A Hard-Sphere Model in Analytic form for Atomic Transport Properties of Liquid Metals

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A HARD-SPHERE MODEL IN ANALYTIC FORM FOR ATOMIC TRANSPORT PROPERTIES OF LIQUID METALS

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Simple analytical forms of hard sphere model are presented for atomic transport properties of liquids, that is the self-diffusion coefficient, D_S, and the shear viscosity, η. The D_S and the back scattering factor have been evaluated based on a recent analytical expression of D_S for hard spheres presented by Speedy, which was obtained by compiling D_S data from many computer simulations for hard spheres. This hard sphere model was applied to test the reliability of recent epoch-making experiment of diffusion in liquids, the measurement of D_S in space for liquid Sn due to Frohberg *et al.*; values of D_S in space are lower than those obtained on earth particularly at higher temperatures than the melting temperature and whose temperature dependence obeys a T^2 law. The former fact seems to indicate that the previous experimental data of D_S on earth may be suffered from gravitational (and thermal) convection effects and the latter fact provides some insights into the mechanism of diffusion in liquids.

The result of this space experiment was well reproduced by this hard sphere model. In addition, the experimental data of D_S and η of liquid Hg was also well reproduced by this hard sphere model, in which an universal reduced relation for the temperature dependence of the hard sphere diameter, σ, was determined by fitting the calculated D_S to the experimental one under microgravity for liquid Sn. The liquid Hg was selected because its experimental values of D_S and η on earth are very reliable. Therefore, a new experimental technique for diffusion coefficients in liquids, the measurement of D_S in liquids under microgravity, seems to be very reliable and should be exploited further.

KEY WORDS: Self-diffusion, viscosity, microgravity.

1 INTRODUCTION

It is well known that the hard sphere (HS) model is quite successful in describing the physical properties of liquid metals near the melting temperature, T_m[1]. However, it has not always been valid to predict their temperature (T) dependences because of the lack of knowledge about the T dependence of the hard sphere diameter, σ, which is essentially derived from the T dependence of the repulsive part in effective pair interatomic potentials[2].

Protopapas *et al.*[3] determined a universal reduced relation for the T dependence of σ so that the expression of the HS model for the self-diffusion coefficient, D_S, might reproduce accurately the experimental T dependence for several liquid metals. However, the shear viscosity, η, was not discussed from this point of view. In addition, unfortunately, experimental data quoted by them were scattered over a quite wide range depending on the data sources and in many cases their predicted values were

situated slightly on the lower side in the range of widely scattered experimental data in a D_S-T diagram.

Recently Frohberg et al.[4] performed an epoch-making new self-diffusion experiment for liquid Sn. This was performed in a space laboratory under microgravity and free from gravitational (and thermal) convection effects. The values of D_S obtained under microgravity for liquid Sn are smaller than experimental values on earth (for example Refs. 5 and 6) particularly at higher temperatures than T_m, as shown in Figure 1. This experimental result in space indicates that present data of D_S for liquids (with high T_m) obtained on earth may be considerably affected by gravitational convections. In addition the temperature dependence for D_S of liquid Sn obtained in space accurately obeys a T^2 law. This fact may provide an important key point for the clarification of mechanism of diffusion. Therefore it is very important to test the reliability of this important experiment.

Tippelskich et al.[7] also applied the HS model to describe the T dependence of viscosity, η, for liquid Hg over a wide temperature range. Similar use of the HS model was made to predict η of liquid Ga by Tippelskich[8]. In these studies the T dependence of σ was determined from the parameter in a van der Waals type equation of state by using experimental data of P, V, T. However, no discussions
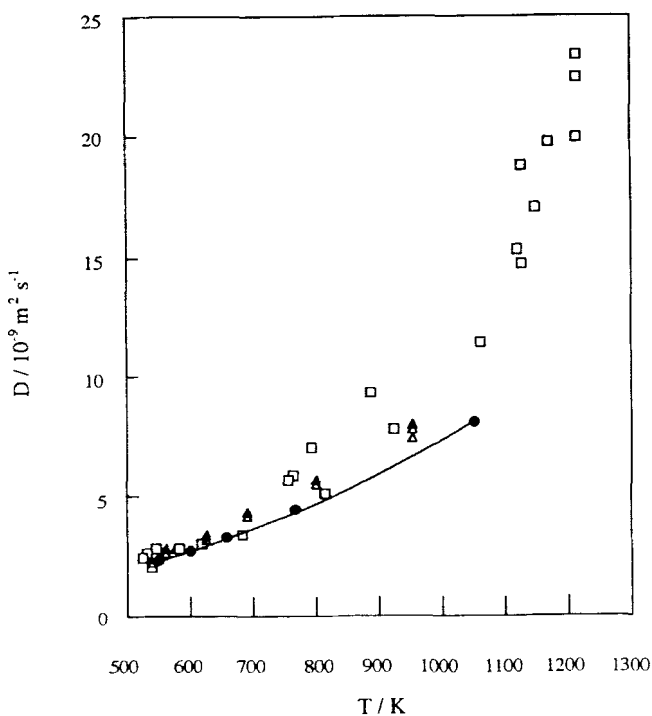
Figure 1 The comparison of self-diffusion coefficient of liquid Sn between the space experiment by Frohberg et al.[4] and conventional experiments on earth due to various authors. —●—: Frohberg et al.[4] ; □ : Ma and Swalin[5] ; △ : Careri et al.[6]

were given for D_S. Most authors believe that values of D_S and η for liquid Hg are the most reliable data on earth among the data on many liquid metals[9]. Therefore it is interesting to examine possibilities that the T dependence of both D_S and η for liquid Hg can be explained based on the HS model by using a common T dependence of σ.

One difficulty for applications of HS model to atomic transport properties is that the so called back scattering factor, C_{BS}, must be referred to the result of D_S of molecular dynamics (MD) simulations "graphically" or by interpolation methods. This is caused by the fact that D_S is given only in a graphic form or in a tabulated form in most MD simulations. The C_{BS} can be "experimentally" determined by the ratio of D_S due to MD simulations for hard spheres relative to D_S given by the Enskog formula, D_{ENS}: in the case of D_{ENS} only binary collisions are taken into account; D_S due to MD simulations "experimentally" takes into account multiple scattering processes or cage effects in addition to binary collision processes; the factor C_{BS} represents the cage effect of surrounding atoms which hinder free advances of the central atom considered.

Fortunately, Speedy[10] succeeded in presenting an "analytic form" of D_S for a hard sphere model from MD simulations of numerous researchers with various ranges of packing fraction, y, The purpose of this study is to present an "analytic form" of atomic transport on the HS model and to apply it to test the reliability of the new experimental technique for diffusion in liquids-the diffusion coefficient measurement under microgravity.

2 THE HARD SPHERE MODEL FOR ATOMIC TRANSPORT IN LIQUID METALS

From the point of view of the HS model, D_S of dense hard sphere liquids, D_S^{HS}, can be written as

$$D_S^{HS} = C_{BS} D_{ENS}. \tag{1}$$

In this equation D_{ENS} represents the so called Enskog formula for D_S, which takes into account only binary collisions of hard spheres and is valid for dilute gases. The explicit form of D_{ENS} is given as follows[1]:

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

where $g_{HS}(\sigma)$ is the radial distribution function of hard sphere system at the hard sphere contact $r = \sigma$. In the dense liquids D_{ENS} must be corrected by the presence of cooperative multiple scattering effects or cage effects. These effects are taken into account in terms of the so-called back scattering factor, C_{BS}.

The estimation of C_{BS} is possible by comparing D_S due to MD simulations for hard spheres, $D_S^{MD,HS}$, with D_{ENS}, as follows:

$$C_{BS} = \frac{D_S^{MD,HS}}{D_{ENS}}. \tag{3}$$

As for $D_S^{MD,HS}$, an excellent analytical form can be employed, that is

$$D_S^{MD,HS} = \left(\frac{\pi D_0}{6y}\right)\left(1 - \frac{6y}{1.09\pi}\right)\left[1 + \left(\frac{6y}{\pi}\right)^2\left\{0.4 - 0.83\left(\frac{6y}{\pi}\right)^2\right\}\right], \tag{4}$$

where D_0 is written as $D_0 = (3/8)\sigma(k_B T/\pi M)^{1/2}$ (k_B denotes Boltzmann's constant; M is the mass of hard spheres with diameter σ). This formula has been presented by Speedy[10] to express the results of D_S for MD simulations of hard spheres performed by a number of workers for various ranges of packing fraction, y.

Therefore the back scattering factor, C_{BS}, can be expressed "analytically" as a function of packing fraction y, as follows:

$$C_{BS} = \frac{(1-y/2)^2}{(1-y)^3}\left(1 - \frac{6y}{1.09\pi}\right)\left[1 + \left(\frac{6y}{\pi}\right)^2\left\{0.4 - 0.83\left(\frac{6y}{\pi}\right)^2\right\}\right] \tag{5}$$

The expression of η for the HS model is given by the Stokes-Einstein relation with the slip boundary condition, as follows[11-13]

$$\eta = \frac{k_B T}{2\pi\sigma D_S^{HS}}. \tag{6}$$

The η can be estimated by inserting the expression for D_S^{HS}, that is Eq. (1) or (4).

3 NUMERICAL CALCULATIONS OF D_S AND η AND ONE TEST OF RELIABILITY OF SPACE EXPERIMENT OF D_S FOR LIQUID Sn

As described above, new experimental techique, the measurement of D_S for liquid Sn under microgravity by Frohberg et al.[4], may provide a warning about the accuracy of present diffusion data for liquids obtained on earth and the reported temperature dependence by them, that is a T^2 law, also may provide an important insight into the mechanism of diffusion in liquids. Therefore it is important to test the reliability of this space experiment by Frohberg et al.[4]

The data of D_S for liquid Sn under microgravity was compared with numerical calculations due to the HS model, Eq. (1) or (4). Calculations were performed for two cases; in one case (case 1) the HS diameter, σ, was assumed to be temperature independent and in the other case (case 2) an empirical relation of Protopapas et al.[3] was assumed for the T dependence of σ. The explicit form of relation due to

Protopapas et al.[3] is written as follows:

$$\frac{\sigma(T)}{\sigma(T_m)} = 1.123 \left\{ 1 - 0.112 \left(\frac{T}{T_m} \right)^{1/2} \right\}. \tag{7}$$

In Figure 2 are shown calculated results of D_S of liquid Sn for these two cases together with experimental results under microgravity due to Frohberg et al.[4]; the result of space experiment is expressed as $D_S = 0.745 \, T^2$ in unit of $10^{-14} \, m^2 s^{-1}$ (T: the absolute temperature). As can be seen in this Figure, it is very important for the HS model to take into account the T dependence of σ. In fact the case 2 is in close agreement with the T^2 law of space experiment in contrast to the case 1.

This close agreement between experiments and calculations in the case 2 encourages us to believe in the reliability of this new space experiment. Unfortunately the employed T dependence of σ is rather empirical[3] and further tests should be performed. In principle, the temperature dependence of σ should be determined theoretically from the knowledge of interatomic potentials, for example, by the perturbation theory of liquids proposed by Weeks, Chandler and Anderson[2]. Unfortunately it is not always easy to obtain accurate information about interatomic potentials
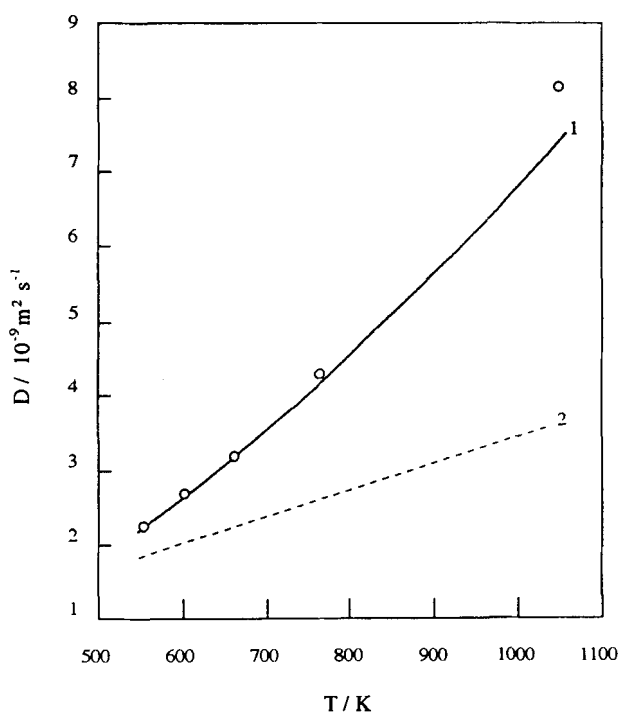
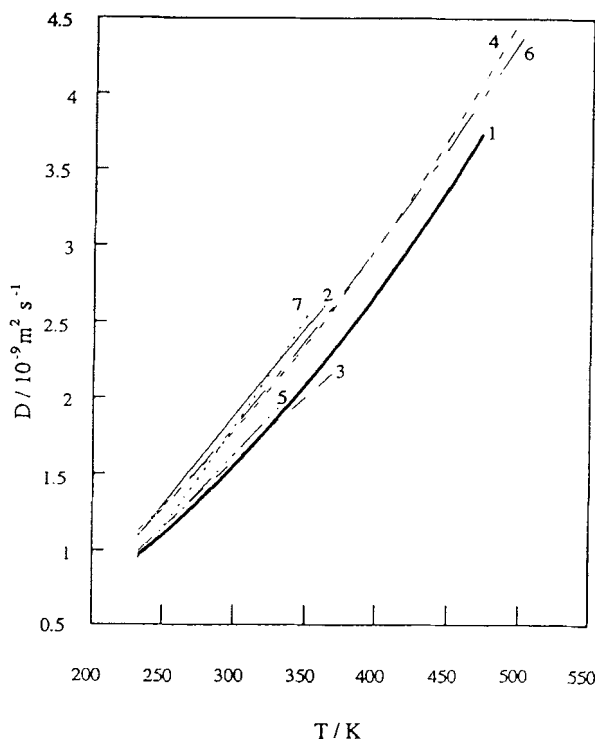**Figure 2** The comparison of self-diffusion coefficient of liquid Sn between calculations of hard sphere model with the space experiment by Frohberg et al.[4] O : The space experiment by Frohberg et al.[4]; solid line 1 : the result of hard sphere model with the temperature dependent σ (case 2: see the text) ; dotted line 2 : that with the temperature independent σ (case 1 : see the text).

experimentally and theoretically. Therefore here the T dependence of σ was determined so that D_S of the HS model, Eq. (1) or (4), might well reproduce the T dependence of D_S in space for liquid Sn[4]. Then, the determined T dependence of σ as an universal reduced form (see Eq. (8)) was employed for the prediction of most reliable data of D_S and η among many present data on earth of liquid metals. The selected system was liquid Hg. The reasons for this selection are as follows: 1) because of its low melting temperature experiments can be performed comparably easily; 2) it does not take too much time to attain an experimental temperature by heating and to quench a concentration profile by cooling; 3) the data of η has been firmly established by the Erk[14] formula[9]. It is to be noted that the data of η is rather free from the gravitational and thermal convection effects due to the shorter experimental time and the forced velocity gradient under experimental conditions.

The calculated D_S and η for liquid Hg are shown respectively in Figures 3 and 4 together with several experimental data on earth[14-20]. As can be seen in these figures, the calculated results for liquid Hg agree well with experiments both for D_S and η. This fact indicates that the space experiment for D_S of liquid Sn is reliable.

It is well known that even on earth the experimental accuracy of measurements of D_S can be improved by adoption of the shear cell technique, which, however, up to
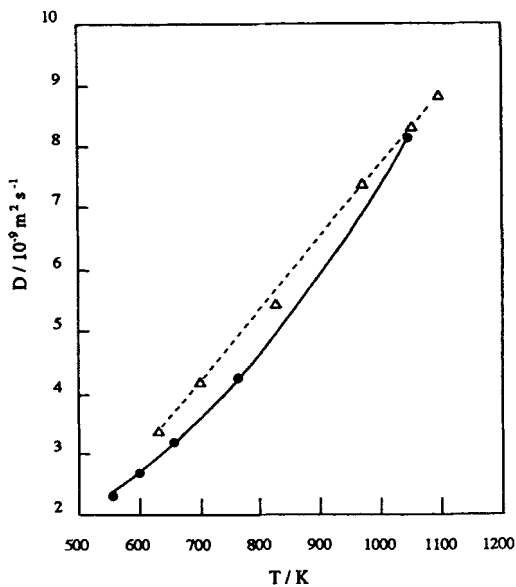

Figure 3   The comparison of self-diffusion coefficient of liquid Hg between a calculation of hard sphere model and experimental results on earth. 1 : The calculated result of hard sphere model ; 2 : Hoffman[15] ; 3 : Nachtrieb[16] ; 4 : Meyer[17] ; 5 : Brown and Tuck[18] ; 6 : Broome and Walls[19] ; 7 : Basu et al.[20].

date, has not adopted very often because of the complexity of the apparatus. For liquid Sn only one such experiment has been performed by Bruson and Gerl[21]. In Figure 5 is shown a comparison between the data of D_S for liquid Sn due to this shear cell technique[21] and those due to the space experiment[4]. As can be seen in this figure, the shear cell result provides slightly larger values of D_S than the space experiment. This may indicate that even by the shear cell technique, measurements of D_S on earth contain some errors due to gravitational convections though much improvement can be obtained. This improvement may imply that the main sources of errors on earth are derived from convection effects on heating before the starting time of diffusion and convection and segregation effects on cooling and solidification after the final time of diffusion. All these sources of error can be diminished as much as possible in the case of the shear cell technique; in this method cell assemblies are composed of a pile of a few or some dozen disks with a hole, which can be rotated coaxially; samples or tracers are contained in each hole in disks. At the start of diffusion time, a liquid column of sample is formed by the rotation procedure of each disk and at the end of diffusion time, a liquid column of sample is cut off into a few or some dozen parts. However, even by adoption of this shear cell technique it may be very difficult to suppress convections in liquid column samples on earth
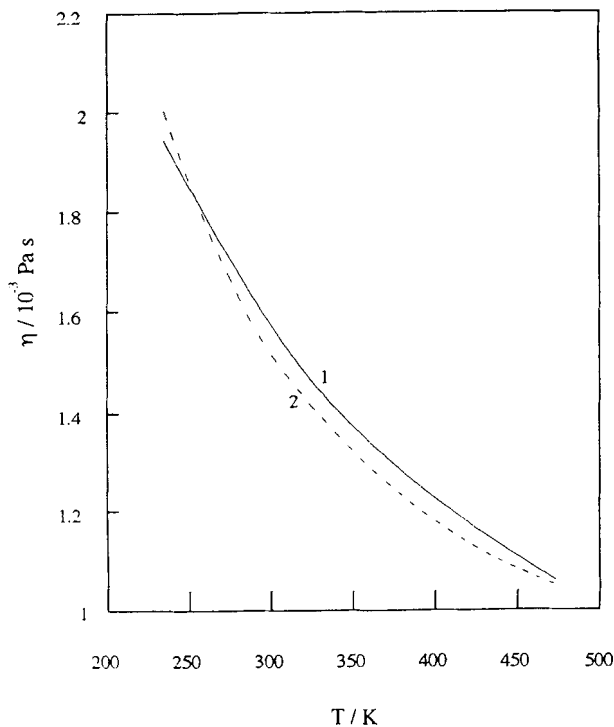

Figure 4 The comparison of viscosity of liquid Hg between a calculation of hard sphere model and the data due to the Frk's formula[14]. 1 : The calculated result of hard sphere model ; 2 : the data due to the Frk's formula[14].

Figure 5   The comparison of self-diffusion coefficient between the space experiment by Frohberg et al.[4] (——●——) and the data due to the shear cell technique on earth by Bruson and Gerl[21] (----△----).
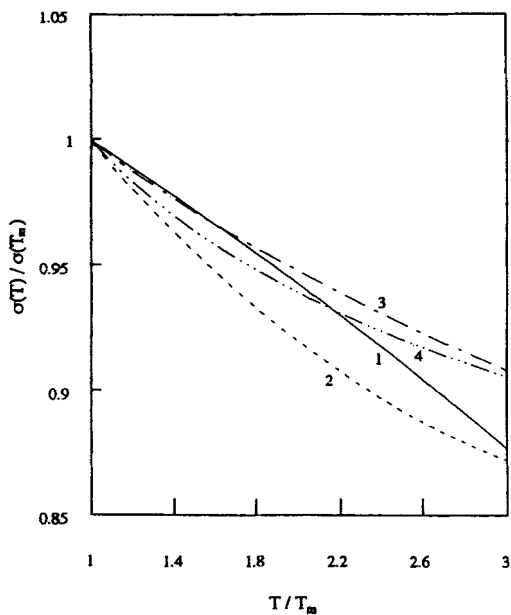
Figure 6   The temperature dependence of σ. 1: The σ determined by the self-diffusion coefficient of hard sphere model with the exact back scattering factor of Eq. (4) to the space experiment due to Frohberg et al.[4]; 2: the σ similarly determined, in which the approximate back scattering factor, $0.33/\xi$, was employed. ; 3: Protopapas et al.[3]; Tippelskirch et al.[7,8]

particularly in the case of liquid alloys whose individual consitituent components have a rather different density. For example, the case of liquid alloys with a miscibility gap may be cited. Measurements of diffusion coefficient in space under microgravity can be expected to become more readily available in future space laboratory age.

4 DISCUSSIONS AND CONCLUSIONS

In this study a new T dependence of σ was determined as universal reduced form by fitting the calculated D_S^{HS} to the space experimental result of D_S for liquid Sn[4], as described above. The explicit form can be summarized as a quadratic form as follows:

$$\frac{\sigma(T)}{\sigma(T_m)} = -4.3851 \times 10^{-3} \left(\frac{T}{T_m}\right)^2 - 0.04427 \left(\frac{T}{T_m}\right) + 1.0487. \tag{8}$$

In this equation $\sigma(T_m)$ denotes the value of the hard sphere diameter, σ at the melting temperature T_m (2.929 Å at 505 K). A different temperature dependence of σ has been proposed by Protopapas et al.[3] and by Tippelskirch et al.[7,8] The former was determined from the data of D_S on earth for many liquid metals and its explicit form is described in Eq. (7). The latter was determined by a certain parameter in the van der Waals type equation of state, which was fitted to observed P, V, T data. The explicit form is $\sigma(T)/\sigma(T_m) = (T_m/T)^{0.0912}$. In Figure 6 these T dependences of σ are shown. It can be seen from this Figure that good agreement is obtained between Eq. (7) and Eq. (8) below $T/T_m = 2$, though a clear discrepancy is observed above $T/T_m = 2$. Because of this agreement below $T/T_m \leqslant 2$, the D_S under microgravity was reproduced in this temperature range by both two T dependences of σ, Eqs. (7) and (8). In this Figure, another T dependence of σ is shown, which was determined by fitting D_S^{HS} with $C_{BS} = 0.33/\xi$ to experimental D_S under microgravity for liquid Sn. The back scattering factor, C_{BS}, has been frequently approximated to be $0.33/\xi$ in the previous studies[1,12,22,23]. However, as can be seen in this figure, σ in this approximate case of C_{BS} accords with σ in the correct case of C_{BS}, Eq. (5), only at T_m and at higher temperatures the discrepancy between them becomes larger. This is derived from the fact that the "traditional analytical" back scattering factor, $C_{BS} = 0.33/\xi$, is only valid at T_m.

Quite recently this type of HS model was applied to reproduce the T dependence of D_S for expanded Rb[24], in which the Enskog formula, Eq. (2), was simply adopted and the T dependence of σ was determined based on the pressure equation of hard spheres. This case corresponds to $C_{BS} = 1$ for a low density range.

In this paper, the formulation of η was performed by using the Stokes-Einstein relation with the slip boundary condition. This relation holds for the hard sphere system, as is known from the computer simulation of Alder et al.[11] Gaskell[25] has succeeded in deriving this relation from the microscopic point of view.

As described above, the T^2 dependence of D_S was found for liquid Sn by the space experiment due to Frohberg et al.[4] A similar T dependence was found by them also for the mutual diffusion coefficient of liquid Sn–In alloys. On the other hand Bruson

and Gerl[21] obtained a linear T dependence of D_S for liquid Sn over a wide T range on earth. As is well known, the T dependence of D_S provides some insights into the mechanism of diffusion. For example, based on the fluctuation theory of liquids, Swalin presented a T^2 dependence of D_S in the first version[26] and a T^1 dependence on the revised version[27]. Rice and Nachtrieb[28] derived several possibilities for the T dependence of D_S from various kinetic theories of liquids. As for this T dependence of D_S, recent computer simulations, have provided a power law of $T^{1.65}$ for liquid Rb[29], that of $T^{2.25}$ for liquid K[30] and the Arrhenius type temperature dependence for liquid Ar[29]. Frohberg[31] derived a T^2 form of D_S based on a vortex theory, which considers a collective motion of group of particles, akin to phonons. For futher understanding of atomic transport in liquids it is essential to clarify the character of collective atomic motions in liquids, which was approximately expressed, for example, by the back scattering factor, C_{BS}, for this simple HS model and phonon-like motions for the vortex theory. Such collective motions on a short time scale have been extensively investigated by microscopic approaches, such as neutron inelastic scattering experiments[24] and molecular dynamic simulations[32-35]. It is also important to determine accurately isotope effects and the T dependence of D_S over a wide temperature range for many liquid metals in order to obtain further understanding of the mechanism of diffusion in liquids. Space experiments are certainly promising for this purpose.

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