Self Diffusion in Liquid Metals

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Self-diffusion coefficients of liquid metals have been calculated according to the linear trajectory prescription. The soft part of the pair potential is being represented by a square well potential. The theoretical liquid structure factor, $S(q)$, calculated under the mean spherical model (MSM) approximation, has been employed in the present calculations. The agreement between theory and experiment is encouraging and shows that the representation of the attractive forces by the square well potential is quite satisfactory for liquid metals.

1. Introduction

It is difficult to calculate the self diffusion coefficient (D) for any real liquid. Many theories, giving reasonable agreement with experiment, have been put forward to describe diffusion in simple liquids[1] and thus have contributed much to our understanding of liquid structure. The friction coefficient ζ, which is related to D, may be obtained in a very direct way by calculating the correlation function of the soft forces according to the linear trajectory prescription[2, 3]. It is proposed, in this paper, to exploit this theory within the framework of the mean spherical model (MSM) to obtain D for liquid metals.

Our recent applications of the MSM approximation on several liquid metals[4–6] and on molecular liquids such as methane[7] yielded quite interesting results for the liquid structure factor, $S(q)$. Presently we extend these studies to calculate D according to the linear trajectory prescription.

2. Theory

The self-diffusion coefficient can be written as,

$$D = k\,T/(\zeta^{\mathrm{H}} + \zeta^{\mathrm{S}} + \zeta^{\mathrm{SH}}) \tag{1}$$

where ζ^{H}, ζ^{S} and ζ^{SH} are the friction coefficients due to the hard core interactions, the soft interactions between neighbouring atoms and the cross-effect between hard and soft forces in the pair potential respectively, k is the Boltzmann's constant and T the temperature. The three friction coefficients in Eq. (1) can be evaluated by the relations[2, 8]

$$\zeta^{\mathrm{H}} = \frac{8}{3}\,\varrho\, g(\sigma)\,\sigma^2 (m\,k\,T)^{1/2} \tag{2}$$

$$\zeta^{\mathrm{S}}_{\mathrm{LT}} = -\frac{1}{3}\,\frac{\varrho}{4\,\pi^2}\left(\frac{\pi\, m}{k\,T}\right)^{1/2} \int\limits_0^\infty q^3\, \widetilde{\Phi}^{\mathrm{S}}(q)\, \widetilde{G}(q)\,\mathrm{d}q \tag{3}$$

and

$$\zeta^{\mathrm{SH}} = -\frac{1}{3}\,\varrho\, g(\sigma)\left(\frac{m}{\pi\,k\,T}\right)^{1/2} \times \int\limits_0^\infty [q\,\sigma \cos q\,\sigma - \sin q\,\sigma]\, \widetilde{\Phi}^{\mathrm{S}}(q)\,\mathrm{d}q \tag{4}$$

where ϱ is the number density, q the momentum transfer, $g(\sigma)$ the value of the pair correlation function, $g(r)$, at $r=\sigma$, m the atomic mass and $\widetilde{\Phi}^{\mathrm{S}}(q)$ and $\widetilde{G}(q)$ the Fourier transforms of the soft part of the pair potential, $\Phi(r)$, and that of $[g(r)-1]$, respectively. σ is the hard core diameter. $\zeta^{\mathrm{S}}_{\mathrm{LT}}$ is the value of ζ^{S} under the linear trajectory assumption[2].

MSM is a perturbation version of the Percus-Yevick[9] (1958) hard sphere model[10]. Presently a square well potential has been taken as a perturbation on the hard sphere potential. The advantage of this method is to have a closed form expression for $G(q)$ as[4, 5]

$$\begin{aligned}\varrho\,\widetilde{C}(q) = -\frac{24\,\eta}{(q\,\sigma)^6}\Big\{ & \alpha(q\,\sigma)^3[\sin q\,\sigma - q\,\sigma\cos q\,\sigma] \\ & + \beta(q\,\sigma)^2\,[2\,q\,\sigma \sin q\,\sigma - (q^2\sigma^2 - 2) \\ & \times \cos q\,\sigma - 2] + \gamma\,[(4\,q^3\sigma^3 - 24\,q\,\sigma) \\ & \times \sin q\,\sigma - (q^4\sigma^4 - 12\,q^2\sigma^2 + 24)\,\cos q\,\sigma + 24] \\ & - \frac{\varepsilon}{k\,T}\,(q\,\sigma)^3\,[\sin\lambda\,q\,\sigma - \lambda\,q\,\sigma\cos\lambda\,q\,\sigma \\ & + q\,\sigma\cos q\,\sigma - \sin q\,\sigma]\Big\}\end{aligned} \tag{5}$$

and

$$\widetilde{G}(q) = \frac{\widetilde{C}(q)}{1-\varrho\,\widetilde{C}(q)} = \frac{1}{\varrho}\,[S(q)-1] \tag{6}$$

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Table 1. Potential parameters.

Liquid	σ (Å)	ε/k (K)	λ
Sodium	3.306	111.60	1.65
Potassium	4.107	96.14	1.65
Rubidium	4.306	96.14	1.65
Cesium	4.808	109.50	1.70
Mercury	2.800	100.00	1.73
Aluminium	2.448	160.00	1.30
Lead	2.970	70.00	1.40
Gallium	2.500	218.00	1.77
Copper	2.253	300.00	1.68
Silver	2.600	500.00	1.75
Gold	2.600	600.00	1.73

where

$$\begin{aligned} \alpha &= (1+2\eta)^2/(1-\eta)^4, \\ \beta &= -6\eta\,(1+\eta/2)^2/(1-\eta)^4, \\ \gamma &= \frac{\eta}{2}\,(1+2\eta)^2/(1-\eta)^4. \end{aligned} \tag{7}$$

Here $\tilde{C}(q)$ is the Fourier transform of the direct correlation function, $C(r)$. The packing fraction, η, is related to the hard sphere diameter σ by $\eta = \pi\varrho\sigma^3/\sigma$, and λ and ε represent the breadth and depth, respectively, of the square well used.

Since the attractive tail used is a square well, its Fourier transform, $\tilde{\Phi}^{S}(q)$, follows as,

Table 2. Friction coefficients, ζ^H, ζ^S, and ζ^{SH} for liquid metals.

Liquid	Temperature	ζ^H (gm·sec^{-1}x10^{-10})			ζ^S (gm·sec^{-1}x10^{-10})		ζ^{SH} (gm·sec^{-1}x10^{-10})		
		Present		Waseda & Ohtani[10]	Present	Waseda & Ohtani[10]	Present		Waseda & Ohtani[10]
		ζ_C^H	ζ_P^H				ζ_C^{SH}	ζ_P^{SH}	
1	2	3	4	5	6	7	8	9	10
Sodium	373	9.184	7.418	2.58 [a]	1.593	4.32 [a]	2.435	1.965	0.43 [a]
	433	9.363	7.625	—	1.398	—	2.137	2.769	—
	473	9.517	7.780	2.99 [a]	1.298	4.53 [a]	1.989	1.626	0.36 [a]
	513	9.515	7.816	—	1.208	—	1.835	1.505	—
	573	9.649	7.971	—	1.102	—	1.663	1.375	—
Potassium	338	9.346	7.523	2.85 [a]	1.628	4.61 [a]	2.480	1.997	0.37 [a]
	408	9.579	7.794	2.96	1.382	4.63 [a]	2.107	1.714	0.24 [a]
Rubidium	313	11.730	9.554	2.65	2.425	5.03	3.410	2.777	0.71
	433	11.840	9.860	—	1.801	—	2.489	2.072	—
	513	11.770	9.917	—	1.543	—	2.088	1.760	—
	513 *	9.005	7.879	—	1.397	—	1.584	1.386	—
	633	11.600	9.924	—	1.272	—	1.666	1.428	—
Cesium	303	15.130	12.030	3.73	3.493	5.81	5.401	4.294	1.36
	573	16.630	13.680	—	1.978	—	3.151	2.582	—
Mercury	238	28.100	22.360	6.94	6.008	14.11	9.968	7.932	2.98
	288	29.930	23.940	—	5.044	—	8.778	7.020	—
	296	30.190	24.160	9.10 [b]	4.922	2.43 [b]	8.614	6.896	−0.21 [b]
	353	31.810	25.610	—	4.217	—	7.610	6.124	—
Aluminium	943	14.420	12.290	4.83	1.940	12.75	1.619	1.379	1.85
	1023	14.660	12.540	—	1.807	—	1.515	1.296	—
Lead	613	30.570	25.600	7.64	2.640	29.46	2.764	2.313	4.18
	823 *	28.160	24.350	—	1.912	—	1.874	1.620	—
	1023 *	26.130	23.120	—	1.494	—	1.398	1.237	—
	1393 *	22.920	20.910	—	1.009	—	0.890	0.808	—
Gallium	323	15.810	13.170	5.28	7.698	10.77	8.722	7.266	3.18
	423 *	15.030	12.870	—	5.698	—	6.374	5.455	—
Copper	1423	38.900	31.960	—	3.772	—	6.521	5.344	—
	1723 *	35.590	30.060	—	3.196	—	4.940	4.169	—
Silver	1323	50.930	42.310	—	11.800	—	10.950	15.830	—
Gold	1373	79.340	2.180	—	12.610	—	23.970	18.760	—

[a] Y. Waseda and K. Suzuki, Act. Met. **21**, 1065 [1973].

[b] ζ_{PY} values from Ichikawa and Shimoji[12].

* Temperature dependent σ has been used (see text).

$$\widetilde{\Phi}^{S}(q) = \frac{4\pi\varepsilon}{q^3}\,[\lambda q\sigma\cos\lambda q\sigma - \sin\lambda q\sigma - q\sigma\cos q\sigma + \sin q\sigma]\,. \tag{8}$$

From Eqns. (3), (4), (6) and (8), we have,

$$\zeta^{S}_{LT} = -\frac{\varepsilon}{3}\left(\frac{m}{\pi k T}\right)^{1/2}\int_0^\infty\left[\frac{\varrho\,\widetilde{C}(q)}{1-\varrho\,C(q)}\right] [\lambda q\sigma\cos\lambda q\sigma - \sin\lambda q\sigma - q\sigma\cos q\sigma + \sin q\sigma]\,dq \tag{9}$$

$$\zeta^{SH} = -\frac{4\varepsilon}{3}\varrho\,g(\sigma)\left(\frac{m\pi}{kT}\right)^{1/2} \cdot\int_0^\infty[(q\sigma\cos q\sigma - \sin q\sigma)/q^3]\,[\lambda q\sigma\cos\lambda q\sigma - \sin\lambda q\sigma - q\sigma\cos q\sigma + \sin q\sigma]\,dq\,. \tag{10}$$

Equations (1), (2), (9) and (10) have been used to calculate D for several liquid metals at various temperatures and densities and the results are presented in Tables 2 and 3.

3. Results

The potential parameters, σ, ε and λ, have been determined by fitting Eq. (6) with the experimental value at the first peak position. The parameters thus obtained are given in Table 1. It is gratifying to note that the above parameters gave very good $S(q)$ values throughout the observable region of q[4, 5].

In Table 2 we present our values for ζ^{H}, ζ^{S} and ζ^{SH} calculated from Eqs. (2), (9) and (10) respectively along with those calculated by Waseda and Ohtani[11] from experimental $g(r)$ and $\Phi(r)$ values. Table 3 shows the values of D obtained from the above ζ values along with the experimental ones and those calculated by Waseda and Ohtani[11]. It is gratifying to note that the present values are in good agreement with the experimental values while the values obtained by Waseda and Ohtani are much higher. In the case of mercury (at 296 K), we compare our results in Table 2 with those reported by Ichikawa and Shimoji[12].

As expected, in the present study ζ^{H} is found to contribute nearly 60% of the total value of ζ. This is because the fundamental assumption underlying MSM is that the structure of liquids is determined primarily by the repulsive forces and that the main effect of the attractive forces between molecules is to provide a uniform background potential in which the molecules move.

Table 3. Self-diffusion coefficient D.

Liquid	Temperature (K)	D (cm$^2\cdot$sec$^{-1}\times 10^{-5}$) Present D_c	Present D_p	Waseda & Ohtani[10]	Experiment
1	2	3	4	5	6
Sodium	373	3.89	4.68	7.02 [a]	4.20 [c]
	433	4.63	5.55	—	5.85 [d]
	473	5.09	6.09	8.28 [a]	8.72 [f]
	513	5.64	6.71	—	—
	573	6.37	7.56	—	—
Potassium	338	3.46	4.18	5.96 [a]	4.01 [c]
	408	4.30	5.17	7.19 [a]	6.45 [e]
Rubidium	313	2.45	2.92	5.15	2.62 [b]
	433	3.70	4.35	—	5.68 [f]
	513	4.59	5.35	—	8.58 [f]
	513 *	5.90	6.63	—	8.58 [f]
	633	6.00	6.91	—	—
Cesium	303	1.74	2.10	2.31 [b]	—
	573	3.63	4.33	9.76 [b]	—
Mercury	238	0.74	0.94	1.66	0.93
	288	0.90	1.10	—	1.17 [g]
	296	0.93	1.13	—	—
	353	1.11	1.35	—	—
Aluminium	943	7.23	8.33	6.17 [b]	—
	1023	7.85	9.02	6.87 [b]	—
Lead	613	2.35	2.76	2.05	2.50 [c]
	823 *	3.55	4.07	—	—
	1023 *	4.86	5.46	—	—
	1393 *	7.74	8.45	—	—
Gallium	323	1.38	1.58	2.32	1.66 [c]
	423	2.15	2.42	—	3.55 [f]
Copper	1423	3.99	4.78	—	4.73 [h]
	1723 *	5.43	6.35	—	—
Silver	1323	2.14	2.61	—	3.16 [h]
Gold	1373	1.63	2.02	—	—

* as in Table 2.

[a] as in Table 2.

[b] calculated value[14].

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In the evaluation of ζ^{H} and ζ^{SH} from Eqs. (2) and (10), $g(\sigma)$ can be calculated either from the compressibility equation of state[13] or from the pressure equation of state. Thus, we present in Tables 2 and 3, two sets of results. The suffixes C and P (see Tables 2 and 3) to ζ^{H}, ζ^{SH} and D represent the equation of state used to evaluated $g(\sigma)$. In general, the results D_p are in good agreement with experiment.

For Na, K, Pb, Cs, Hg and Al, the temperature dependence of D has been evaluated using the potential parameters listed in Table 1 while for Pb, Ga and Cu, the temperature dependence of σ has been employed. The temperature dependence of σ has been obtained from an equation proposed by Protopapas et al.[14] (their Eq. (2.11)).

The agreement between theory and experiment (see Table 3) is quite encouraging and shows that the present potential represents the structure of liquid metals quite satisfactorily. The present results are much nearer to the experimental ones than those calculated from long-range oscillatory potentials derived from experimental $S(q)$ values[11]. The latter results[11] depend much upon the accuracy of the experimental $S(q)$ values, especially in the low q region[15]. The present theoretical model (MSM) gives good results in the above region and hence the theory is more reliable than the experiment, especially in the low q region of $S(q)$. Thus, the present potential satisfies the important condition that an acceptable potential should generate D[16, 17].

Finally it is worthy to point out that the potential parameters listed in Table 1 yield good values not only for $S(q)$ over the whole observable region of q[4, 5] but also for its isothermal pressure derivatives[18] and for isothermal compressibilities calculated in an entirely different context from Barker-Henderson's (1967) perturbation theory[19]. Thus, the representation of the attractive forces by the square well potential is quite satisfactory for liquid metals.

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