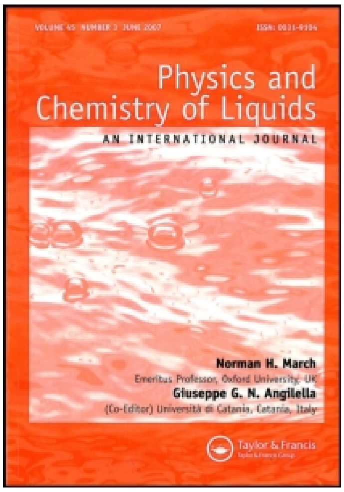

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Temperature Dependence of Self Diffusion in Liquid Metals

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To cite this Article Chhabra, R. P. and Sridhar, T.(1983) 'Temperature Dependence of Self Diffusion in Liquid Metals', Physics and Chemistry of Liquids, 13: 1, 37 — 46

To link to this Article: DOI: 10.1080/00319108308080761

URL: http://dx.doi.org/10.1080/00319108308080761

Phys. Chem. Liq., 1983, Vol. 13, pp. 37–46
0031-9104/83/1301-0037$18.50/0

Printed in Great Britain

Temperature Dependence of Self Diffusion in Liquid Metals

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(*Received July 9, 1982*)

After presenting a brief summary of the previous work, Hildebrand's fluidity model for the liquid state has been combined with a general equation for self diffusion in liquids to elucidate the temperature dependence of self diffusion in liquid metals. The analytical form for the temperature dependence presented herein is obeyed by the sixteen metals for which experimental values of self diffusion coefficient at various temperatures are available in literature. The article is concluded by suggesting a method for predicting self diffusion in liquid metals.

INTRODUCTION

Studies on diffusion in the liquid state have spanned over a period of a century. Perhaps the most important unsettled question in this field concerns the temperature dependence of diffusion coefficients. Our understanding of the liquid state is still in a preliminary stage of development and diffusivity data can provide important checks on the proposed model. Theories for diffusion in liquid metals have in general borrowed heavily from the theories of the liquid state and in some areas developed in a rather unique fashion. A coherent theory encompassing liquids and liquid metals is yet to emerge.

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Recent data on diffusion in liquid metals over a wide temperature range has made it possible to test rigorously the various theoretical predictions. This paper examines the effect of temperature on the diffusion coefficient and shows how an earlier theoretical analysis which proved quite successful for simple liquids, also applies to liquid metals. Excellent reviews of diffusion in liquid metals are available.[1,2]

PREVIOUS WORK

Two different approaches have been taken in order to understand diffusion in liquids. On one hand there are the idealized structural models that attempt to relate diffusion coefficients to macroscopic properties of the liquid. The more fundamental approaches attempt to calculate transport properties from the pair correlation function without appeal to a preconceived structure of the liquid. These approaches have yielded equations for predicting transport properties.[3] In this paper we are interested in the form of temperature dependence that these theories predict.

The hole theory of liquids draws heavily upon the similarity with vacancy theory for solids. It arose due to the perception that a high degree of local order persists in the liquid state. It was assumed that molecular mobility is constrained by the nearest neighbours just as in crystalline solids. This theory gives rise to an exponential dependence of the diffusion coefficient on temperature. It postulates the need for a hole of molecular dimensions before motion can occur. The need for displacements of the order of molecular size has been criticised by Alder and Wainwright[4] and Hildebrand.[5]

The activated state theories require a localization of the energy density in order to overcome a barrier to motion. This approach also leads to an exponential form of the temperature dependence. Over small temperature ranges such a dependence is in agreement with experiments; however, in such cases it is also possible to fit the data to a simple linear function of temperature. The chief value of the activated state theory has been its use to parameterize a kinetic process.[6]

The free volume theories envisage the available free volume in liquids to be assembled into holes of molecular dimensions by a statistical rearrangement. This theory predicts that at constant volume, the diffusion coefficient should vary according to $T^{1/2}$. The experimental data of Ozelton and Swalin[7] do not support this prediction.

Swalin's model[8] for diffusion in liquid metals is based on the concept that atoms make diffusive movements over a continuous distribution of distances. He used the Morse potential function to describe the potential energy-distance relationships. This theory leads to a T^2 dependence of diffusion coefficients. Comparison with experimental data for liquid tin was shown to be satisfactory.

Nachtrieb[6] conducted a survey of all published data on self diffusion in liquid metals. Examining the temperature dependence of diffusion coefficients, it is found that none of the data follow a $T^{1/2}$ or T^2 dependence as predicted by free volume theory or Swalin's model[8] respectively. For Tin and Indium both log D versus $(1/T)$ and D versus T yield equally good straight lines. None of the above-mentioned forms describe the data for Mercury. Nachtrieb[6] concluded that the actual temperature dependence could be a more complicated function involving temperature dependent physical properties. There appeared to be little advantage in presuming anything other than a simple linear dependence on temperature.

Broome and Walls[9] used a modified shear cell to measure self diffusion in Mercury. They attempted to fit the data to several functional forms as given below:

$$\ln D = \frac{A_1}{T} + B_1 \qquad \text{(Arrhenius)}$$

$$D = A_2 T^{1/2} + B_2 \qquad \text{(Kinetic Theory)}$$

$$D = A_3 T + B_3 \qquad \text{(Harmonic Oscillator Model)}$$

$$D = A_4 T^{3/2} + B_4 \qquad \text{(Dynamic Analysis)}$$

$$D = A_5 T^2 + B_5 \qquad \text{(Swalin's Model}^{8}\text{)}$$

$$D = A_6 \frac{T}{\mu} + B_6 \qquad \text{(Stokes–Einstein)}$$

A statistical analysis of the above-mentioned equations applied to the data on Mercury failed to confirm the applicability of any particular model.

Statistical mechanical theories envisage molecular motion takes place in small steps in a random walk fashion. In these theories the friction coefficient in Brownian motion is related to the auto correlation function of the force acting on the molecule. It provides a sophisticated approach to the problem of relating molecular friction coefficients to the properties of the liquid. Bearman,[10] in a review, shows the similarities between rate theories and statistical mechanical theories in relating mutual and self diffusion coefficients. The Lamm-Dullien approach[11,12,13] is based on a similar concept. We shall use their approach to analyse existing data on self diffusion in liquid metals.

ANALYSIS AND DISCUSSION

Dullien[13] using Lamm's theory evaluated a molar average friction coefficient. Observing that the molar average friction coefficient and viscosity are two different ways of averaging friction coefficients, he derived the following equation for self diffusion,

$$\delta = \left[\frac{2\mu V D}{RT}\right]^{1/2} \tag{1}$$

This equation is not based on any particular model of the liquid state and is expected to hold for Newtonian liquids. The parameter δ is the average momentum transfer distance. Dullien[13] showed that the above equation is consistent with elementary kinetic theory.

Recently, Hildebrand[5] presented a large body of evidence suggesting that the temperature dependence of viscosity μ (or fluidity, ϕ) is best represented by assuming that the extent of fluid flow is determined by free volume rather than being limited by the availability of an activation energy such as Eyring postulates; see e.g. Glasstone *et al.*[14] Thus Hildebrand[5] wrote,

$$\phi = \frac{1}{\mu} = B\left[\frac{V - V_0}{V_0}\right] \tag{2}$$

This linear relation between fluidity and molal volume was shown to be valid for liquids, liquid metals and compressed gases. It has been extended to dilute macromolecular polymer solutions,[15] binary liquids [16–18], diffusion of free radicals in solution,[19] thermal conductivity of simple liquids,[20] and molten salts.[21] The range of applications shows the versatility of this simple approach. Equation (2) can be incorporated into equation (1) to obtain,

$$D = \frac{BR\delta^2}{2}\frac{T}{V}\left(\frac{V - V_0}{V_0}\right) \tag{3}$$

This equation relates diffusion coefficient to temperature and molal volume. Chhabra *et al*[20] showed that the above equation correctly predicted the temperature dependence of self diffusion coefficient of simple liquids. We now test the applicability of equation (3) to liquid metals.

Figures 1, 2 and 3 show plots of self diffusion coefficient D versus $T(V - V_0)/VV_0$ for a variety of liquid metals over a wide temperature range, as indicated in Table I. Self diffusion coefficient values, except for Thallium, have been taken from the compilation by Nachtrieb[6] and density data was taken from Smithells.[22] For Thallium, the densities at different temperatures have been estimated from the equation presented by Crawley,[23] while the values of diffusion coefficients have been taken from Cahill and

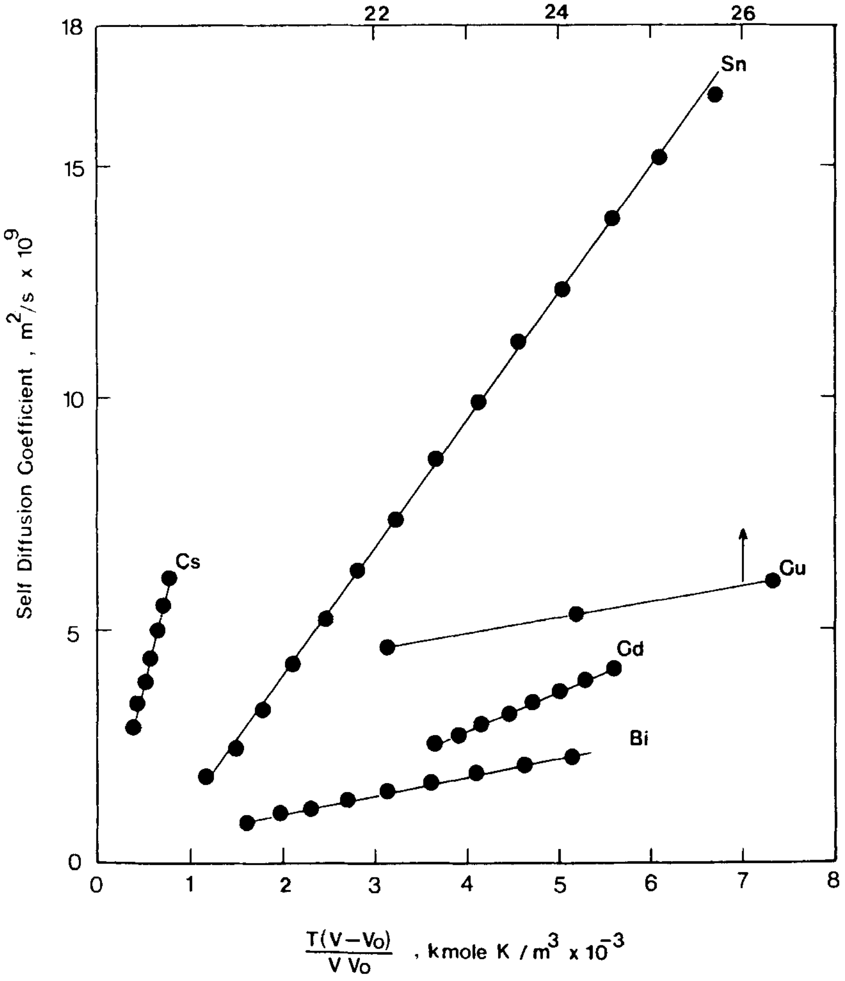

FIGURE 1 Dependence of diffusion coefficient on molal expansion for Cesium, Tin, Copper, Cadmium and Bismuth.

Grosse[24] who calculated diffusion coefficient from viscosity data based on Frenkel's kinetic theory via the Stokes–Einstein relationship. Their calculated values are in agreement with the experimental values reported by Barras *et al.*[25] The values of V_0 were taken from Hildebrand[5] and could also be calculated using viscosity data. The excellent linearity of these plots needs to be emphasized. The slopes and regression correlation coefficients are given in Table I. Using the values of these slopes and B, as listed by Hildebrand,[5] the mean momentum transfer distance δ can be calculated. Dullien[26] has

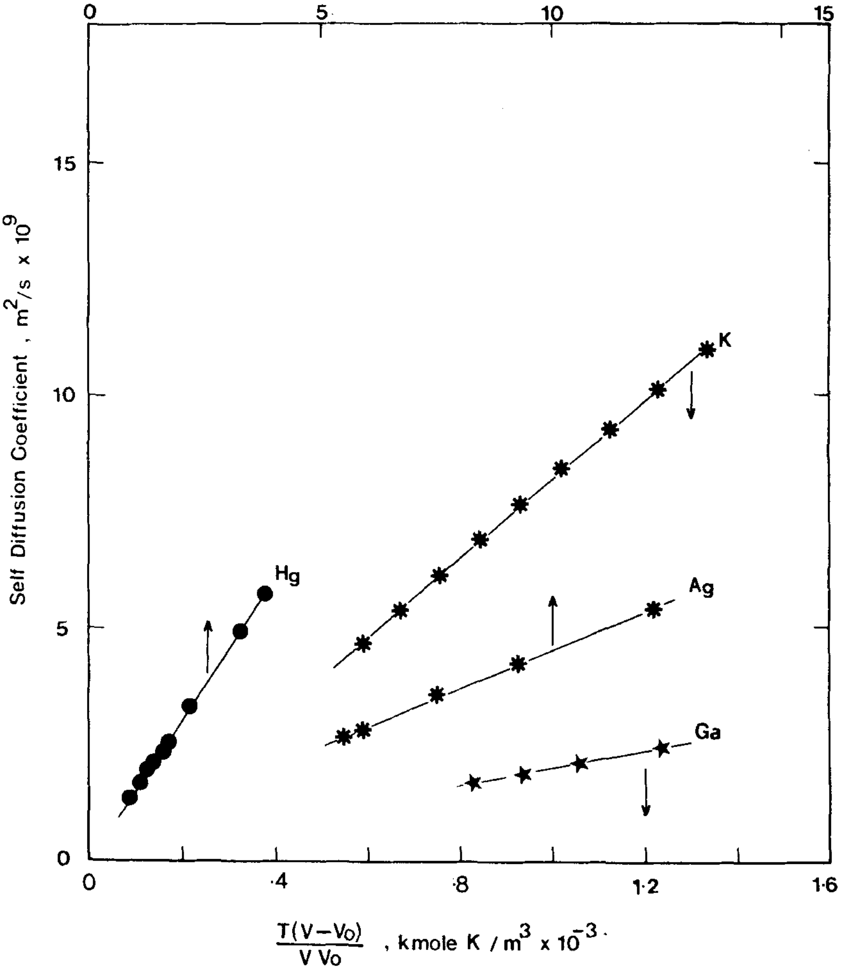

FIGURE 2 Dependence of diffusion coefficient on molal expansion for Mercury, Potassium, Silver and Gallium.

related δ to the molecular diameter for simple liquids as

$$\delta = 0.63\ \mathrm{d} \qquad (4)$$

Figure 4 shows the variation of the momentum transfer distance (δ) as a function of atomic diameter. Beyer and Ring[27] has given a compilation of Goldschmidt atomic diameters. The data seem to indicate that equation (4) is obeyed, if d is taken as the atomic diameter. The experimental values of δ (calculated from the slopes of plots in Figures 1 to 3) are compared with the

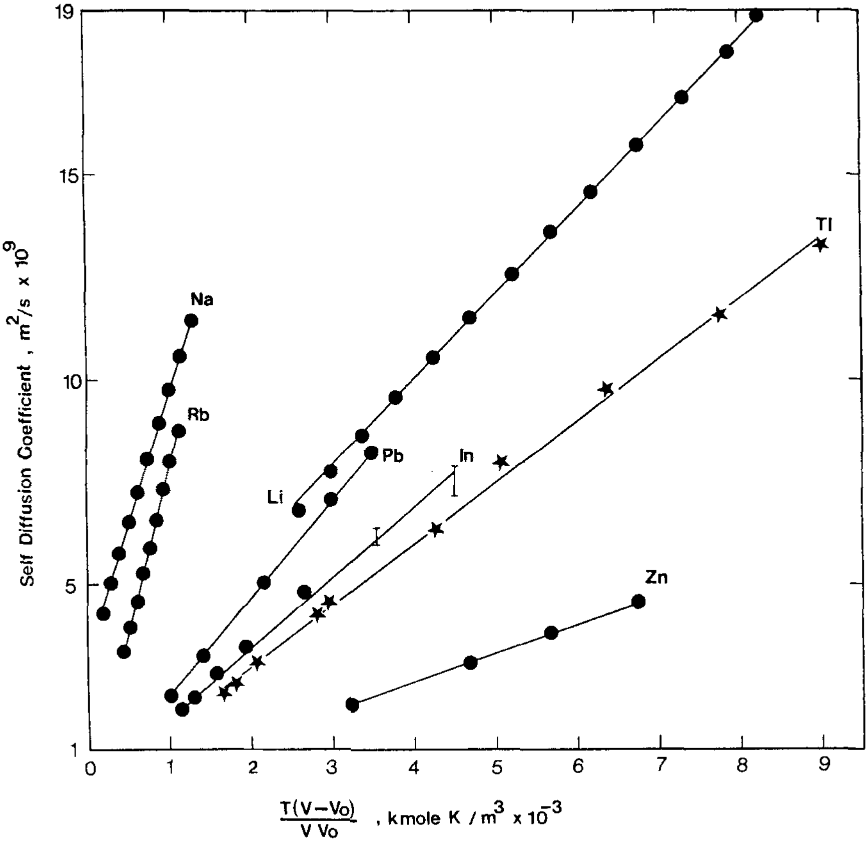

FIGURE 3 Dependence of diffusion coefficient on molal expansion for Sodium, Rubidium, Lithium, Lead, Indium, Thallium and Zinc.

prediction of Eq. (4) in Table I. The agreement is quite satisfactory except for the case of Bismuth. No immediate reason for this discrepancy can be given.

The form of Eq. (3) explains why the various expressions cited previously have had some success. Over limited temperature ranges, the quantity $(V - V_0)/VV_0$ can be considered to be a constant and thus leading to a linear dependence of diffusion coefficient on temperature. If the molar V is considered to be independent of temperature, the Stokes–Einstein equation results and so on. The fact that the slope of these plots can be predicted from atomic diameters suggests that we have herein a method for predicting self diffusion coefficients in liquid metals. In most cases the error involved can be estimated from Table I to be of the order of 10 % and is equal to the errors involved in predicting value of mean momentum transfer distance δ.

TABLE I

Metal	Temp. range (K)	Slope × 10^{12} $m^5/K/k$ mole/s	Corr. Coeff.	δ calculated from Slope (Å)	d Å	$\delta = 0.63\,d$ Å
Ag	1248-1623	0.411	0.9989	1.592	2.88	1.814
Bi	550-950	0.379	0.9950	0.965	3.64	2.293
Cd	623-763	0.824	0.9999	1.991	3.04	1.915
Cs	333-453	8.061	0.9995	3.084	5.40	3.402
Cu	1413-1533	0.342	0.9999	1.89	2.56	1.613
Ga	303-372	1.72	0.9997	1.661	2.70	1.701
Hg	303-566	1.486	0.9991	1.733	3.10	1.953
In	448-873	1.398	0.9959	1.640	3.14	1.978
K	363-523	8.359	0.9992	2.729	4.76	3.000
Li	473-713	2.0668	0.9989	1.852	3.14	1.978
Na	373-553	6.409	0.9983	2.390	3.84	2.420
Pb	606-930	2.424	0.9998	2.574	3.50	2.205
Rb	333-493	8.115	0.9993	2.689	5.04	3.175
Sn	560-1150	2.744	0.9992	2.253	3.16	2.000
Tl	644-1279	1.468	0.9976	1.873	3.40	2.142
Zn	693-873	0.7192	0.9999	1.742	2.74	1.726

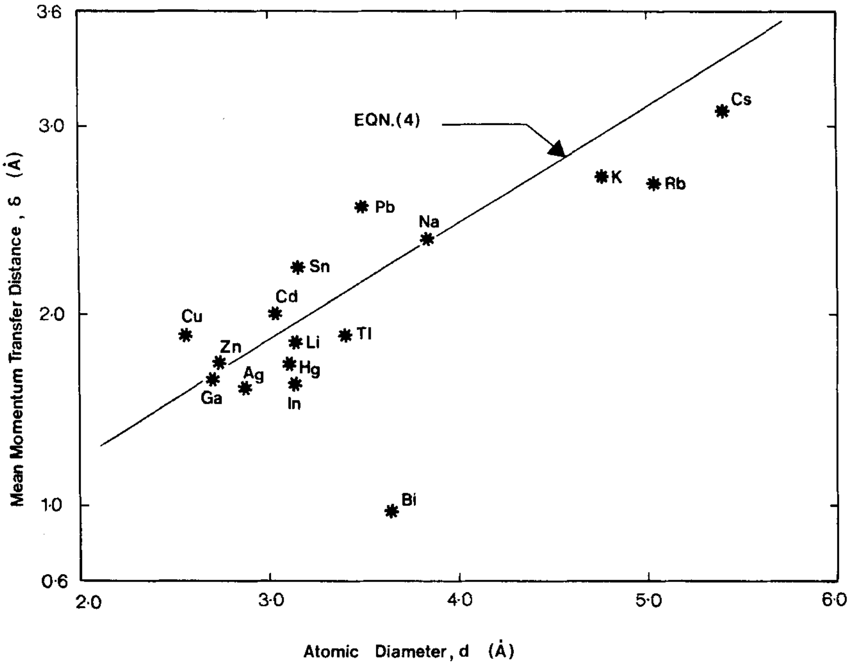

FIGURE 4 Relationship between mean momentum transfer distance and Goldschmidt atomic diameter.

CONCLUSIONS

The present paper has given an analytical form for the temperature dependence of self diffusion in liquid metals. The equation is obeyed by all the sixteen liquid metals for which data were available. The temperature dependence of diffusion coefficients in liquid metals is similar to that in simple liquids. The form of the temperature dependence is such that over small temperature ranges and particular liquids it can be simplified into a number of equations. This possibly explains why a variety of empirical equations have had at least limited success. However, the fact that the present equation works equally well for scores of simple liquids as well as for liquid metals suggests that the formulation presented here merits serious consideration.

LIST OF SYMBOLS

$A_1, \ldots, A_6$ $B_1, \ldots, B_6$	Constants in various empirical equations
B	Constant in Eq. 2
D	Self diffusion coefficient
δ	Mean momentum transfer distance
d	Goldschmidt atomic diameter
R	Gas constant
T	Absolute temperature
V	Molal volume
V_0	Molal volume corresponding to zero fluidity
μ	Viscosity
ϕ	Fluidity

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