and to clarify the role played by the particular feature in the short range order in Ge on the diffusion phenomena.

- (2) In order to investigate the effect of the variation of the degree on the complexity in liquids, impurity diffusion measurements in liquid Ge will be conducted with the impurity of Si, which should make covalent bond with Ge, and Sn with no covalent bond with Ge, respectively. The second aim is to verify whether chemical bonds will play a role on the diffusion mechanism. Based on the deviation of observed impurity diffusion coefficients from values predicted by the hard sphere model (Hypothesis C), we can know whether the effect of chemical bonds is present or not on the diffusion mechanism in liquid Ge.

C. HYPOTHESES

C.1 Hypothesis A

Hypothesis A, derived from the hard sphere model, states that there exists a common temperature dependence among the diffusion coefficients of liquid group IVB elements in spite of the difference in their liquid structures (see Figure 2).

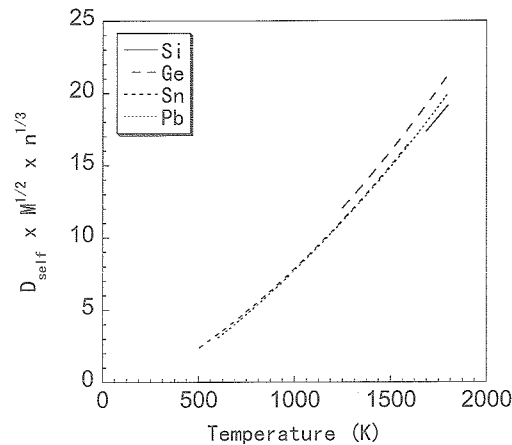


Figure 2. Temperature dependence of $D_{\text{self}} \times M^{1/2} \times n^{1/3}$ based on the hard sphere model (D_{self} : self diffusion coefficient; M : atomic mass; n : number density of atoms)

Melts of group IVB elements can be classified into two kinds of liquids, the densely packed liquids and the loosely packed liquids. Liquid Pb and liquid Sn belong to the former group while liquid Ge and liquid Si belong to the latter group. In spite of such a difference, there exists a common temperature dependence (diffusion law) among the self-diffusion coefficients of liquid group IVB elements.

According to the hard sphere model [6], the self-diffusion coefficient, $D_{\text{self}}^{\text{HS}}$, can be expressed by

$$D_{\text{self}}^{\text{HS}} = C_{\text{BS}} D_{\text{ENS}}. \quad (1)$$

In this equation, D_{ENS} is so called the Enskog formula, which represents the self-diffusion coefficient of dense gases. The explicit form of D_{ENS} is given by

$$D_{ENS} = \frac{8}{3} \sigma \left(\frac{k_B T}{M} \right)^{\frac{1}{2}} \left\{ \frac{6y g_{HS}(\sigma)}{\pi} \right\}^{-1}. \quad (2)$$

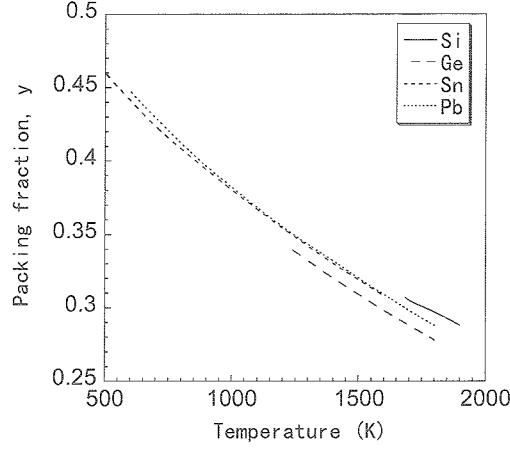


Figure 3. Temperature dependence of packing fraction of liquid IVB elements calculated from the entropy

In this equation, k_B , T and M are respectively the Boltzmann constant, the absolute temperature and the atomic mass. The parameters, y and σ , are respectively the packing fraction and the hard sphere diameter. These two parameters are related each other by the relation, $y = \frac{1}{6} \pi n \sigma^3$, where n is the number density. The symbol $g_{HS}(\sigma)$ designates the radial distribution function at the hard sphere contact. The particular feature of the hard sphere model is that the liquid structure can be expressed only by the packing fraction y (or σ). In liquids, the movement of a tagged particle is hindered by surrounding atoms due to the high liquid density. This cage effect is taken into account by the back scattering factor, C_{BS} . C_{BS} depends only on the packing fraction if one assumes the hard sphere pair interactions. Therefore, from a viewpoint of the hard sphere model, the (normalized) self-diffusion coefficient, D_{self} divided by the factor $(\sqrt{M}n^{1/3})^{-1}$, is only a function of T and y (Note the relation, $\sigma = \left(\frac{6y}{\pi n}\right)^{1/3}$).

The packing fraction, y , can be determined by fitting the calculated values of entropy, S , to the experimental data [7,8]. The entropy is one of structure sensitive physical quantities. The explicit expression of the entropy on the hard sphere model is given as Eq. (3). (Note that Eq. (3) corresponds to the excess entropy, namely, the entropy of liquids minus that of ideal gas [9].)

$$\Delta S_{HS} = N k_B \frac{y(3y-4)}{(1-y)^3}. \quad (3)$$

Packing fraction of liquid group IVB elements calculated from the entropy is shown in Figure 3 as a function of temperature. From this figure we conclude that there is an almost unique y vs. T relationship in the liquid group IVB elements. In the case of the loosely packed liquids (Si and Ge), the values of packing fraction near the melting point are lower, 0.3~0.35. On the other hand, they are larger, ~0.45, for the densely packed liquids (Sn and Pb). It is well known that y is nearly 0.45 at the melting point for simple metals [10]. The loosely packed structure of liquid Si and liquid Ge may be closely related to the loosely packed structure of diamond lattice in the solid state.

In spite of such a difference, the calculated result of the (normalized) self-diffusion coefficient, $D_{self} \sqrt{M} n^{1/3}$, shown in Figure 2, indicates that there exists a common temperature dependence in the self-diffusion coefficients

of the liquid group IVB elements. This temperature dependence can be represented by the power law, $D_{self} = AT^n$ (A: constant) with the power index (n), 1.5 ~ 1.7 for all liquid IVB elements. In order to verify the “Hypothesis A”, whether the power index is in 1.5 ~ 1.7 or not, the experimental error must be lower than 5 %.

C.2 Hypothesis B

Hypothesis B, derived from the molecular dynamics study, states that the temperature dependence of the self-diffusion coefficient in liquid Ge is different from that of liquid Sn due to the difference of the degree of the complexity, or due to the different degree of the existence of the shoulder as shown in Figure 4.

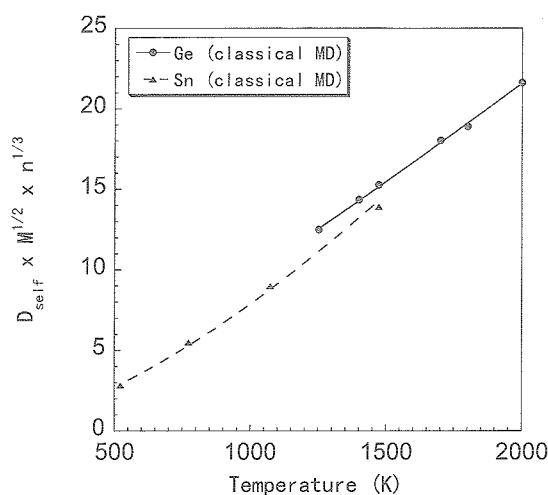


Figure 4. Temperature dependence of $D_{self} \times M^{1/2} \times n^{1/3}$ due to the classical molecular dynamics simulations

At present, we have some results for liquid Sn and liquid Ge obtained through the classical molecular dynamics. The interatomic potential of liquid Sn was obtained from the experimental $S(Q)$ [1] based on the inverse problem method developed by Munejiri and Hoshino [11,12]. Interatomic potential of liquid Ge was obtained from the pseudopotential theory of cohesive energy in liquid metals [10, 13]. We could successfully reproduce the experimental static structure factor, $S(Q)$, by these classical molecular dynamics.

Figure 5 shows the velocity autocorrelation function (VAF) of liquid Ge and liquid Sn calculated by the classical molecular dynamics. The calculated VAF of liquid Sn damps with oscillation around zero; the negative value of VAF implies a high probability of large-angle deflection of atom in its motion. Since a tagged atom is enclosed in a cage formed by its neighboring atoms, the atom cannot diffuse easily but vibrates in the cage for a relatively long time. On the other hand, VAF of liquid Ge does not oscillate but decays monotonously without taking negative values. This means that the cage effect does not exist so much and atoms can propagate over larger distances without any collision.

Obtained temperature dependence of self-diffusion coefficient in liquid Ge can be represented by the power law with the power index of 1.2, which is smaller than that of liquid Sn, 1.7, as shown in Figure 4. In order to verify the difference of the power index, the experimental accuracy of 5% is required.

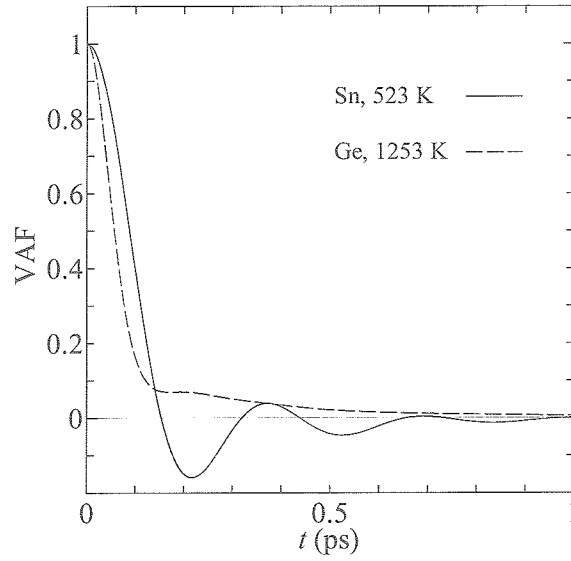


Figure 5. Velocity autocorrelation function of liquid Sn and liquid Ge calculated by the classical molecular dynamics

C.3 Hypothesis C

Hypothesis C states that the impurity diffusion in liquids can be predicted by the hard sphere model. If the observed impurity diffusion coefficient deviates from this prediction, we can tell the effect of the chemical bonds on the diffusion mechanism in liquids.

The impurity diffusion coefficient, D_{impurity} , can be written as Eq. (4) on the hard sphere model [10] in the form of the ratio to the self-diffusion coefficient, D_{self} , i.e.

$$\frac{D_{\text{impurity}}}{D_{\text{self}}} = \frac{\sigma_{\alpha\alpha}^2 g_0(\sigma_{\alpha\alpha})}{\sigma_{\alpha\beta}^2 g_{0\alpha\beta}(\sigma_{\alpha\beta})} \left(\frac{M_\alpha}{M_{\alpha\beta}} \right)^{1/2} = \frac{\sigma_{\alpha\alpha}^2 g_0(\sigma_{\alpha\alpha})}{\sigma_{\alpha\beta}^2 g_{0\alpha\beta}(\sigma_{\alpha\beta})} \left\{ \frac{1}{2} \left(1 + \frac{M_\alpha}{M_\beta} \right) \right\}^{1/2}. \quad (4)$$

In this equation, $\sigma_{\alpha\beta}$ is the average of hard sphere diameters of the species α and β . The symbol $g_0(\sigma_{\alpha\alpha})$ is the radial distribution function of pure liquids at the distance $\sigma_{\alpha\alpha}$. The symbol $g_{0\alpha\beta}(\sigma_{\alpha\beta})$ is the radial distribution function of liquid mixtures at the distance $\sigma_{\alpha\beta}$. $M_{\alpha\beta}$ is the reduced mass between atomic mass M_α of the species

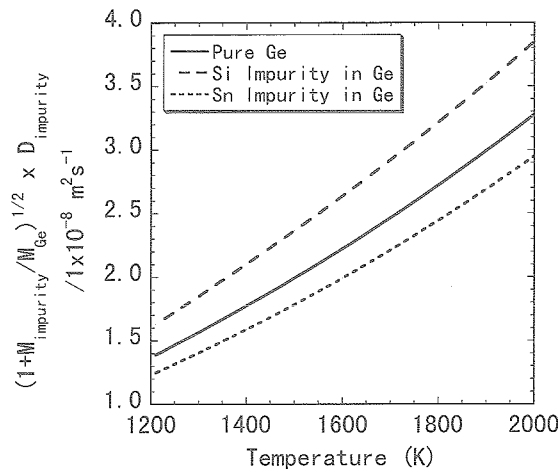


Figure 6. Temperature dependence of $(1 + M_{\text{impurity}}/M_{\text{Ge}})^{1/2} \times D_{\text{impurity}}$ of IVB elements in liquid Ge (D_{impurity} : impurity diffusion coefficient; M_{impurity} : atomic mass of impurity)

α and M_β of species β . If experimental impurity diffusion coefficients deviate from the predicted values from the hard sphere model, the effect of chemical bond must be present on the diffusion in liquids. In this case, the liquid diffusion model must take account of the effects of chemical bonds. If the agreement between experimental values and the predicted values is satisfactory, the effect of chemical bond may be small. In this study we select Si atom and Sn atom as an impurity in liquid Ge. It is well known that the phase diagram of Ge-Si system shows the complete mutual solubility each other both in the solid and liquid states. That is, Ge atoms tend to mix with the impurity Si atoms randomly. On the other hand, the phase diagram of Ge-Sn system is eutectic type, whose eutectic composition is in the extremely Sn rich side, 0.3%Ge. This indicates that the tendency of agglomeration of Ge atoms prevails compared with the tendency of mutual random mixing. Therefore, the effect of covalent bond, if present, may be expected not for Sn impurity but for Si impurity. The effect of chemical bonds may be investigated by the impurity diffusion of Si and Sn in liquid Ge.

The predicted values of the hard sphere model itself are shown in figure 6 for the impurity diffusion coefficient of Si and Sn together with the self-diffusion coefficient in liquid Ge. In this figure the explicit dependence on atomic mass is excluded by multiplying the factor, $(1 + M_{\text{impurity}} / M_{\text{Ge}})^{1/2}$, and D_{impurity} . The impurity diffusion coefficients of Sn in Ge are predicted to be 10 % lower than the self-diffusion coefficients of Ge, and those of Si are predicted to be 17 % higher than the self-diffusion of Ge. Since the self-diffusion of Ge will be measured with less than 5 % error, the impurity diffusion experiments must be performed with the accuracy of less than 4% to detect the effect of liquid structure on D_{impurity} on the hard sphere model.

D. BACKGROUND AND SIGNIFICANCE

Clarification of the roles played by the short range order on the physico-chemical properties in metallic and semiconductor melts belongs to the most advanced fields in the today's condensed matter science. We plan to give a clear answer to this problem through the proposed diffusion studies in liquid group IVB elements. These elements show a systematic trend in their liquid structure ranging from Si, that shows the distinct shoulder in the structure factor, to Pb that shows a typical liquid metal type of structure with no shoulders (see Figure 1).

The self-diffusion coefficients of Sn were measured by Froberg et al. during the D1 mission [3] and by Yoda et al. [4] and Itami et al. [5] during the MSL-1 mission. Froberg et al. also measured the self-diffusion coefficients of Pb during the D2 mission [2]. A good agreement was obtained between the hard sphere model and the self-diffusion coefficients of the liquid Pb and Sn. Structure of liquid Pb is typically liquid metal like, and liquid Sn shows a small shoulder in the first peak of the structure factor, $S(Q)$. The structure of liquid Ge is more complex and shows a distinct shoulder in its structure factor. It is very interesting to investigate the temperature dependence of self-diffusion coefficient of liquid Ge. Up to now, self-diffusion coefficient of liquid Ge has been measured by Itami et al. [14] and also by Yoda et al. [15] under the microgravity condition provided by the TR-1A 5 rocket flight. Itami et al. used the long capillary method while Yoda et al. adopted the shear cell technique. The shear cell technique gave an excellent concentration profile, that could be well fitted to the solution of Fick's second law. However, its measurement was made at only one temperature, the microgravity time was a little too short as will be discussed later. Thus, this shear cell data for liquid Ge cannot be considered more than a preliminary data. In the case of long capillary method, the diffusion experiment suffered from the volume dilation of solidifying Ge. It was concluded through this experience that the shear cell should be adopted in the diffusion experiments for liquids which show volume dilation on solidification. Also, it is important to allocate a long microgravity period for the diffusion experiments in liquid Ge.

If the effects of the short range order on the diffusion in liquid group IVB elements are clarified from the systematic study, the diffusion of Si, which has the lighter atomic mass in group IVB, can be evaluated. Si is the most important material for the semiconductor industry, but it is also the most difficult material for diffusion measurements because of its high reactivity. This will set the stage for the study of more complex melts, such as melts of III-V semiconductors.

Our project is organized involving various scientists for diffusion experiments, liquid structure measurements and liquid theories. The diffusion experiment group includes the development of the shear cell techniques and the numerical analysis of the fluid dynamics. Many of our members also have experiences of conducting diffusion experiments in microgravity as shown in Table 1. Especially their experiences were with the shear cell technique. We have succeeded in shearing and dividing the samples in all previous experiments.

The liquid structure measurement group employs the small angle X-ray scattering and the neutron elastic [16,17] and inelastic scattering [18] to obtain the microscopic information of static and dynamic structure of liquids. The neutron scattering experiments are conducted in cooperation with Japan Atomic Energy Research Institute.

The liquid theory group will clarify the diffusion mechanism and will produce a diffusion model. They use the hard sphere model, the classical molecular dynamics [19], the *ab initio* molecular dynamics [17] and the mode coupling theory [20]. The *ab initio* molecular dynamics, being free from the assumption on interatomic interactions, may in principle be the most accurate tool for the study of atomic motion. However, the *ab initio* molecular dynamics needs to confirm the system size dependence of simulations, that may exceed the capacity of even the present supercomputers. On the other hand, although the classical molecular dynamics is free from such a problem, it requires suitable interatomic potentials for simulations, which is not always available for complex liquids. The essential feature of hard sphere model is in its “simplicity”, and the “analytical expressions” for many physical quantities. The features in liquid structures essentially depend on a single parameter, the packing fraction η which is the ratio between the fractions of the repulsive region per atom to the whole region per atom. The hard sphere model has an additional advantage of grasping the global feature of liquids. Our theoretical and experimental expertise in combination with all the tools available in our disposal will enable us to establish a new diffusion model for the complex materials.

Table 1. The microgravity experimental experiences of the project members

Experiments (Method)	Mission (year)	Reference
Interdiffusion of lead-tin-telluride (Long capillary)	TEXUS ^{*1} ('88, '90, '92), TR-1A4 ^{*2} ('95), MSL-1 ^{*3} ('97)	[21,22]
Self-diffusion of Ge (Long capillary)	TR-1A 5 ^{*2} ('96)	[14]
Self-diffusion of Ge (Shear cell)	TR-1A 5 ^{*2} ('96)	[15]
Self-diffusion of Li (Long capillary)	TR-1A6 ^{*2} ('97)	[23]
Self-diffusion of Sn (Long capillary)	MSL-1 ^{*3} ('97)	[5]
Self-diffusion of Sn (Shear cell)	MSL-1 ^{*3} ('97)	[4]
Interdiffusion of Ag-Cu (Shear cell)	TR-1A 7 ^{*2} ('98)	[24]

*1 TEXUS : German sounding rockets

*2 TR-1A : Japanese sounding rockets

*3 MSL-1 : The First Microgravity Science Lab, a space shuttle mission

E. MICROGRAVITY ENVIRONMENT

E.1 Necessity of Long Microgravity Period

In spite of the efforts to suppress convection flows in melts, measuring accurate diffusion coefficient by the ground experiments has not been as successful as the microgravity experiments. Self-diffusion or impurity diffusion measurements should be performed under isothermal condition on the ground, however it is difficult to achieve such condition in practice especially at temperatures as high as 1300 K. Numerical simulations show that material transport is surely enhanced by convection. According to a numerical analysis even a temperature difference of less than 0.5 K across the sample at the vertical capillary configuration can cause flows in liquid samples even though calculated concentration profiles show good fits for the Fick’s second law with apparent diffusion coefficient [25]. The measurement error is still higher than 10-20% on the ground due to convection. Recently, there have been attempts to measure diffusion coefficients under application of strong magnetic fields to reduce convection on the ground. Mathiak and Froberg [26] performed the experiments concerning the strong magnetic fields on interdiffusion. They compared their results with microgravity measurements. The mean diffusion coefficient in magnetic field was 6.4% higher than that in microgravity even at the relatively low diffusion temperature, 523 K. The experimental errors in diffusion coefficients should increase with temperature increase because of the lower viscosity and higher temperature inhomogeneity, and the error won’t be low enough to verify our hypothesis.

In order to develop and verify our liquid diffusion model, we are aiming for the accuracy of measured diffusion coefficients within 4%. This requirement of accuracy comes from the necessity to verify our Hypotheses A, B and C. Our previous microgravity experience assures us that the necessary experimental accuracy can be readily obtained by our refined experimental method if the diffusion coefficients are measured in the space microgravity environment.

The shear cell method will be employed to prevent the concentration profile in liquids from the flow caused by the volume dilation on solidification, as described above. The demerit of the shear cell method is in the flow that is generated in the sample during the “shearing” procedures (joining and dividing of a sample). A long diffusion period is needed to make this error as small as possible in order to precisely measure the diffusion coefficients. It was reported that the length of the disturbance by shearing was about as long as sample radius [27]. We assumed that the disturbance occurred about ± 2 mm at the beginning of the experiments with 2 mm diameter sample. Therefore, the error due to the division of a liquid sample at the end of a experiment is negligibly small if the shear cell thickness is larger than the sample diameter. However, we need to clarify the initial disturbance from joining of the sample. We calculated the error from this disturbance with various diffusion times. Table 2 shows the calculated errors in the diffusion coefficients due to the initial disturbance of joining. It was found that 7000 seconds (117 minutes) is needed to make the error under 1 %. In order to satisfy the total error under 4 %, more than 2-hour microgravity period is needed.

Table 2. The errors in the diffusion coefficients due to the initial disturbance of joining

Diffusion time	2000 s (33.3min)	4000 s (66.7min)	6000 s (100.0min)	7000 s (116.7min)	8000 s (133.3min)
The error in the diffusion coefficient	2.9 %	1.7 %	1.1 %	0.9 %	0.8 %

E.2 Gravitational Disturbance in ISS

Our experiment will be designed to minimize the effects of convection flows which might affect the diffusion measurements. Concentration profiles will be readily disturbed by the flows which might be induced by the residual gravity and the g-jitters existing in the ISS environment. The experimental condition has to be optimized to carry out highly precise diffusion experiment in microgravity. Therefore, a numerical analysis of the effects of convection on diffusion measurements has been performed to estimate the experimental error and to optimize experimental conditions. A three-dimensional model with a container was employed for this analysis. The convection was induced by both temperature and concentration gradients. The diameter of a specimen was varied from 0.5 mm to 2.0 mm. The magnitude of residual gravity and g-jitter used in the analysis was chosen based on the data estimated by NASA for the ISS. The residual gravity was $2 \mu\text{g}$ and its direction was inclined 45 degrees against the specimen axis. The g-jitters used in the numerical analysis, which was artificially produced by summing sinusoidal vibrations ranging from 0.01 to 100 Hz, were added in random direction simulating the ISS g-environment. The result predicted a significant effect of the convection flows to the diffusion measurements. In the case of specimen 2 mm in diameter, the maximum flow velocity was $25 \mu\text{m/s}$ and the apparent diffusion coefficient became 3.6% higher than the pure diffusion, leading us to the conclusion that the experimental results might be spoiled by the convection. In the case of the 1mm diameter specimen, the error in diffusion coefficient was less than 1%. Hence, specimens with diameter less than 1 mm should be selected in order to avoid the effect of gravitational disturbances in the diffusion experiments conducted in the ISS environment.

One concern that is associated with the use of small specimen might be the wall effect. The wall effect can be considered as the Marangoni convection due to the roughness of crucible walls and as the rapid surface diffusion. The rapid surface diffusion is discussed frequently for the solid surface at rather low temperatures, where the difference of chemical potential between bulk and surface is important. It hasn't been found for liquids at high temperatures and can't be thought to affect the diffusion experiments in liquids because it occurs, if present, only in one atomic layer near the surface. The Marangoni convection at the crucible wall can be suppressed by reducing the free surface area, which can be achieved by using springs to push the samples during melting and also by reducing the crucible roughness to less than $50 \mu\text{m}$.

The experimental error due to the gravitational disturbance can be suppressed less than 1 % by using a 1 mm diameter sample, a spring and a crucible with less than $50 \mu\text{m}$ roughness even under the residual gravity and g-jitter in ISS.

F. EXPERIMENTAL DESIGN AND METHODS

To limit the experimental error to less than 4 % as required by our specific aims, the experiment is designed as follows:

F.1 Shear Cell Method

Diffusion measurements will be carried out with a diffusion couple method, in which a diffusion couple of two samples having two different concentrations will be melted. The concentration profile after a diffusion experiment will be analyzed. There are two ways in the diffusion couple method. One is the long capillary method in which a diffusion couple is kept even during heating and cooling periods. The other one is the shear cell method. In this method, each part of the diffusion couple is separated during heating process. Then a liquid column of diffusion is formed at the start of the diffusion, and it is divided into many segments at the final period

of diffusion. Finally, the small segments are cooled and solidified. These processes are described in Figure 7. The merit of shear cell method is that the diffusion time is precisely defined, and the effect of solidification, namely, the segregation and the flows caused by the volume change on solidification can be completely removed.

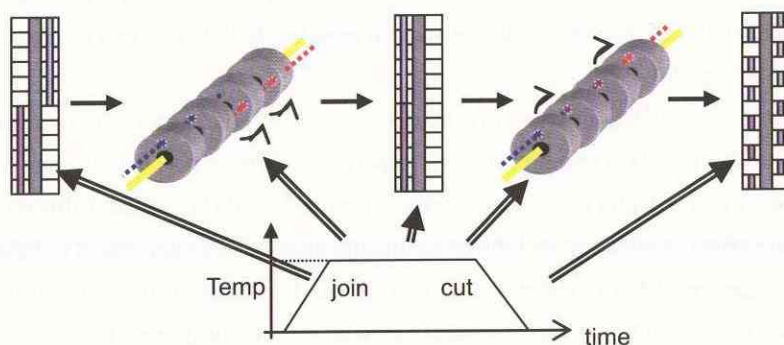


Figure 7. Concept of the shear cell method

For the material showing volume dilation on solidification, the shear cell method should be employed as described above. The demerit of the shear cell method is the disturbance on the concentration profile due to the flow on joining and dividing. A long diffusion time can make the error of this disturbance due to the flow on forming a liquid column less than 1%. The effects of the shearing on dividing sample into many segments can be neglected if the length of divided samples is longer than the sample radius as reported in Ref.27. At present, several experiments and simulations are in progress to clarify the effects of shearing and to optimize parameters that are needed for the shear cell operation and cell design. An additional demerit of the shear cell is the fact that the number of analytical points is limited by the number of segments which is not so large in practice. The number of analytical points also determines the error of the diffusion coefficients. According to the error theory the number of segments should be more than 10.

F.2 Sample Configuration

The sample cell consists of diffusion samples, springs for compensation of change of the sample volume, cell segments, a shaft to rotate the cell segments, a spring to keep the cell segments in tact, and thermocouples, as shown in Figure 8. The concept of each part design is described below.

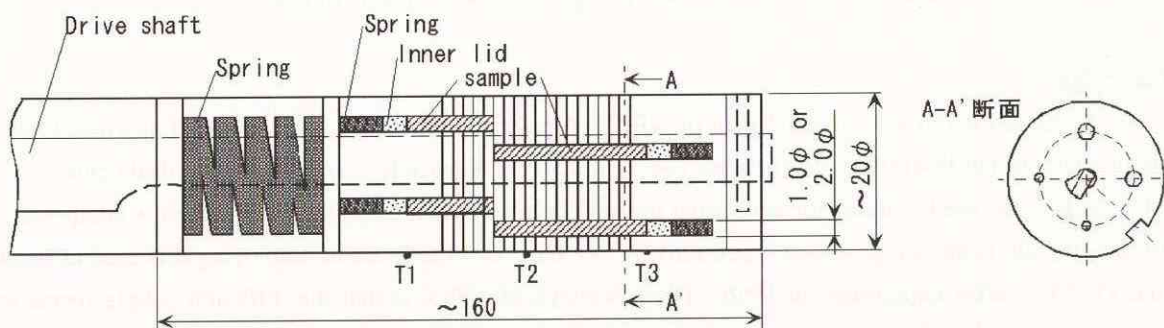


Figure 8. Shear cell sample configuration (unit: mm)

1) Sample

A self-diffusion sample consists of a natural Ge and a Ge enriched by stable isotopes. The sample is designed to minimize the sample weight difference, as shown in Table 3. It is possible to study the isotope effect on the diffusion in this sample design. Impurity diffusion samples consist of a pure Ge and a Ge doped by specific impurities. The impurity level of the initial sample may be about 0.1 % that is imposed by the detection limit of the analysis (SIMS and ICP-Mass).

The sample radius is selected to be 1 mm (g-jitter insensitive) and 2 mm (g-jitter sensitive). The sample length should be 50 mm for the 7000 second diffusion experiment. The experimental error from the flow due to g-jitter can be less than 1% if a 1 mm diameter sample is used. Also, 7000 second diffusion experiment is long enough to eliminate the effect of shearing and the experimental error can be suppressed to below 1 %.

Since the vapor pressure of Ge is about 4.8 Pa at 1800 K, it is needed to fill argon or helium gas in the cartridge. If necessary, it is possible to adopt the shear cell with sealing machinery [28].

Table 3. Concentration of sample for self-diffusion experiment

Atomic mass	70	72	73	74	76	Total atomic mass
Ratio in natural Ge (%)	20.5	27.4	7.8	36.5	7.8	72.71
Ratio of enriched Ge (%)	32.5	0	0	67.5	0	72.70

2) Shear cell

The cell material should have low wettability to the sample from the viewpoint of spring mechanism and should not react chemically with the sample liquid. We measured contact angles of boron nitride, pyrolytic boron nitride, glassy carbon and graphite to liquid Ge. The contact angles were around 160 degrees for all materials even after heating at 1773 K for 1 hour. We will do the same test for liquid Ge containing Si or Sn as impurity.

The dimensional tolerance of the cell alignment should be less than 50 micrometer for the 1 mm diameter sample. This estimation was derived from a calculated result that less than 5 % of misalignment has to be maintained to keep the error less than 1 %.

Graphite springs will be used after testing the changes in length and in spring constant at high temperatures. A shaft which rotates the cell segments will be made of mullite, a compound material of Al_2O_3 and SiO_2 which has low thermal conductivity and high strength even at high temperature, about 1800K.

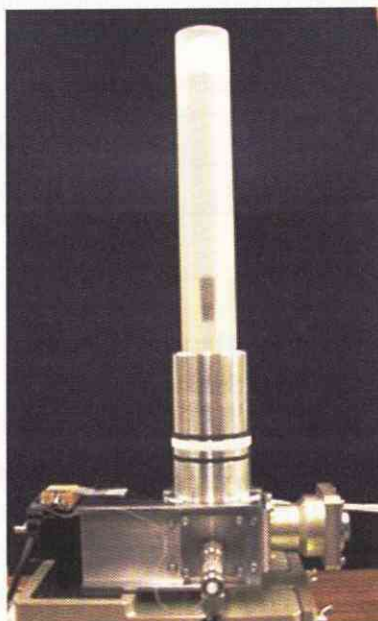
3) Cartridge

We are preparing our experimental plan by AFEX (Advanced Furnace for microgravity Experiments with X-ray radiography) or DMI (Diffusion Module Insert) in Material Science Research Rack described below.

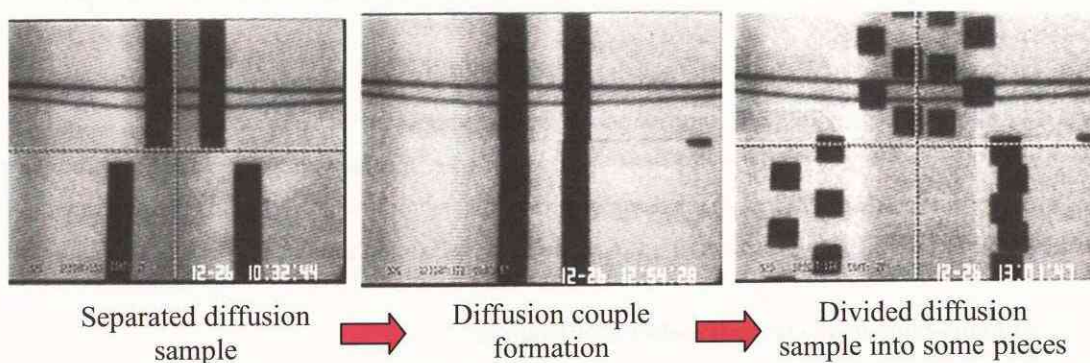
For AFEX, we need a heater for isothermal heating. We will use a ceramic heater, which is composed of pyrolytic graphite heater on pyrolytic boron nitride. We have an experience of employing this type of heater on the TR-IA5 rocket experiment in 1996. The advantage of AFEX is that the diffusion couple formation and separation can be observed during experiments by X-ray. We will seal the cell and heater in a sapphire or a glassy carbon cartridge, which has high transmissivity for X-ray and the ability to maintain the vacuum. Photograph 1 shows a shear cell cartridge for ground experiments using AFEX BBM (Bread Board Model). Photograph 2 shows the X-ray image of AFEX during a diffusion experiment using the shear cell technique. This

is the first direct observation of the shear cell operations, formation of the liquid diffusion column and division into small pieces.

For DMI, we will use a tantalum cartridge which was tested up to 1773 K through the MSL-1 mission in 1997.



Photograph 1. The shear cell cartridge for AFEX BBM



Photograph 2. X-ray image of a diffusion sample during a shear cell experiment

4) Safety

Most of the materials including the samples, Ge, Sn, and Si, in our proposal have already been used in the previous space shuttle experiments. The total sample weight in one shear cell is about 2 g. The sample will be sealed in a cartridge as described above, and the cartridge will be decompressed during the experiments. The decompression has an advantage for the safety requirement.

F.3 Experimental Condition

- 1) Atmosphere : argon gas
- 2) Temperature homogeneity : +/- 10 K for 50 mm length at 1773 K (1800 K if possible)
- 3) Experimental condition : 5 temperatures (1250 ~1773 K (1800 K if possible)) as shown in Table 4
- 4) Number of cartridges : 15 (5temperatures x (1self-diffusion+2impuritydiffusion samples))

Table 4. Experimental conditions

Temperature (K)	1250	1400	1550	1700	1773 (1800 if possible)
Diffusion time (s)	7000	5580	4550	3780	3400

G. DATA ANALYSIS

G.1 Concentration Analysis and Calculation of Diffusion Coefficients

ICP-MASS (Inductive Coupled Plasma Mass Spectroscopy) will be used for the isotope analysis of self-diffusion samples and for Sn impurity diffusion sample analysis. ICP-MASS can't be used for Si impurity diffusion sample analysis because the mass of Si is near to that of nitrogen or nitrogen compounds. Therefore, SIMS (Secondary Ion Mass Spectroscopy) will be used for Si impurity sample analysis.

Fick's second law is used to calculate diffusion coefficients. If the diffusion coefficient, D, doesn't depend on the concentration as in self- and impurity diffusion, the following equation will apply:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.$$

(5)

The numerical or the analytical solutions will be used to reproduce the concentration distribution of experiments.

G.2 Analysis

We will organize various microscopic information of atomic structures and atomic dynamics as described below. As the results of this project, we will present a new diffusion mechanism along with a new model for the atomic dynamics and diffusion in liquids of complex structures taking into account those factors such as the covalency, the dynamics of local environment (life time), the multi-relaxation time.

1) *Ab initio* and many-body force classical molecular dynamics

Based on the *ab initio* molecular dynamics, we will analyze the atomic motion, which is strongly related to the diffusion mechanism, as follows:

- i) The electron density distribution function for the verification of covalent bonds.
- ii) Analysis of local configuration around a moving particle (angle distribution of three body distribution function).
- iii) Analysis of residence time distribution function around local configuration. Also, the role of the many body force of atomic interaction will be examined for liquids with the effect of covalent bonds by using the many-body force classical molecular dynamics.

2) Neutron elastic and inelastic scattering experiments in cooperation with Japan Atomic Energy Research Institute (JAERI)

The particular feature in the structure factor, $S(Q)$, of liquid group IVB elements is the existence of shoulders in the high Q side of the first peaks. We will use the neutron facility at JAERI and analyze the existence of shoulders as a function of temperature up to 1800K-2000K by the neutron elastic scattering. The experimental results will be analyzed to clarify the short range order in liquid Sn and liquid Ge.

We will also perform the neutron inelastic scattering and quasi-elastic scattering experiments for liquid Sn and liquid Ge to obtain the information about van Hove space-time correlation functions, which is the direct experimental information of microscopic atomic dynamics.

3) Small angle X-ray scattering experiments

The clusters in liquids, if present, can be detected experimentally by the small angle scattering either of X rays or neutrons by the liquids. Small angle X-ray diffraction apparatus was installed in NASDA. Using this apparatus we will analyze the structures of clusters in liquid Sn and Ge as a function of temperature.

4) Mode coupling theory coupled with large scale molecular dynamics and neutron inelastic scattering experiments

Mode coupling theory is a prevailing theory for the studies of dynamic atomic properties in liquids, glass forming liquids and liquid metals. In the present study, we will analyze the velocity auto-correlation function and the space-time correlation function given by the large-scale molecular dynamics along with the neutron inelastic scattering experiments. We will also clarify the role played by the correlation between density and current of atoms.

H. EXPECTED RESULTS AND POTENTIAL TO THE FUTURE

At first we will obtain the temperature dependence of the self-diffusion coefficient in liquid Ge and of the impurity diffusion coefficients of Si and Sn respectively in liquid Ge. These data can be employed as reliable reference data. It can help us to improve the ground diffusion measurement technique, for example, in magnetic field application, and thus it may help us to measure diffusion coefficients with low experimental errors enough for industrial application.

The next activities will be concentrated on the data analysis for theoretical modeling. We are deeply interested to find out whether or not the chemical bonds will affect the diffusion mechanism. If “Hypothesis A” and “Hypothesis C” from the hard sphere model is found to be right, the chemical bonds doesn’t affect the diffusion mechanism, and there will be some cancellation effects between the complexity of liquids and loosely packed structures. This point offers an interesting viewpoint that will constitutes a subject of the fundamental science. For the applied science, self-diffusion and impurity diffusion coefficients in liquid group IVB elements can be estimated from “Hypothesis A” and “Hypothesis C”, respectively. It means the possibility that even the self- and impurity diffusion in liquid Si may be estimated from these hypotheses. As is well known, Si is the most important material for the semiconductor industry but, because of its high reactivity, it is the most difficult material to measure its diffusion coefficient. This will provide the starting point for the study of more complex melts, such as melts of III-V semiconductors (GaAs etc.).

If the “Hypothesis B” is found to be right, the microscopic details of liquid structures must be taken into

account for the diffusion model in such melts. Up to now the effect of short range order has been discussed only on the static liquid structures. Therefore, if correct, the “Hypothesis B” also provides a new branch of the fundamental science that concerns with the effect of short-range order on the atomic dynamics in liquids. The new model is required to explain the diffusion in liquid group IVB elements having different degrees of complexity.

The final goal of our proposal is to clarify the roles played by the loosely packed structures of liquids and the covalent bonds, and to reflect these in the diffusion model of complex liquids such as melts of Ge, Si and GaAs. We are confident that the results that will be born out of the presently proposed research project will be much appreciated by the semiconductor industry as much as by the many-body physicists in the fundamental science.

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