

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Empirical Relationships between Transport Coefficients of Liquid Metals over a Range of Thermodynamic States

J. Ascough^a; R. G. Chapman^a; N. H. March^a

^a Theoretical Chemistry Department, University of Oxford, Oxford, England

To cite this Article Ascough, J. , Chapman, R. G. and March, N. H.(1988) 'Empirical Relationships between Transport Coefficients of Liquid Metals over a Range of Thermodynamic States', *Physics and Chemistry of Liquids*, 18: 3, 253 – 267

To link to this Article: DOI: 10.1080/00319108808078599

URL: <http://dx.doi.org/10.1080/00319108808078599>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Empirical Relationships between Transport Coefficients of Liquid Metals over a Range of Thermodynamic States

J. ASCOUGH, R. G. CHAPMAN and N. H. MARCH

*Theoretical Chemistry Department, University of Oxford,
South Parks Road, Oxford, OX1 3TG, England.*

(Received 5 April 1988)

Assuming the Wiedemann-Franz law, measured data for electrical conductivity σ of liquid Cs and Rb is converted to λ_e , the electronic contribution to the thermal conductivity λ . While the major part of the measured thermal conduction is thereby accounted for, the "residual" ionic contribution, defined as $(\lambda^{-1} - \lambda_e^{-1})^{-1}$, does not simply increase as the metal-insulator transition is approached along the coexistence curve.

Since λ is dominated by λ_e , it is surprising that a hard sphere model, which predicts $\lambda/\eta = 5k_B/2M$ with η the shear viscosity and M the ionic mass, still gives correctly a relatively constant ratio, though a difference in behaviour of λ/η as a function of thermodynamic state is noted for liquid Rb and Cs compared with liquid argon.

A generalization of Andrade's formula for shear viscosity at the melting point is also discussed, including the work of Zwanzig relating the self-diffusion coefficient D to η via the bulk viscosity.

Key Words: Self diffusion, viscosity, Wiedemann-Franz law.

1 INTRODUCTION

Considerable understanding of electronic transport in simple liquid metals now exists. The object of the present paper is to explore therefore whether microscopic theory of electronic conductivity σ (known to intimately involve the liquid structure factor $S(k)$, the bare ion pseudo-potential v_b , and the dielectric function $\epsilon(k)$ in the region of the triple point), can be utilized to make first-principles predictions of atomic transport in the simple sp liquid metals.

To this end, we have explored therefore, first of all, the thermal conductivity λ of the liquid metal. The Wiedemann-Franz law¹ relates the electronic conductivity σ to the electronic contribution, λ_e say, to the thermal conductivity. The precise relation is

$$\frac{\lambda_e}{\sigma T} = \text{const} = L \quad (1.1)$$

where the Lorenz number L has the theoretical value $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$.

We have therefore, in Section 2 below, first utilized experimental data on σ , which we know can be convincingly interpreted from microscopic theory near the triple point, to calculate λ_e for some sp metals over a range of thermodynamic states. For a few cases, λ_e thus obtained can be brought into contact with direct measurements of the thermal conductivity λ . Though as expected, λ_e is the dominant contribution to λ in the dense metallic fluids under discussion here, the "residual" contribution from the ions shows somewhat surprising features, though, it must be stressed, the deviations of λ_e from λ are quantitatively small.

Attention is then shifted, in Section 3, to the shear viscosity η of simple liquid metals over a similar range of thermodynamic states. Here, the analysis of empirical relationships has been guided by the melting point formula:

$$\eta(T_m) = \text{const } T_m^{1/2} M^{1/2} \rho^{2/3} \quad (1.2)$$

with T_m the melting temperature, M the atomic mass, and ρ the atomic number density (N/V) for N atoms in volume V . To build up confidence in the formula (1.2), which was obtained using Green-Kubo theory of transport, plus an assumption of a well defined Debye frequency in the frequency spectrum of a liquid metal, by Brown and March,² Table 1.1 is reproduced from their work. This shows, with a constant chosen following Andrade,³ whose kinetic theory arguments would not find ready acceptance¹ today, that the quantitative agreement between theory and experiment at the melting temperature is quite remarkable. Therefore, we regard Eq. (1.2) as a further pillar, in addition to Eq. (1.1), in building up quantitatively useful empirical relationships between transport coefficients. The other relation that has motivated the data analysis presented in Section 3 comes from an entirely different (and less physical for simple liquid metals with small ion cores) line of argument, namely a hard sphere model of transport in dense fluids. Here, the work, for example, of Longuet-Higgins and Pople,⁴ following

Table 1.1 Data for the shear viscosity of various metals at their melting temperatures.

Liquid	Exptl. (poise)	Theory (poise) $\alpha(MT_m)^{1/2} \Omega^{-2/3}$
Li	0.0060	0.0056
Na	0.0069	0.0062
K	0.0054	0.0050
Rb	0.0067	0.0062
Cs	0.0069	0.0066
Cu	0.0410	0.0420
Ag	0.0390	0.0410
Au	0.0540	0.0580
In	0.0190	0.0200
Sn	0.0210	0.0210

N.B. M and Ω are respectively atomic mass and volume.

earlier studies by Collins and Raffel,⁵ obtained by Boltzmann transport theory the hard-sphere relationship:

$$\frac{\lambda}{\eta} = \frac{5k_B}{2M} \quad (1.3)$$

with k_B , as usual, denoting Boltzmann's constant. Though Eq. (1.3) is not verified, of course, by experimental data on liquid metals over a range of thermodynamic states since λ is dominated by λ_e , yet it does predict correctly the approximate constancy of λ/η over a range of thermodynamic conditions.

Section 4 is then concerned with the relation between the self-diffusion constant D and the shear viscosity η . It has, in fact, been known for a long time that there is indeed an intimate connection between D and η , which in the early literature is most frequently expressed by the Stokes-Einstein formula

$$\frac{D\eta a}{k_B T} = c \quad (1.4)$$

where a is a molecular diameter while c is a numerical constant.⁶ In their work on Green-Kubo transport theory, Brown and March² found for liquid metals with a well defined Debye edge that, by invoking Lindemann's law of melting, the self-diffusion coefficient D at the melting temperature of simple metals had the form⁷

$$D_m = \frac{\text{constant } T_m^{1/2}}{M^{1/2} \rho^{1/3}}. \quad (1.5)$$

Taking the product of Eqs (1.2) and (1.5), Eq. (1.4) is regained when one utilizes the known constancy of the packing fraction at the melting point of metals. Though Eq. (1.5) was derived by Brown and March² from a physical argument specific to liquid metals with a sharp Debye edge, earlier work by Ascarelli and Paskin⁸ using a modification of Enskog theory applied again to the hard sphere model led back to the form (1.5), with a generalization they proposed away from the melting temperature T_m : see also Section 4 below.

Subsequently, and quite recently, Zwanzig,⁹ using also Green-Kubo formulae and a Debye-like assumption, has proposed a relation between D and η having the form

$$\left(\frac{D\eta}{k_B T}\right)\rho^{-1/3} = 0.0658\left(2 + \frac{\eta}{\eta_l}\right) = C, \quad (1.6)$$

which now involves the ratio η/η_l of shear to longitudinal viscosity. As Zwanzig points out, C , though dependent on η/η_l , can only vary between 0.13 and 0.18. Zwanzig also showed Eq. (1.6) to be consistent with experimental data on the insulating liquids tetramethylsilane at $T = 293$ K and 373 K, and on benzene at $T = 393$ K. As was suggested earlier, taking the product of Eqs (1.2) and (1.5) we obtain

$$D_m \eta_m \alpha \rho_m^{1/3} T_m. \quad (1.7)$$

This equation is, of course, in contrast to Eq. (1.6), specific to the melting point. One of us⁷ has subsequently pointed out that Zwanzig's assumptions closely parallel those made by Brown and March² at the melting point of liquid metals. The prediction (1.6) will therefore be brought into contact with liquid metal transport coefficients in Section 4.

Finally, Section 5 consists of a discussion of the utility of the above formulae for liquid metals, their theoretical basis, as well as a brief summary.

2 ELECTRONIC CONTRIBUTION TO THERMAL CONDUCTIVITY DERIVED USING WIEDEMANN-FRANZ LAW

We have first taken a restrictive set of data for measured electrical conductivity σ at atmospheric pressure.¹⁰ (Calculations have been performed by other workers which theoretically extend this data set—we include these results also.) It must be stated though, that even as the theoretical to experimental error may be of the order of 2% for

Table 2.1a Data for thermal conductivity for liquid Rb.

T/K	$\lambda_{total}^{calc}/W\ m^{-1}\ K^{-1}$	λ_{total}^{exp}	λ_e MaH	λ_e , Eq. (1.1)
312.5	32.7	32.70	—	—
350.0	32.5	32.11	—	—
400.0	31.9	31.31	45.5	33.53
450.0	31.1	30.49	—	—
500.0	30.2	29.66	46.8	32.02
550.0	29.2	28.82	—	—
600.0	28.3	27.96	47.0	30.31
650.0	27.4	27.09	—	—
700.0	26.4	—	46.6	28.61
800.0	24.7	—	46.0	26.96
900.0	22.9	—	44.3	25.30
1000.0	21.2	—	42.2	23.62
1100.0	19.5	—	39.3	21.87
1200.0	17.7	—	35.3	20.19
1300.0	16.0	—	31.2	18.23
1400.0	14.3	—	26.9	16.41
1500.0	12.7	—	23.0	14.64

N.B. λ_e , Eq. (1.1) was calculated assuming L has the value given below Eq. (1.1). MaH denotes Mattheissen approach.

Table 2.1b Data for thermal conductivity of liquid Cs.

T/K	$\lambda_{total}^{calc}/W\ m^{-1}\ K^{-1}$	λ_{total}^{exp}	λ_e MaH	λ_e , Eq. (1.1)
301.7	18.4	18.3	—	—
350.0	18.4	18.3	—	—
400.0	18.4	18.3	25.3	20.25
450.0	18.4	18.3	—	—
500.0	18.3	18.3	27.7	20.68
550.0	18.1	18.4	—	—
600.0	17.9	—	29.7	20.62
650.0	17.5	—	—	—
700.0	17.1	—	30.7	20.24
800.0	16.3	—	31.6	19.62
900.0	15.3	—	31.2	18.83
1000.0	14.3	—	30.4	17.89
1100.0	13.1	—	28.2	16.74
1200.0	11.9	—	25.3	15.43
1300.0	10.2	—	22.2	13.97
1400.0	9.4	—	18.3	12.43
1500.0	8.1	—	14.7	10.89

Data calculated as in Table 2.1a.

measurements up to 700 K, the errors for predictions of σ at temperatures greater than 700 K are not easily determined.

Using Eq. (1.1), we have calculated λ_e at various temperatures shown in Tables 2.1a and b. These data are shown in curves 1 and 3 of Figure 2.1 for Rb and Cs respectively.

If calculation of λ_e from λ_{total} via Mattheissen's Rule is carried out, one obtains curves 5 and 6 of Figure 2.1. The estimate for the ionic contribution was made from the work of Liebfried and Schlomann.¹¹ Their relationship is simply¹¹ $\lambda_i^j = A_0^j (k_B/h)^3 M \Omega^{1/3} \theta_D^3 / (\gamma_G^2 \cdot T)$. A_0 is generally a function of γ_G and hence the superscript refers to different values prescribed for the parameters A_0^j ; M and Ω refer to the atomic mass and volume respectively.

As might be expected, the relationship for the component contributions to the total thermal conductivity is:

$$\frac{1}{\lambda_{\text{total}}} = \sum_j \frac{1}{\lambda_j} \quad (2.1)$$

where j denotes the different mechanisms of scattering. Hence

$$\lambda_e^{-1} = \frac{\lambda_i - \lambda_{\text{total}}}{\lambda_i \lambda_{\text{total}}} \quad (2.2)$$

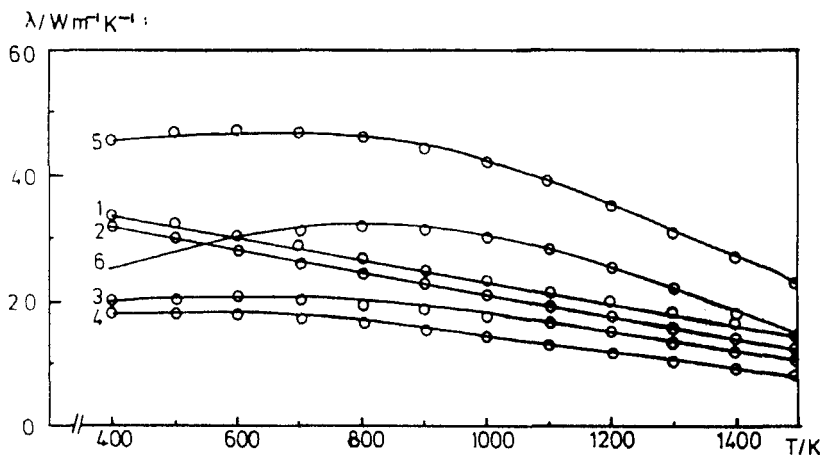


Figure 2.1 Contributions to thermal conductivity λ , in units of $\text{W m}^{-1} \text{K}^{-1}$ as a function of temperature. *Curve 1.* Electronic contribution λ_e for liquid Rb, calculated from Eq. (1.1) using measured electrical conductivity σ as given by Cook *et al.* (Ref. 10). *Curve 2.* Curves of λ_{total} for Rb. *Curve 3.* Same as Curve 1 but for liquid Cs. *Curve 4.* Curves of λ_{total} for Cs. *Curve 5.* λ_e for Rb as calculated via Mattheissen approach. *Curve 6.* λ_e for Cs as calculated via Mattheissen approach.

the subscript i indicating ionic contribution.

This relationship is derived from Mattheissen's Rule which essentially states that for all component scattering processes the inverse total relaxation time equals the sum of the component inverse relaxation times for those scattering processes. Hence, the total resistivity equals the sum of the component resistivities.

The residual ionic contribution, as in Liebfried and Schlomann,¹¹ is estimated by assuming that there is almost a solid-like character to the liquid. This is to say that there is a characteristic vibrational frequency even though the system is disordered.

3 RELATION BETWEEN SHEAR VISCOSITY AND THERMAL CONDUCTIVITY

The next question we shall attempt to answer is whether the hard-sphere formula^{5,6} displayed in Eq. (1.3), though not as it stands appropriate of course, can motivate nevertheless a useful route to estimating η in liquid metals. The data used here can only be treated as relatively close estimates for the ratio λ/η when the states for λ and η are close lying. The ratio itself is only weakly dependent on the thermodynamic state.

The data presented here for the ratio λ/η was obtained by calculating η using the hard-sphere model with comparison (i.e. substitution) of λ from experiment. This data is recorded in Tables 3.1 and 3.2, again for liquid Rb and Cs.

Equation (1.3) is incomplete for metallic liquids and hence it should not be surprising that the figures presented for λ/η are one or two orders of magnitude in disagreement with those of the theoretical prediction—i.e. 1.56×10^2 and 2.43×10^2 for caesium and rubidium respectively. λ_e is (cf. Section 2) the major contributor to λ and it must, we feel, raise the question as to whether a two-component (ions + conduction electrons) model will eventually be required for a full understanding of shear viscosity of simple s-p liquid metals.

Using measured η for Cs in $(\lambda_e/\eta)^{\text{MaH}}$ (MaH—Mattheissen) one obtains values having an order of magnitude of 5 in comparison with theory which predicts 2. Comparing the input of measured data for λ with hard-sphere input for η to plot the curves of λ/η vs. T one observes in Figures 3.1a and b a peak in the range $1000 \text{ K} \leq T \leq 1100 \text{ K}$, and also the curve has roughly the same shape. One might note that for both Rb and Cs T_{max} is approximately 1020 K which might imply T_{max} is a characteristic temperature for the two alkalis and, perhaps, for the group. Further work will be needed to see if this is verified.

Table 3.1 Measured shear viscosity η for Rb and Cs.

<i>Shear viscosity of Rb:</i> ¹²			
<i>T/K</i>	<i>η/cP</i>		
311	0.6734		
312	0.6713		
313	0.6630		
318	0.6441		
323	0.6258		
372.7	0.4844		
413.5	0.4133		
452.0	0.3634		
493.1	0.3234		
<i>Shear viscosity for Cs:</i> ¹³			
<i>T/K</i>	<i>Visc/mP</i>	<i>T/K</i>	<i>Visc/mP</i>
408	3.87	1171	1.41
489	3.05	1230	1.34
505	2.87	1297	1.25
593	2.48	1378	1.20
693	2.12	1456	1.15
770	1.86	1470	1.12
829	1.80	1581	1.02
798	1.86	1621	0.97
918	1.59	1673	0.93
1008	1.53	1745	0.91
1088	1.41	1783	0.87
1063	1.54	1828	0.83
		1878	0.79

The condition for the maximum to occur is:

$$\frac{d \ln \eta}{dT} = \frac{d \ln \lambda}{dT} \quad (3.1)$$

which may give a route to evaluating T_{\max} . We note the following estimates:*

$$\left. \frac{d \ln \eta}{dT} \right|_{T=1020\text{K}} \approx (1390\text{K})^{-1}, \quad \left. \frac{d \ln \lambda}{dT} \right|_{T=1020\text{K}} \approx (1130\text{K})^{-1} \quad (3.2)$$

For $1000\text{K} \leq T \leq 1100\text{K}$, $d \ln \eta/dT \approx \text{const}$ but $d \ln \lambda/dT$ is not. The curvature of the plot of $\ln \lambda$ vs. T is variable over this range and hence

* Given Eq. (1.1), $\frac{d \ln \lambda}{dT} = \frac{1}{T} + \frac{d \ln \sigma}{dT} \sim \frac{1}{T}$.

Table 3.2 Ratio of thermal conductivity λ to shear viscosity η for heavy liquid alkalis.

<i>Rubidium</i>		
T/K	$\rho/\text{kg m}^{-3}$	$\frac{\lambda}{\eta} \times 10^4/\text{kg}^{-1} \text{JK}^{-1}$
400	1451.99	1.10
500	1411.40	1.13
600	1370.19	1.15
700	1328.31	1.19
800	1285.68	1.23
900	1242.20	1.25
1000	1197.75	1.27
1100	1152.15	1.27
1200	1105.14	1.25
1300	1056.41	1.21
1400	1005.48	1.17
1500	751.74	1.12
<i>Caesium</i>		
T/K	$\rho/\text{kg m}^{-3}$	$\frac{\lambda}{\eta} \times 10^3/\text{kg}^{-1} \text{JK}^{-1}$
400	1791.28	5.38
500	1738.36	5.93
600	1684.70	6.54
700	1630.23	7.16
800	1574.84	7.76
900	1518.40	8.14
1000	1460.70	8.49
1100	1401.49	8.39
1200	1346.41	8.18
1300	1277.00	7.86
1400	1210.68	7.19
1500	1140.52	6.52

N.B. Pressure is taken as ~ 10 MPa.

the gradients may match for this temperature interval. This is in contrast to λ/η versus T for the insulating liquid argon,^{14,15} shown in Figure 3.2: see also Table 3.3.

4 STOKES-EINSTEIN RELATION AND ZWANZIG'S GENERALIZATION

Bearing on the above comment about a two-component model of liquid metals, it should occasion no surprise that, when considering the self-diffusion coefficient D of the ions in a liquid metal, one should have in

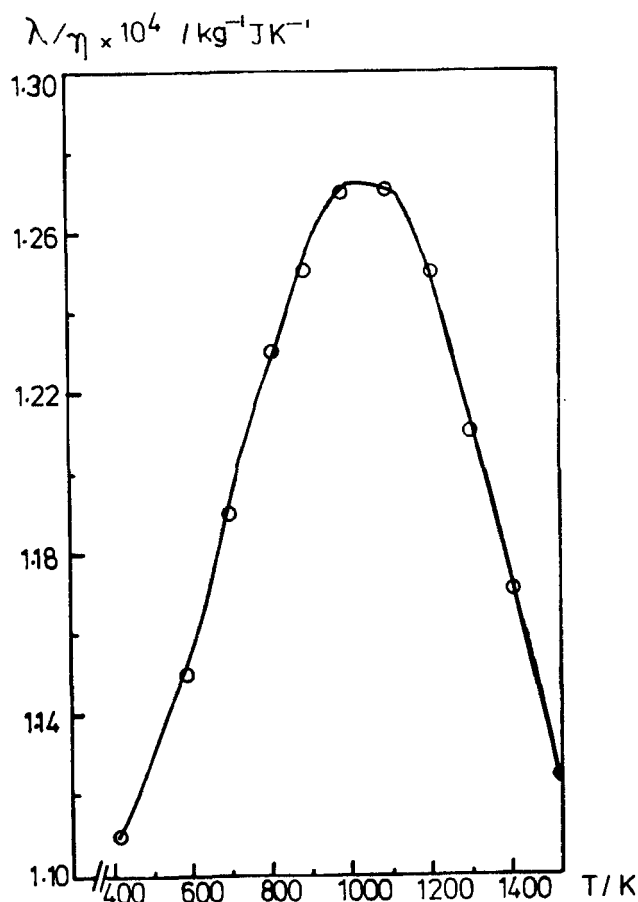


Figure 3.1a Ratio of thermal conductivity λ to shear viscosity η for liquid Rb, versus temperature T . While measured data is employed for λ , the shear viscosity does not appear to have been measured over an equivalent temperature range. Hence η used in constructing this plot has been calculated from model of Paskin and Ascarelli.⁸ Note that while $\lambda/\eta \sim 1.2 \times 10^4 \text{ kg}^{-1} \text{ JK}^{-1}$, there is evidence for a maximum around $T \sim 1000 \text{ K}$, in marked contrast to the behaviour for liquid argon shown in Figure 3.2 below.

mind a picture of an ion “carrying around its own screening cloud,” but, of course, diffusion occurring in interaction with the other screened ions via forces which are mediated by the electrons. Notwithstanding such a picture, the work of Brown and March² already demonstrated a type of Stokes–Einstein relationship between D and η at the melting point of metals.

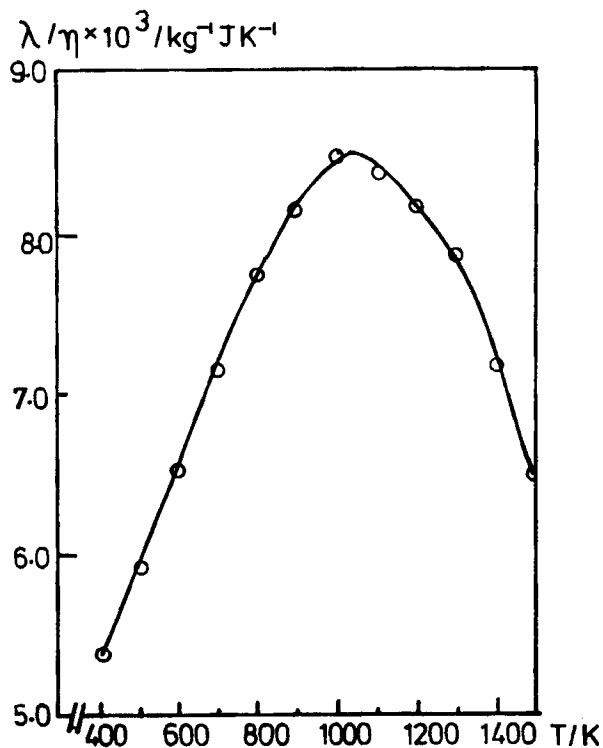


Figure 3.1b Same as Figure 3.1a but for liquid Cs.

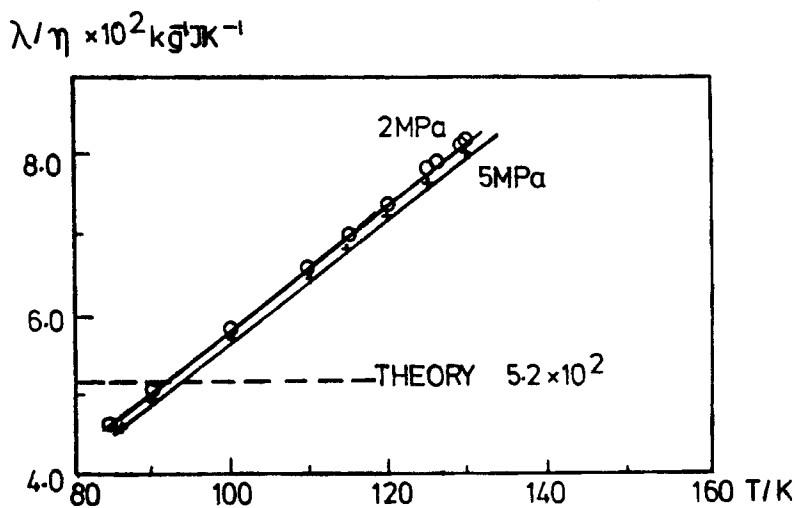


Figure 3.2 λ/η versus T for liquid argon, following Janaf tables.¹⁴

Table 3.3 Shear viscosity and thermal conductivity of liquid argon¹⁴.

2 MPa			
T/K	$\eta \times 10^{-6}/\text{Pa.s}$	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	$\frac{\lambda}{\eta} \times 10^2/\text{kg}^{-1} \text{ JK}^{-1}$
84.280	290.0	0.1350	4.655
90.000	245.0	0.1250	5.102
100.000	187.0	0.1100	5.882
110.000	146.0	0.0969	6.637
115.000	129.0	0.0908	7.039
120.000	114.0	0.0847	7.430
125.000	99.9	0.0785	7.858
126.000	97.2	0.0772	7.942
128.000	91.9	0.0746	8.118
129.714	87.2	0.0721	8.268
5 MPa			
T/K	$\eta \times 10^{-6}/\text{Pa.s}$	$\lambda/W \text{ m}^{-1} \text{ K}^{-1}$	$\frac{\lambda}{\eta} \times 10^2/\text{kg}^{-1} \text{ JK}^{-1}$
85.62	292.0	0.1350	4.673
90.00	253.0	0.1270	5.020
100.00	194.0	0.1120	5.773
110.00	152.0	0.0992	6.533
115.00	136.0	0.0935	6.875
120.00	121.0	0.0877	7.248
125.00	107.0	0.0820	7.664
130.00	95.0	0.0762	8.021
135.00	83.0	0.0702	8.458
136.00	81.1	0.0690	8.508
138.00	76.5	0.0665	8.693
140.00	72.0	0.0639	8.875
142.00	67.3	0.0614	9.123

Here, our main concern is with the generalization (1.6) proposed by Zwanzig. Unfortunately there is still very little known about the bulk viscosity η_v of liquid metals, related to the longitudinal viscosity η_l in Eq. (1.6) by

$$\eta_l = \frac{4\eta}{3} + \eta_v. \quad (4.1)$$

Zwanzig refers to $\eta_v = \eta/3$ as "typical," to get $C = 0.171$ in Eq. (1.6). Of course, it may well be that η/η_l varies with thermodynamic state in practice. The data shown in Table 4.1 is itself comparable with experiment, e.g., D_{melting} for Rb is approximately 2.7×10^{-5} , at least as

Table 4.1 Self-diffusion coefficient D for liquid Rb and Cs.

Rubidium (Rb)		
T/K	$\rho/\text{kg m}^{-3}$	$D (10^{-4} \text{ cm}^2 \text{ s}^{-1})$
500	0.1411	0.1962
600	0.1370	0.2873
700	0.1328	0.3898
800	0.1286	0.5020
Caesium (Cs)		
T/K	$\rho/\text{kg m}^{-3}$	$D (10^{-4} \text{ cm}^2 \text{ s}^{-1})$
500	0.1738	0.1722
600	0.1685	0.2544
700	0.1630	0.3466
800	0.1571	0.4467

regards magnitude. It seems that Zwanzig's model is reasonably good at predicting, at least, the magnitude of D (see Figure 4.1 also). From this data it is difficult to predict what the best value of η/η_i might be.

Evidently, diffusion in a metal is involving electron screening of ions, relating to the strength of electron-ion interaction, which is intimately involved already in the microscopic theory of electrical conductivity. The outstanding question here is whether the generalization of the Stokes-Einstein relation does, in fact, involve, in a significant quantitative way, the bulk viscosity η_v . This is involved in interpreting sound-wave attenuation: an area clearly worthy of further study in the present context.

5 DISCUSSION AND SUMMARY

It seems natural at this point to return to Eqs (1.1)–(1.6) set out in the Introduction. The question of the fundamental validity of the Wiedemann-Franz law (1.1) has recently been reopened by Castellani *et al.*,¹⁶ following earlier work by Langer.¹⁷ The work of Castellani *et al.* considers the theory of thermal conductivity of disordered interacting systems, the crucial input being the validity of Fermi-liquid theory. Given that, Castellani *et al.* demonstrate the continuing validity of the law (1.1) in such systems over a range of thermodynamic states wide

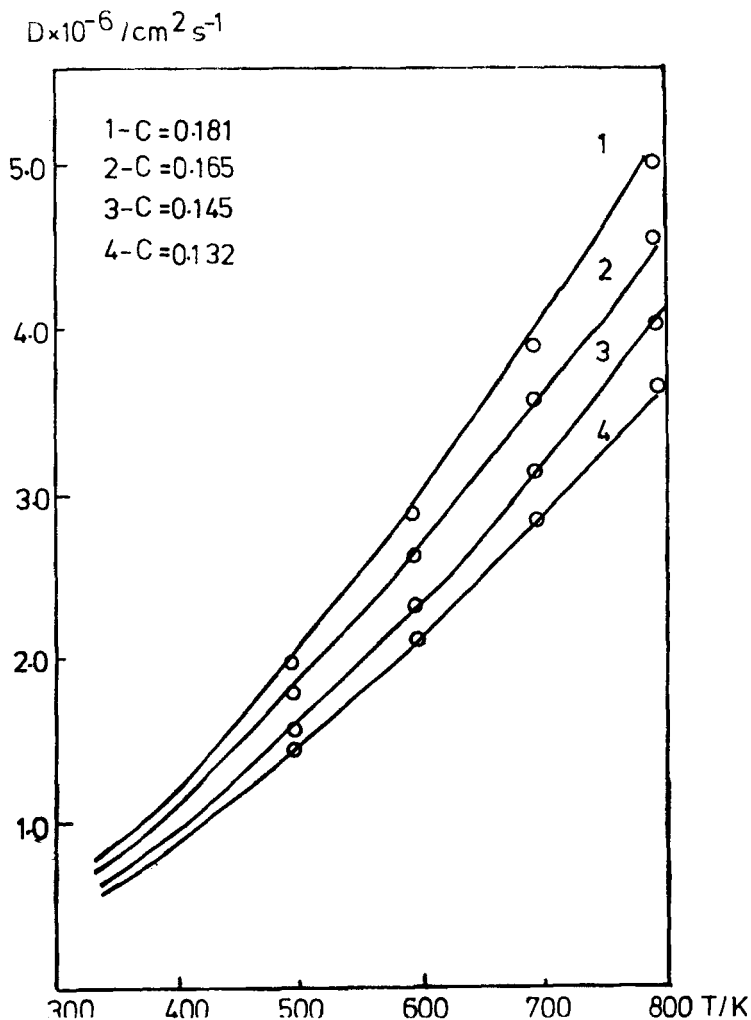


Figure 4.1 Shows self-diffusion coefficient D versus T for liquid Rb. Various curves were calculated from Zwanzig formula (1.6). However, different curves correspond to different choices of "constant" C which is dependent on bulk viscosity. In constructing these curves, other input was a theoretical estimate of shear viscosity η from work of Paskin and Ascarelli.⁸

enough to embrace the metal-insulator transition. However, this assumption of a Fermi liquid, as Chapman and March¹⁸ have recently pointed out with specific reference to expanded fluid Cs, is too restrictive for such a liquid metal. Their work demonstrates, on the coexistence curve and towards the metal-insulator transition, a cross-

over in the magnetic susceptibility from Fermi liquid-like behaviour to a Curie law regime. This does not necessarily deny the importance of the arguments of Castellani *et al.* for the validity of Eq. (1.1) over quite a wide range of thermodynamic states of liquid metals. Nevertheless, we consider, with Langer,¹⁷ that there is a real possibility, though perhaps under the rather extreme conditions met on approaching the metal-insulator transition, that mean free path effects will eventually influence σ and λ in rather different ways. Finally, with reference to the metal-insulator transition, and because of the technological importance of liquid Na as a reactor coolant, it would be of great interest to have data such as given in Ref. 19 extended over the widest possible range of thermodynamic states for other alkalis than Rb and Cs.

Acknowledgement

J. Ascough and R. G. Chapman wish to acknowledge the awards of SERC postgraduate studentships throughout the course of this work.

References

1. See, for example, T. E. Faber, Introduction to the theory of liquid metals (Cambridge: University Press), 1972.
2. R. C. Brown and N. H. March, *Phys. Chem. Liquids*, **1**, 141 (1968).
3. E. N. da C. Andrade, *Phil. Mag.*, **17**, 497 (1934).
4. H. C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.*, **25**, 884 (1956).
5. F. C. Collins and H. Raffel, *J. Chem. Phys.*, **22**, 1728 (1954).
6. See, for instance, the review by H. J. Parkhurst and J. Jonas, *J. Chem. Phys.*, **63**, 2698, 2705 (1975).
7. N. H. March, *J. Chem. Phys.*, **80**, 5345 (1984).
8. P. Ascarelli and A. Paskin, *Phys. Rev.*, **165**, 222 (1968).
9. R. Zwanzig, *J. Chem. Phys.*, **79**, 4507 (1983).
10. J. G. Cook, M. P. van der Meer and D. J. Brown, *Can. J. Phys.*, **60**, 1311, 1759 (1982).
11. G. Liebfried and H. Schlomann, *Nachr. Acad. Wiss. Gottingen, Math. Phys. Klasse.*, **4C**, 171 (1954).
12. Landolt-Bornstein, *Zahlenwerk und Funktionen 5 Tiel.*, Springer, Berlin, 122 (1965).
13. H. C. Tsai, *High Temp. S*, **6-7**, 142 (1974).
14. J. Janaf, *J. Phys. Chem. Ref. Data*, **11**, Suppl. 1 (1982).
15. See also D. M. Heyes, *Can. J. Phys.*, **64**, 773 (1986) for molecular dynamics calculations of η and λ in insulating Lennard-Jones liquids.
16. C. Castellani, C. DiCastro, G. Kotliar, P. A. Lee and G. Strinati, *Phys. Rev. Lett.*, **59**, 477 (1987).
17. J. S. Langer, *Phys. Rev.*, **128**, 110 (1962).
18. R. G. Chapman and N. H. March, *Phys. Rev. B*, in press. (1988).
19. Handbook of Thermodynamic and Transport Properties of Alkali Metals, Cook and Fritsch, Section 7.2, IUPAC, Blackwell Scientific Publications. Ed. W. H. Ohse (1985).