Title	Estimations of Some Unknown Viscosities and Self-diffusivities for Liquid Metals
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Citation	Transactions of JWRI. 1973, 2(2), p. 196-202
Version Type	VoR
URL	https://doi.org/10.18910/7787
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Estimations of Some Unknown Viscosities and Self-diffusivities for Liquid Metals[†]

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Abstract

Both viscosity and self-diffusion of liquid metals obey approximately a simple form of exponential (the Arrhenius) equation.

It is shown that simple empirical relationships exist between the temperature dependences (activation energy) of viscosity and self-diffusion for liquid metals and their melting points. The constant in the exponential equation can be obtained from the expressions which have been derived by authors previously.

The temperature dependences of viscosity and self-diffusion of liquid metals are clasified into two groups; one is normal metals (typical metals) and the other is semi-metals.

The structure factors for liquid metals can be clasified into two groups as well as the temperature dependences of viscosity and self-diffusion.

Consequently, viscosities and self-diffusivities can be estimated in cases where experimental data is lacking.

1. Introduction

Transport processes are concerned with the flow of mass, momentum, and energy in fluids in nonuniform states. For normal liquids near equilibrium, the transport rates are proportional to gradients of concentration, mass velocity, and temperature; and diffusivity, viscosity, and thermal conductivity are the respective proportionality constants. The theory of thermal conductivity is less well developed and more complex than the first two, and avialable data is also few, because of the considerable difficulty in the experimental techniques.

Interest in the viscosity and diffusion of liquid metals today stems both from technological considerations of welding, metallurgy or nuclear engineering (atomic reactor coolants), and from theoretical considerations, such as the fact that their structural simplicity marks them good media to test the current theories of liquid state.

Academically, for equilibrium properties, the pair potential and pair distribution function are the starting point and the calculation proceeds via equilibrium statistical mechanics. By such approach, the information regarding time variation of particle positions is not considered. In contrast, for transport coefficients the calculation proceeds via a detailed atomic (molecular) dynamics method. That is, the transport coefficients themselves are integrals over time[1]. These integrals can not be expressed in a simple way in terms of the pair potential and pair distribution functions, and they can not be calculated in a similar way as to the equilibrium cases. Therefore, for transport coefficients, rigorous expressions have not been derived at present. In such cases approximate expressions are commonly employed. For this reason, it is usual to propose models of liquid first and then calculate the transport coefficients for the models. Intuitively, the viscosity or diffusivity will depend upon three fundamental parameters: pair potential (the interatomic bond strength), the atomic size (the atomic weight), and the coordination number (the tadial distribution function, that is, the structure of liquid metals).

Experimental viscosity and diffusion data exist for only about 50% of all metallic elements (metals are the elements consisting over three-fourths of the periodic table), excluding the rare-earth group. And a practical determination of these properties for many of the remaining metals would prove difficult experimentally, owing to their chemical reactivity, their refractoriness, or their scarcity. Therefore, several mathematical or empirical methods have been suggested for calculating viscosities and diffusivities of liquid metals, but none are successfull expect for few metals.

From the practical standpoint, it would be useful that viscosities and diffusivities of many liquid metals can be estimated by simple expressions in cases where experimental data is lacking. According to experimental results, both viscosity and self-diffusion obey approximately the general form of Arrhenius equation. Simple empirical relationships exist between the temperature dependences (activation energy) of

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viscosity and self-diffusion for liquid metals and their melting temperatures. Furthemore, the constant in the Arrhenius equation can be calculated from the expressions which have been derived by present authors[2), 14)] previously. The temperature dependences of viscosities and self-diffusivities for liquid metals have been clasified into two groups: one is normal metals* (typical metals) and the other is semi-metals.** Furthermore, they correspond to the structure factors which have been determined by means of X-ray or neutron diffraction and have been calculated from hard sphere model. These approaches have usually involved a discussion of the analytical relationship between viscosity and self-diffusion.

It is propossed to estimate viscosities and self-diffusivities of liquid metals, whose metals are not so far studied experimentally. It should be understood that this simple relationship represents a first approximation only.

2. Estimations of some unknown viscosities for liquid metals

The beginnings of the modern theory of transport processes in liquids were set forth by Kirkwood[3)], and by Born and Green[4)]: Rigorous expressions for viscosity were derived which applied equally to liquid and gas. They consist of two parts due to the thermal motion and molecular (atomic) forces respectively, of which the first is dominant for the gas, and the second for liquid. By approximating the rigorous formular, viscosity of liquids was obtained by Born and Green[4)]. Born and Green[4)] thought that a method of successive approximations could overcome the calculational difficulties of the formular, but unfortunately this has not yet been accomplished.

A simple form expresses the relationship between viscosity η and temperature T in °K., as follows:

$$\eta = A \cdot \exp\left(\frac{H_\eta}{RT}\right)$$

or

$$\log \eta = \frac{H_\eta}{2.303R} \frac{1}{T} + \log A \tag{1}$$

The experimental values $\log \eta$ all fall on straight lines when plotted against 1/T. Where A is a constant, R the gas constant and H_η the slope of ($\log \eta$, 1/T) (if the mechanism of viscosity is an activated process, H_η is the energy of activation for viscous flow). In addition, from a general kinetic theory of liquids, Born and Green[4)] found that the approximately exponential temperature dependence exists. The simple exponential representation is a useful engineering correlation of viscosity for liquid metals. Many pure metals, however, do not show exactly linear plots $\log\eta$ vs.1/T over wide temperature range. A number of alternatives to equation (1) have been proposed which are more successful for particular group of liquids. But even if these have greater justification, the limited-accuracy of the available data probably does not justify a more complex equation than equation (1).

If the constants A and H_η are given, viscosities can be estimated from equation (1). From the theoretical and experimental standpoint, it has been suggested that any kind of relationships between viscosity and the other physical properties of liquid metals. It was found by Grosse[5)] that a simple empirical relationship exists between H_η, the slope of ($\log\eta$, 1/T) of viscosity for liquid metals and their melting points. This was shown in log-log plot. Grosse[5)] observed a monotonic function of the melting temperature of the metal. (According to Eyring's views[6)], H_η is proportional to the energy of vaporization.) Consequently, use of this empirical relationship makes it possible to estimate the variation of liquid metal viscosities with temperature.

However, from the experimental and theoretical investigation of the physical properties of liquid metals (the structure factors or radial distribution functions) it would be considered that viscosity and diffusion at or near the melting point, being sensitive to the structure of liquids, correspond to the crystal structure in solid state. Furthermore, the experimental viscosity data of liquid metals which was taken by Grosse[5)], is quetionable today, because experimental difficulties normally encountered in viscosity measurements of liquid metals precluded accurate measurements with early techniques.

A consideration of the best data now available appears in **Table 1.** They are obtained from the recent review by Wilson[7)] and have in some instances been supplemented by Takeuch and Iida[8)]. Relationship between H_η and melting point (T_m) is shown graphically in **Fig. 1.** As can be seen from **Fig. 1,** the slope of ($\log\eta$, 1/T), H_η is described by $H_\eta = 1.3RT_m$ for semi-metals and $H_\eta = 1.7RT_m \sim 3.5RT_m$ for normal metals. From experimental data, Hrbek[9)] has proposed $H_\eta = 3RT_m$ for many liquid metals. From **Fig. 1,** however, relationship between H_η and T_m can inadequatly be expressed only a straight line. That is, the temperature dependences

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* Normal metals (typical metals) are defined as those that crystallize in the bcc, fcc, or hcp structure.

** Semi-metals are defined as those that crystallize into (more) complex crystal structures.

Table 1. Slope of (log η, 1/T) (activation energy) for viscosity in pure liquid metals.

Metal	T_m (°K)	H_η (K cal·mole^{-1})	Ref.
Li	453.7	1.33	7
Na	371.0	1.25	7
K	336.4	1.2	7
Rb	312	1.23	7
Cs	301.8	1.15	7
Mg	923	7.3	7
Ca	1123	6.5	7
Al	932	3.95	7
Cu	1357	7.3	7
Ag	1234	5.3	7
Au	1336	5.1	7
Zn	692.7	2.7	8
Cd	594	3.0	8
Hg	234.3	0.53	8
Ga	302.9	1.0	8
In	429.3	1.25	8
Sn	505	1.25	8
Pb	600.6	1.9	8
Sb	903	2.6	8
Bi	544.5	1.25	8
Fe	1809	9.9	7
Co	1768	10.6	7
Ni	1725	12.0	7
Pu	913	3.1	7

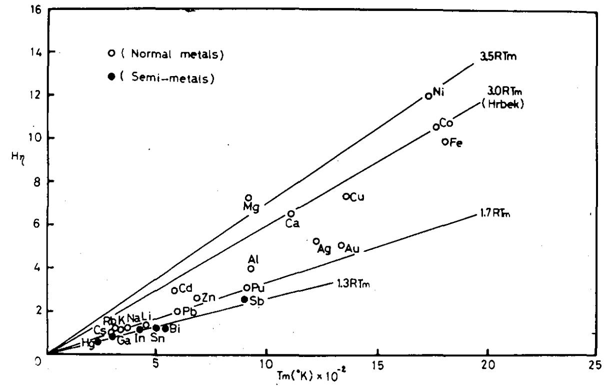

Fig. 1. H_η, slope of (logη, 1/T) (activation energy) for viscosity in pure liquid metals as a function of melting temperature.

of viscosities of liquid metals should be clasified into two groups: one is normal metals and the other is semi-metals. The slope of (logη, 1/T) vs. melting temperature relationship is shown graphically in **Fig. 2.** As Fig. 2 indicates, it can be clasified into the two groups. Furthermore, fairly linear relationships exist between H_η and T_m, respectively. As can be seen from Fig. 2, the slopes of (logη, 1/T) of viscosity for

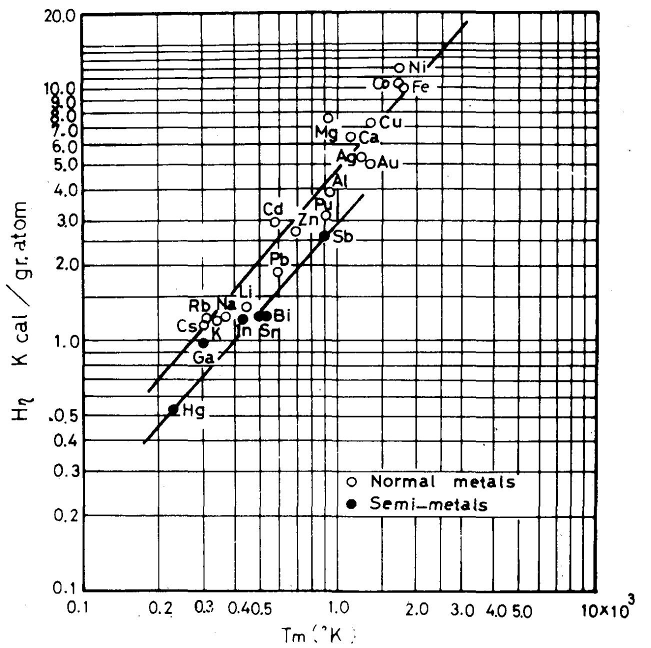

Fig. 2. Slope of (logη, 1/T) (activation energy) for viscosity in pure liquid metals vs. melting point.

liquid metals are described by $H_\eta = 1.21 T_m^{1.2}$ for normal metals and $H_\eta = 0.75 T_m^{1.2}$ for semi-metals.

The constant A is obtained by the expression of viscosity which have been derived by present authors[2] previously. The expression is:

$$\eta = \frac{4}{3}\nu P(T)\, m\rho^2 \int_0^a g(r)\, r^4 dr \qquad (2)$$

where ν is a vibrating frequency of atoms, P(T) means the life time which corresponds to the probability of atom to vibrate at each site, m is atomic mass, ρ is the average number of atoms per unit volume, and g(r) is the radial distribution function. At the melting point, viscosity η_m (equation (1)) is expressed as follows:

$$\eta_m = 5.7\times10^{-4}\,\frac{(M\,T_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}} \qquad (3)$$

where M is the atomic weight and V_m is liquid atomic volume at the melting point. Expression of this type has been derived before by Andrade[10]. Consequently, the constant A is as follows:

$$A = \frac{5.7\times10^{-4}\,(M\,T_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}\exp(H_\eta/R\,T_m)} \qquad (4)$$

Finaly, viscosities of liquid metals are given by the following expression;

$$\eta = \frac{5.7\times10^{-4}\,(M\,T_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}\exp(H_\eta/R\,T_m)}\exp\left(\frac{H_\eta}{RT}\right) \qquad (5)$$

3. Estimations of some unknown self-diffusivities for liquid metals

An analogous Arrhenius expression to that used for viscosity is found to fit all available data in diffusivity;

$$D = D_0 \exp\left(-\frac{H_D}{RT}\right)$$

or (6)

$$\log D = -\frac{H_D}{2.303R}\frac{1}{T} + \log D_0$$

where D_0 is a constant and H_D the slope of (log D, 1/T) (If the mechanism of diffusion is an activated process, H_D the activation energy for self-diffusion). It is suggested for self-diffusion as well as viscosity that simple relationships exist between H_D and the melting point. Saxton and Sherby[11] have studied viscosity and atomic mobility in liquid metals, and have proposed, in an interesting phenomenological analysis of viscosity and self-diffusion data for liquid metals, $H_D = 3.0\ RT_m$ for normal liquid metals and $H_D = 2.75\ RT_m$ for semi-metals. On the other hand, Nachtrieb[12] has proposed a empirical relation $H_D = 3.35\ RT_m$ for pure metals. From the recent review by Hachtrieb[12] and for alkali metals more recent data by Larsson et al[13] (**Table 2**), relationships between H_D and T_m are shown in **Fig. 3.** As can be seen from Fig. 3, Saxton and Sherby's observation is found for semi-metals. For normal metals, however, both Saxton and Sherby's observation and Nachtrieb's observation are rough approximations. That is, the relationships are inadequately represented with a straight line for normal metals.

Table 2. Slope of (log D, 1/T) (activation energy) for self-diffusivity in pure liquid metals.

Metal	T_m (°K)	H_D (K cal·mole^{-1})	Ref.
Li	453.7	2.87	13
Na	371.0	2.22	13
K	336.4	2.02	13
Rb	312	1.98	13
Cs	301.8	(1.86)	13
Cu	1357	9.71	12
Ag	1234	7.66	12
Zn	692.7	5.09	12
Hg	234.3	1.16	12
Ga	302.9	1.12	12
In	429.3	$\begin{pmatrix}2.43\\2.55\end{pmatrix}$	12
Sn	505	2.58	12
Pb	600.6	4.45	12
Sb	903	5.0	11
Bi	544.5	3.0	11
Fe 4.6%C 2.5%C	1809	$\begin{pmatrix}12.2\\15.7\end{pmatrix}$	12

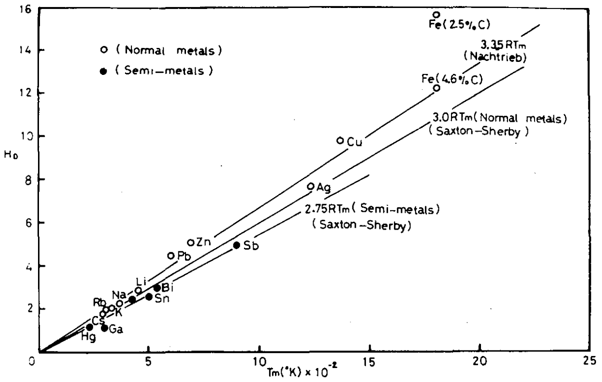

Fig. 3. H_D, slope of (log D, 1/T) (activation energy) for self-diffusion in pure liquid metals as a function of melting temperature.

Log-log plots of the H_D, the slope of (log D, 1/T) against the melting temperature are shown in **Fig. 4.** It can be seen that fairly good straight lines are obtained for normal metals and semi-metals, respectively. Namely, the temperature dependences of self-diffusivities of liquid metals can be clasified into two groups (normal metals and semi-metals) as well as viscosities. The empirical relationships $H_D = 2.5T_m^{1.15}$ for normal metals and $2.0T_m^{1.15}$ for semi-metals are found from Fig. 4.

As have been shown by present authors[14], self-diffusivities of liquid metals at the melting point are given by the following simple expression;

$$D_m = 3.5\times10^{-6}\left(\frac{T_m}{M}\right)^{\frac{1}{2}} V_m^{\frac{1}{3}} \tag{7}$$

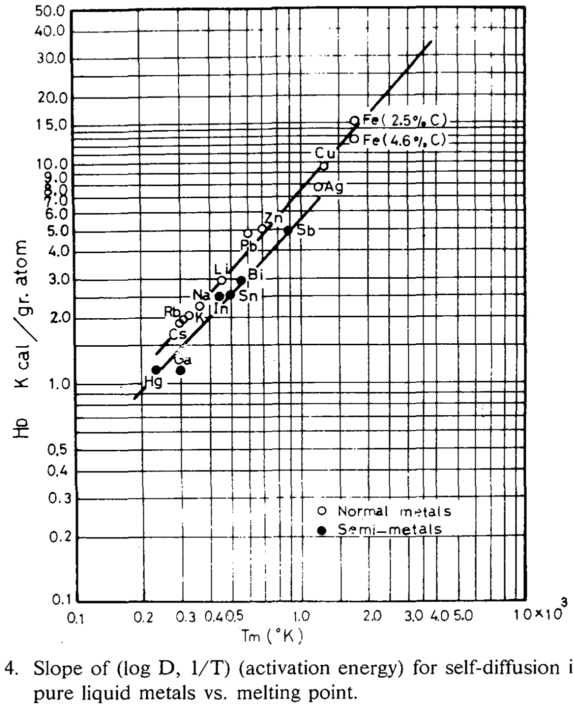

Fig. 4. Slope of (log D, 1/T) (activation energy) for self-diffusion in pure liquid metals vs. melting point.

By combining above expression with equation (1), the constant D_0 can be obtained.

$$D_0 = \frac{3.5\times10^{-6} T_m^{\frac{1}{2}} V_m^{\frac{1}{3}}}{M^{\frac{1}{2}} \exp(-H_D/RT_m)} \tag{8}$$

Consequently, self-diffusivities of liquid metals are expressed as follows;

$$D = \frac{3.5\times10^{-6} T_m^{\frac{1}{2}} V_m^{\frac{1}{3}}}{M^{\frac{1}{2}} \exp(-H_D/RT_m)} \exp(-\frac{H_D}{RT}) \tag{9}$$

On the other hand, Nachtrieb[12] has suggested D =constant·T

$$D = C \cdot T \tag{10}$$

From the equation (7) and (10), self-diffusivities of liquid metals are represented;

$$D = \frac{3.5\times10^{-6} V_m^{\frac{1}{3}}}{(MT_m)^{\frac{1}{2}}} \cdot T \tag{11}$$

It is considerable importance that the physical properties of liquid metals, such as viscosity and diffusion, can be clasified into two groups; one of normal metals and the other of semi-metals. This fact has a meaning in engineering parameters as well. For instance, as shown in **Fig. 5**, the ratio of surface tension (γ) to viscosity (i. e. ideal penetration coefficient in engineering) of liquid metals is also clasified into the same groups. As can be seen from Fig. 5, the values of $(T_m/M)^{\frac{1}{2}}$ for tin and lead are nearly equal to each other, but the value of (γ_m/η_m) for tin (ideal penetration coefficient at the melting point) is considerably larger than that for lead.

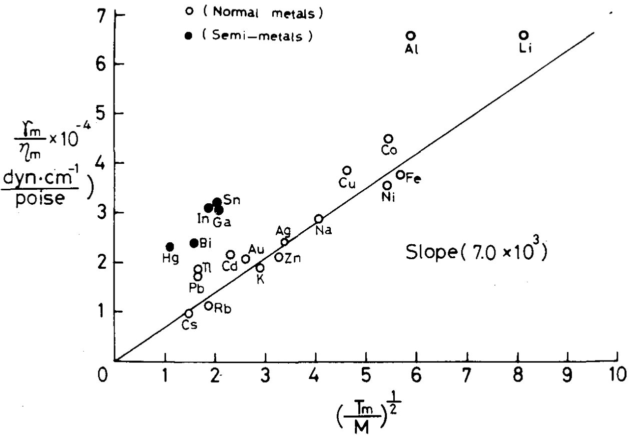

Fig. 5. Ratio of surface tension to viscosity for pure liquid metals at their melting point vs. (melting yemperature, °K/atomic weight, g·more^{-1})$^{\frac{1}{2}}$. (molar volume, cm^3·mole^{-1})$^{\frac{1}{3}}$.

4. Relationships between the temperature dependences of viscosities and self-diffusivities of liquid metals and their structure factors

A complete treatment of the transport properties of a liquid requires a discussion of the position and momentum of each atom at each instance of time[1]. Thus it is useful to define more general distribution functions involving position ($\vec{r}$), momentum ($\vec{p}$) and time (t), which describe the distribution at some time t_2 relative to the initial distribution at t_1. The simplest of these is the general pair distribution function, namely $f(\vec{r}_1, \vec{p}_1, t_1; \vec{r}_2, \vec{p}_2, t_2)$ is the probability of finding an atom at $\vec{r}_2$ with momentum $\vec{p}_2$ at time t_2, if there was an atom at ($\vec{r}_1$, $\vec{p}_1$, t_1). Many transport properties may be discussed in terms of a simpler function (G) involving only space and time, i. e.;

$$G(\vec{r}_1 - \vec{r}_2,\ t_2 - t_1) = \iint f(\vec{r}_1, \vec{p}_1, t_1; \vec{r}_2, \vec{p}_2, t_2)\, d\vec{p}_1\, d\vec{p}_2$$

Phisically, G is proportional to the probability of finding an atom at $\vec{r}_2$ at the time t_2, if there was an atom at ($\vec{r}_1$, t_1). It depends only upon the space and time difference because the system is in thermal equilibrium. These differences will be denoted by $\vec{r}_1 - \vec{r}_2 = \vec{r}$ and $t_2 - t_1 = \tau$. $G(\vec{r}, \tau)$ is known as the van Hove correlation function or total space-time correlation function. The theory of space-time-dependent correlation function ($G(\vec{r}, t)$), in viscosity and diffusion, has not been developed to the point where rigorous expressions may be derived. In these cases approximate expressions, based on models, are commonly employed.

For each of the solid and gaseous states there is an ideal model which is good approximation to reality and forms the basis for theoretical discussion. These are the ideal crystal lattice and the ideal gas models, respectively; for the former, emphasis is on structural order modified slightly by the thermal motion of atoms while, for the latter, the model describes the random thermal motion of the atoms from random atomic positions. On the other hand, at present there is no ideal model which gives a good approximation to liquid state. If such a model is found it would (in constrast to the crystal and gas models) need to cover structural and thermal properties with equal emphasis.

The mechanism of an activated process, based on cell model (hole, lattice or free volume model) in a liquid is not well understood, but a jump process, such as is usually visualized in solids, does not seem likely and is certainly not supported by the evidence from neutron diffraction experiments.

Intuitively, viscosity or diffusion will depend upon the structure of liquids. North et al[15] have determined the structure factors for four liquid metals (Zn, Tl, Sn and Bi) a temperature close to the melting point, by means of neutron diffraction. The data for

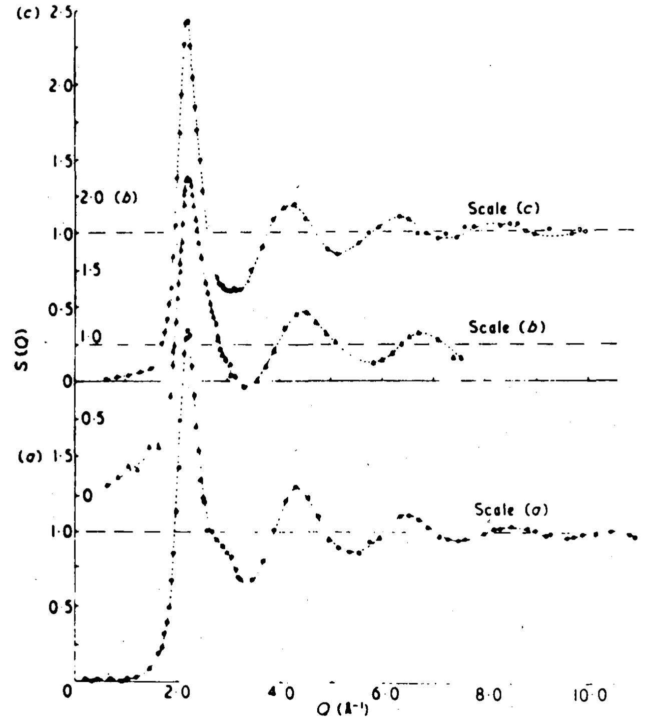

Fig. 6. Structure factors S(Q) for liquid Sn and Tl (Scale (a): Sn at 250°C; Scale (b): Sn at 600°C; Scale (c): Tl at 320°C) (after North et al).

liquid tin and thallium are shown in **Fig. 6.** As can be seen from Fig. 6, the result of tin at 250°C confirms the existence of a shoulder (subsidiary maximum) on the high Q side of Q_m. In contrast, the results of liquid thallium and tin at 600°C do not.

Intensity patterns have been obtained by X-ray diffraction from liquid bismuth up to 652°C by Isherwood and Orton[16], and the experimental structure factor (a(K)) curves were compared with those caluculated from hard sphere model. The results are shown in **Fig. 7.** The experimental information obtained from their investigation is the high temperature diffraction pattern at 652°C. This temperature coresponds to one-third range (melting point to boiling point) and, as can be seen from **Fig. 7,** a subsidiary maximum is still present. When the peak heights of the experimental and hard sphere a(K) curves are compared, there are two main differences between the best fitting hard sphere a(K) curves and those of bismuth. One is the small difference in position the first peak and the other is the presence of the subsidiary maximum. The first peak position of hard sphere a(K) curves lies between the main and subsidiary peakes of experimental curve.

Ashcroft and Lekner[17] were comparing the hard sphere curves with experimental curves from the alkali metals, which do not show a subsidiary maximum. The results for potassium and rubidium are

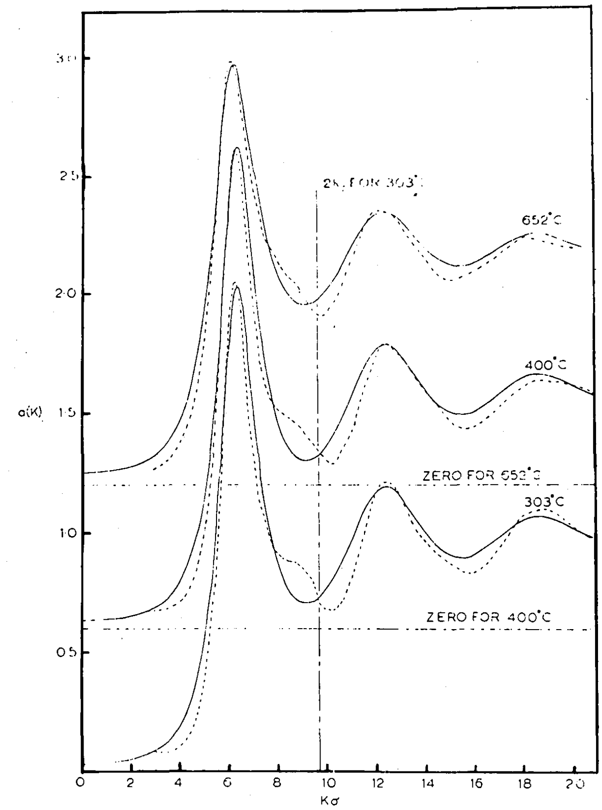

Fig. 7. Experimental and hard sphere a(K) (structure factor) curves. ——Hard sphere a(K) with origin changed.--- Experimental a(K). Note: $2K_f$ does not change much with temperature. (after Isherwood and Orton).

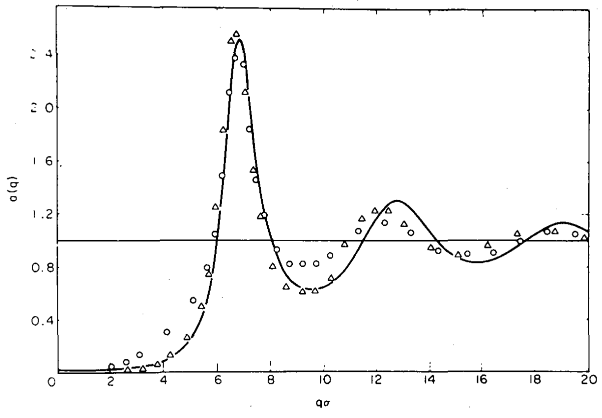

Fig. 8. Interference functions for liquid K (curcles) and Rb (triangles) compared with that predicted by Percus-Yevick hard-sphere theory (full curve). a(q) is structure factor and σ the hard-sphere diameter. (after Ashcroft and Lekner).

shown in **Fig. 8.**

The structure factors for liquid metals can be also clasified into two groups as well as the temperature dependences of viscosity and diffusion; one is normal metals and the other is semi-metals. The subsidiary maximum (shoulder) is a minor structural effect. Consequently, it influences the transport properties, such as viscosity or diffusion.

5. Conclusion

Viscosities and self-diffusivities for pure liquid metals can be estimated in such cases where experimental data is lacking.

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