Temperature Dependence of Self-Diffusion Coefficient in Liquid Hg and Sn: a Modified Hard-Sphere Description

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ABSTRACT

Analytical expressions based on a modified hard-sphere model are presented for atomic diffusion in condensed matter. The temperature dependence of a hard-sphere diameter is essential to explain the experimental diffusion coefficient in liquid Hg and Sn. The formula proposed by Protopapas *et al.* /10/ works well at low temperatures but fails to describe the temperature dependence of a hard-sphere diameter as the temperature is increased. A universal reduced form obtained by Itami and Sugimura /4/ is better than Protopapas *et al.*'s formula at high temperatures.

Keywords: Dzugutov's scaling law, Excess entropy, Self-diffusion coefficient, Hard-sphere model

1. INTRODUCTION

During the last quarter of the 20th century, considerable progress was made in calculating atomic transport properties of liquid metals through the development of the hard-sphere theory /1-3/. A number of model theories for diffusion have been proposed so far. However, as pointed out by Itami and Sugimura (IS) /4/, these theories have not always been successful in predicting the temperature dependence (T-dependence) of self-diffusion coefficient in liquid metals. This is due to the lack of knowledge about the T-dependence of a hard-sphere diameter, which is known to be essentially some average of the repulsive part of a pair interaction. A recent work reported by Yokoyama /5/, for example, is one of the investigations along this line. Yokoyama has studied the T-dependence of sound velocity and self-diffusion coefficient in liquid alkali metals up to elevated temperatures of approximately 1300 K above the melting point. It turned out that agreement between theory and experiment for both the sound velocity and self-diffusion coefficient is quite good if the T-dependence of a hard-sphere diameter is properly taken into account including an entropy contribution arising from the softness of the interatomic forces.

The purpose of the present paper is to examine if this approach can account for the T-dependence of self-diffusion coefficient in liquid Hg and Sn. The reason why we selected liquid Hg and Sn for investigation is that their experimental values of self-diffusion coefficient are reliable and that these elements have been studied by IS /4/ on the basis of the hard-sphere model, so that we can compare our results with theirs to check the usefulness of the approach we used for liquid alkali metals.

In the next section we mention the theories and approximations to be employed. Results of numerical calculations are presented and compared with those of IS as well as available experimental data in Section 3. We then discuss the validity of the approximations. Conclusions drawn from this work will be presented in the final section.

2. MODEL THEORIES

2.1 Dzugutov's scaling law

The basic formula derived from Dzugutov's scaling law /6-7/ for atomic diffusion in condensed matter is given as

$$D_{HS} = 0.049\Gamma_E\,\sigma^2\exp(S_E/Nk_B), \tag{1}$$

where D_{HS} is the self-diffusion coefficient in the hard-sphere fluid,with σ being a hard-sphere diameter, Γ_E is the collision frequency, and S_E is the excess entropy of ion disorder alone(i.e., configurational entropy), which is given in Eq.(5) below. Γ_E can be calculated for the absolute temperature T and the number density of ions ρ as

$$\Gamma_E = 4\sigma^2 g(\sigma)\rho(\pi k_B T/m)^{1/2}, \tag{2}$$

where m is the atomic mass, k_B is the Boltzmann constant and $g(\sigma)$ is the hard-sphere pair correlation function at the core, given by

$$g(\sigma) = (1 - \xi/2)/(1 - \xi)^3, \tag{3}$$

using the Carnahan-Starling formula /8/. Here, ξ is the packing fraction defined by

$$\xi = \pi\rho\sigma^3/6. \tag{4}$$

On the other hand, S_E is given by

$$S_E = S_{pack} + S_S, \tag{5}$$

in which S_{pack} is the excess entropy due to the finite packing of the hard spheres, best described via the negative Carnahan-Starling expression

$$S_{pack}/Nk_B = -\xi(4 - 3\xi)/(1 - \xi)^2. \tag{6}$$

S_S is an entropy contribution arising from the softness of the interatomic forces /9/, given by

$$S_S/Nk_B = \pi\rho f(\sigma_0 - \sigma_m)(T/T_m)^{1/2}\sigma^2 g(\sigma), \tag{7}$$

where σ_0 is the location of the minimum in the pair potential and σ_m refers to the melting point, T_m. Here $\sigma_0 = 1.0878(\rho_m)^{-1/3}$ as given by Protopapas *et al.* /10/ and ρ_m refers to the number density of ions at the melting point. f is a parameter related to the soft-force part of the pair potential and is approximated as ~ 0.35 for all systems at all temperatures.

The T-dependence of σ is estimated by the use of the empirical formula proposed by Protopapas *et al.* /10/.

$$\sigma(T) = 1.126\sigma_m[1 - 0.112(T/T_m)^{1/2}] \tag{8}$$

or

$$(\partial\ln\sigma/\partial\ln T)_V = -(0.056\sigma_0/\sigma(T))(T/T_m)^{1/2}, \tag{9}$$

where the relation $\sigma_m = 0.888\sigma_0$ is used.

2.2 Speedy's expression

Speedy /11/ presented an analytical formula for D_{HS}, which was obtained from analyses of molecular dynamics simulations of hard-sphere fluids performed by a number of workers,

$$D_{HS} = (D_0/(6\xi/\pi))(1 - (6\xi/\pi)/1.09)(1 + (6\xi/\pi)^2(0.4 - 0.83(6\xi/\pi)^2)) \tag{10}$$

where $D_0 = (3/8)\sigma(k_B T/\pi m)^{1/2}$. According to Speedy, Eq. (10) is accurate over the whole density range from the ideal gas limit, where it is exact, to the highest density $\xi = 0.565$ at which the metastable fluid has been studied. The work of Speedy is well paraphrased in the work of IS/4/.

3. RESULTS

As reported by Yokoyama /12/, we can extract the value of ξ through Eqs. (5)-(7). The value of ξ is 0.463 for liquid metals near the melting point, with which the experimental structure factor data /13/ of liquid Hg and Sn are moderately well described by the hard-sphere structure factor. The value of σ at T_m is extracted from

Eq.(4) using the observed density and the value of 0.463 for ξ. Then, the T-dependence of σ is estimated by Eq.(8) or Eq. (9). The value of ξ at elevated temperatures is determined from Eq.(4) using Eq.(8) and the observed densities. Thus, the value of D_{HS} can be estimated from Eq.(1) or Eq.(10). Numerical results of such calculations are summarized in Tables 1 and 2 in comparison with the experimental values.

Three kinds of experimental data of liquid Sn are quoted for comparison, which depend on the fitting procedures to self-diffusion data of liquid Sn under microgravity (see Ref. /15/ for more details).

4. DISCUSSION

As seen from Table 1, both Eq. (1) and Eq. (10) describe the experimental data reasonably well, but a better description is given by Eq. (10). The results obtained from Eq. (10) is in good agreement with the hard-sphere results obtained by IS (see Fig. 3 of Ref. /4/). Predicted values of Eq. (1) are quite good up to T = 353 K, but a deviation from the experimental data starts at T = 423 K, which corresponds to ξ = 0.393. The deviation becomes large as ξ is decreased. This is due to the breakdown of Dzugutov's scaling law as shown

Table 1

Comparison of D in liquid Hg between calculated and experimental results.

T (K)	ρ (10^3Kg m^{-3})	ξ	D (10^{-9}m^{2}s^{-1}			
			Eq. (1)	Eq. (10)	Expt (1)	Expt (2)
238	13.68	0.463	1.15	1.00	1.00	1.11
273	13.60	0.448 (0.449)	1.45 (1.44)	1.32 (1.31)	1.32	1.48
293	13.55	0.440 (0.441)	1.61 (1.61)	1.51 (1.50)	1.50	1.69
353	13.40	0.417 (0.416)	2.13 (2.14)	2.15 (2.18)	2.01	2.40
423	13.23	0.393 (0.388)	2.71 (2.77)	2.98 (3.11)	2.56*	3.29
473	13.08	0.377 (0.368)	3.11 (3.20)	3.62 (3.90)	2.90*	3.98
523	12.87	0.360 (0.343)	3.52 (3.59)	4.38 (4.97)	3.22*	4.71

Expt (1): from $D = D_0 \exp[-Q/RT]$ where $D_0 = 8.5\times10^{-5}$ (10^{-4}m^{2}s^{-1}),
Q = 1.01(4.184KJmol^{-1}) and R = 8.314JK^{-1}mol^{-1} (see Table 3.1 and (1.4.41) of Ref./2/)
Expt (2): from $D = 4.34\times10^{-13}T^{3/2} - 4.81\times10^{-10}$(m^{2}s^{-1}) (see Table 7.2 of Ref./3/)
( ): obtained from Eq.(11); *: extrapolated value

Table 2

Comparison of D in liquid Sn between calculated and experimental results.

T (K)	ρ (10^3Kg m^{-3})	ξ	D (10^{-9}m^{2}s^{-1}				
			Eq. (1)	Eq. (10)	Expt (1)	Expt (2)	Expt (3)
523	6.93	0.463	2.34	2.04	2.04	2.10	2.67
573	6.90	0.453 (0.454)	2.74 (2.70)	2.46 (2.42)	2.45	2.53	3.15
973	6.64	0.384 (0.378)	5.89 (6.03)	6.71 (7.06)	7.05	9.36	8.19
1173	6.58	0.360 (0.346)	7.20 (7.40)	8.96 (9.93)	10.25	10.72	11.49
1373	6.49	0.338 (0.312)	8.36 (8.49)	11.43 (13.60)	14.04	14.73	15.27

Expt (1): from $D_S = 0.745\times10^{-14}\ T^2$ (m^{2}s^{-1}) (see Ref. /4/)
Expt (2): from $D = 6.91338\times10^{-15}T^{2.01697}$ (m^{2}s^{-1}) (see Fig. 8 of Ref. /15/)
Expt (3): from $D = 3.2499\times10^{-14}T^{1.8077}$ (m^{2}s^{-1}) (see Fig. 6 of Ref. /15/)
( ): obtained from Eq.(11)

in Fig. 1 of Ref. /14/ (see also Fig. 2a of Ref. /6/).

As for liquid Sn, both Eq. (1) and Eq. (10) seem to work well at low temperatures up to T = 573 K, but begin to undershoot the experimental data as the temperature is increased. Predicted values of Eq. (1) again start to deviate from the experimental data at T = 973 K, which corresponds to $\xi = 0.384$. The deviation becomes large as ξ is decreased. This is due to the breakdown of Dzugutov's scaling law just mentioned in the case of liquid Hg. The results obtained from Eq. (10) are in good agreement with hard-sphere results obtained by IS (see Fig. 2 of Ref. /4/). From this discussion, it is suggested that Eq. (8) proposed by Protopapas *et al.* works well at low temperatures but fails to describe the T-dependence of σ as the temperature is increased. In relation to this problem, a universal reduced form was proposed by IS, which is given by

$$\sigma(T)/\sigma(T_m) = -4.3851\times10^{-3}(T/T_m)^2 - 0.04427(T/T_m) + 1.0487. \qquad (11)$$

In this equation $\sigma(T_m)$ denotes the value of the hard-sphere diameter at the melting temperature T_m (2.929 A at 505 K). Equation (11) was obtained by fitting the calculated D_{HS} to the space experimental data of the self-diffusion coefficient in liquid Sn (see Ref. /4/ for more details). We tried comparing Eq. (11) with Eq. (8). Our calculated results, shown in brackets in Tables 1 and 2, are slightly improved at high temperatures by the use of Eq. (11) as seen from the tables. Another reduced form slightly different from Eq. (11) is proposed by Itami *et al.* /15/, but we did not try this in the present work.

5. CONCLUSIONS

We have studied the temperature dependence of the self-diffusion coefficient in liquid Hg and Sn. The conclusions drawn from this work are as follows.

(1) Both Eq.(1) and Eq.(10) describe the experimental data reasonably well, but a better description is provided by Eq.(10) over a wide range of temperatures.

(2) Equation (11) proposed by Itami and Sugimura is better than Eq.(8) at high temperatures. This was confirmed for liquid Hg as well.

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