J. Plasma Physics (1997), *vol.* 57, *part* 1, *pp.* 121–127

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Thermal conduction in strongly coupled plasmas: especially liquid alkali metals

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(Received 4 April 1996)

In earlier work, we have noted on semi-empirical grounds that the electrical conductivity σ in strongly coupled plasmas can be written as a linear form $\sigma = \sigma_0 \Gamma$ in terms of the usual plasma coupling parameter Γ. Here, this is combined with the Wiedemann–Franz law to yield a zeroth-order treatment of thermal conductivity κ in such strongly coupled plasmas. Some refinement is needed to explain the properties of the heavier liquid alkali metals beginning with Na. This refinement follows from the nearly free-electron theory of electrical resistivity $\rho = \sigma^{-1}$. Finally, a relation is forged between ρ, κ and the shear viscosity η at the freezing point of liquid alkali metals.

1. Introduction

In his early work Professor David Montgomery was intimately concerned with dynamical structure in fluids: a major theme of our present study. Thus in 1969 he was already working on the problem of calculating distribution function autocorrelations for a monatomic fluid, in which a generalized BBGKY hierarchy was used (Montgomery 1969) and the relationship with the Boltzmann equation was established. This was followed by a study of Brownian motion from Boltzmann's equation (Montgomery 1971*a*). Among his early papers was the use of the Kubo formula (compare (14) below) to evaluate the bulk electrical conductivity of a magnetized two-dimensional plasma (Montgomery 1971*b*), this work being later generalized with Tappert to treat three-dimensional plasma problems (Montgomery and Tappert 1972).

The aim of the present study is to present a semi-empirical analysis of the thermal conductivity κ in strongly coupled plasmas. The resulting formula for κ will then be confronted with experimental data (Barasoni *et al.* 1968; see also Sittig 1956) on the heavier liquid alkali metals beginning with Na.

For insulating liquids, the thermal conductivity κ is strongly correlated with the shear viscosity η. The motivation for such a relation in insulators is afforded by studies on a dense hard-sphere liquid (Collins and Raffel 1954; Longuet-Higgins and Pople 1956). This leads to the relationship $\kappa/\eta = 5k_B/2M$, with M the atomic mass. However, when κ/η is plotted versus temperature T for liquid argon, variation of κ/η by a factor of about 2 occurs over a temperature range from 85 to 130 K (Ascough *et al.* 1988). The order of magnitude of the ratio is given correctly by the dense hard-sphere liquid model. Of course, it is well

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https://doi.org/10.1017/S0022377896005223 Published online by Cambridge University Press

known that in liquid metals, the thermal conductivity κ is dominated by the electrons. One of us (Tosi 1992) has, in contrast, shown that for the liquid alkali metals the longitudinal viscosity $\frac{4}{3}\eta+\zeta$, with ζ the bulk viscosity, is dominated by the bare ion–ion interaction within a strongly coupled electron–ion plasma model, electronic scattering providing a 'correction' that is, at most, about 10 %. Furthermore, the theory indicates that the bulk viscosity ζ is an order of magnitude smaller than the shear viscosity η. Nevertheless, as pointed out by Ascough *et al.* (1988), there is still a correlation between thermal conductivity κ and shear viscosity η in liquid alkali metals, and this aspect will therefore also be considered below.

The mainly electronic origin of thermal transport in liquid metals underlies the Wiedemann–Franz law, asserting constancy of the ratio $\kappa/\sigma T$, with σ the electrical conductivity (see e.g. March 1990). The validity of this law does not depend upon specific assumptions about the shape of the Fermi surface, the density of electron states, the nature of the scattering potential or the inclusion of electron–electron interactions via a Fermi liquid model, but only involves the general assumption that the scattering is elastic. This assumption is well justified for liquid metals. We turn immediately to the use of the Wiedemann–Franz law to estimate the thermal conductivity κ in strongly coupled plasmas.

2. Estimate of thermal conductivity in strongly coupled plasmas

In recent work we have studied the scaling of electrical conductivity σ in strongly coupled plasmas, with reference especially to experiments on Cu plasmas (DeSilva and Kunze 1994) and to expanded liquid alkali metals (see e.g. Winter *et al.* 1994). For such monovalent assemblies, the ionic plasma coupling parameter Γ defined by

$$\Gamma = \frac{e^2}{ak_B T}, \tag{1}$$

with a the mean interparticle separation, was found to play a major role. In particular, it was found semi-empirically that the electrical conductivity for large Γ ($\Gamma > 10$) took the linear form

$$\sigma = \sigma_0 \Gamma. \tag{2}$$

Equation (2), with σ_0 a system-dependent empirical constant, describes the dependence of the electrical conductivity on the thermodynamic state over wide ranges of density and temperature.

Here, we shall first combine (2) with the Wiedemann–Franz law, which relates σ to the thermal conductivity κ via

$$\frac{\kappa}{\sigma T} = L, \tag{3}$$

with L the so-called Lorenz number. Theory for free electrons in the quantal regime yields $L = \pi^2 k_B^2/3e^2 = 2.45\times10^{-8}\,\mathrm{J^2\,C^{-2}\,K^{-2}}$, and the measured values of

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L for a number of liquid metals agree with this theoretical value within $\pm 10\,\%$ (see e.g. March 1990). Noting from (1) and (2) that the product σT appearing in (3) can be written as

$$\sigma T = \frac{\sigma_0 e^2}{a k_B}, \tag{4}$$

one arrives at a 'zeroth-order' approximation to the thermal conductivity κ of a strongly coupled plasma as

$$\kappa = \frac{L e^2 \sigma_0}{k_B a}. \tag{5}$$

We turn to confront this semi-empirical prediction (5) for strongly coupled plasmas with data from experiment and from microscopic theory on the heavier liquid alkali metals at constant density.

3. Data from experiment and from microscopic theory on liquid alkali metals, especially Na to Cs

In Fig. 1 we reproduce data on electrical resistivity ρ at constant density taken from the experimental work of Endo (1963) and Lien and Sivertsen (1969) and from the Bhatia–Krishnan–Ziman nearly free-electron theory as applied to these liquid alkali metals by Pastore *et al.* (1981).

As is clear from the experimental data in Fig. 1, the electrical resistivity is almost linear in temperature T over the range of the measurements, in support of the form of σ given by (2) and (1). This prompts us to write $\rho = \sigma^{-1}$ in terms of properties at the melting temperature T_m, namely

$$\rho(T) = \frac{\rho_m T}{T_m}, \tag{6}$$

where $\rho_m = \rho(T_m)$ is the electrical resistivity at the melting temperature.

We next note that from microscopic theory, initiated by Krishnan and Bhatia (1945) and brought to full fruition using pseudopotentials by Ziman (1961),

$$\rho(T) = \frac{12\pi m^2}{\hbar^3 n e^2 k_F^2} \int_0^1 |V_{ei}(k)|^2 S(k) \left(\frac{k}{2k_F}\right)^3 d\left(\frac{k}{2k_F}\right), \tag{7}$$

with n the electron density and k_F the Fermi wavenumber. The microscopic formula (7) of the nearly free electron (NFE) theory involves knowledge not only of the structure factor $S(k)$ but also of the electron–ion scattering matrix element $V_{ei}(k)$. In Fig. 1 the continuous curves show that the NFE theory is in excellent agreement with experiment over the temperature range of the measurements. However, over a wider range of temperature it is clear from the microscopic theory that the temperature coefficient of ρ/T is negative, and hence it follows from the Wiedemann–Franz law (3) that the temperature coefficient of κ is positive, in agreement with experiments on liquid Na (Sittig 1956).

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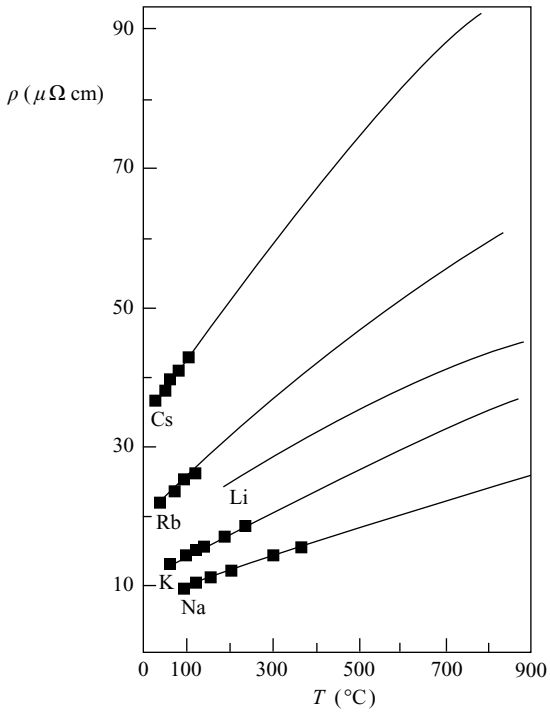


Figure 1. Electrical resistivity ρ of liquid alkali metals versus temperature T at constant density. The squares are experimental data from Endo (1963) and Lien and Sivertsen (1969). The lines are the results of NFE theory. From Pastore *et al.* (1981).

4. Relation between transport coefficients κ, ρ and η at freezing temperature of liquid alkali metals

Let us return in this section to the relation of thermal conductivity κ to shear viscosity η. The early work of Andrade (1934) (see also Faber 1972) gave the viscosity at the melting temperature T_m of liquid metals as ($\eta(T_m) \equiv \eta_m$)

$$\eta_m = 5.1 \times 10^{-4} (MT_m)^{1/2} n^{2/3} \text{ poise}$$
$$\equiv A(MT_m)^{1/2} n^{2/3}. \tag{8}$$

Whereas the kinetic arguments of Andrade were considered by Faber (1972) to be oversimplified, Brown and March (1968) gave an approximate argument from Green–Kubo formulae (see e.g. March and Tosi 1976) leading to (8). Using the value of A as given by Andrade in (8), his formula is compared with experiment in the first two rows of Table 1, for liquid alkali metals at freezing. The agreement is seen to be quantitative.

4.1. Ion–electron plasma theory of (longitudinal) viscosity of liquid alkali metals

In the present context, it is highly relevant to emphasize the recent work of one of us, in which the so-called longitudinal viscosity $\eta_l = \frac{4}{3}\eta + \zeta$, with ζ the bulk viscosity, has been evaluated for the liquid alkali metals using an ion–electron plasma approach.

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Table 1. Shear viscosities of liquid alkali metals at freezing (in centipoise).

	Li	Na	K	Rb	Cs
Experiment	0.60	0.69	0.54	0.67	0.69
Equation (8)[a]	0.56	0.62	0.50	0.62	0.66
Equation (14)[b]	0.56	0.64	0.54	0.55	0.56

[a] Calculated with Andrade's coefficient.
[b] Values of $\eta+\frac{3}{4}\zeta$, where η is shear and ζ is bulk viscosity as in the text.

The starting point is afforded by the work of Postogna and Tosi (1980), who treat a liquid alkali metal as a classical monovalent ionic plasma embedded in the fluid of conduction electrons. Under the assumption of weak electron–ion interactions, but to all orders in the ion–ion and electron–electron interactions, the dynamic response function $\chi(k,\omega)$ of mass-density fluctuations in the absence of coupling to energy fluctuations (i.e. neglecting the damping due to thermal conductivity as a lower-order effect), with k the wavenumber and ω the angular frequency, takes the form

$$\chi(k,\omega)=\frac{\chi_0(k,\omega)}{1-v(k,\omega)\,\chi_0(k,\omega)}. \tag{9}$$

In (9), $\chi_0(k,\omega)$ is the corresponding function of the one-component classical plasma (OCP), while $v(k,\omega)$ is the indirect ion–ion interaction involving screening by the conduction electrons. This is given by (Tosi 1992)

$$v(k,\omega)=\frac{k^2v^2(k)}{4\pi e^2}\left[\frac{1}{\epsilon(k,\omega)}-1\right], \tag{10}$$

where $v(k)$ is the bare electron–ion pseudopotential, which, when statically screened to yield the effective electron–ion interaction with due account of exchange and correlation, enters the NFE formula (7) for the electrical resistivity ρ.

Tosi (1992) adopts the following form for the electronic dielectric function in (10):

$$\epsilon(k,\omega)=1-\frac{\omega_p^2}{\omega^2-s_e^2\,k^2+i\omega k^2\Lambda}, \tag{11}$$

with ω_p the electronic plasma frequency and $s_e=\omega_p/k_e$, k_e being the inverse screening length of the interacting electron gas, which in turn is related to its compressibility. The form assumed in (11) for the damping term is applicable under the condition $kl_e\ll 1$ for the electronic mean free path, as obtains in sound-wave propagation experiments in liquid metals. The expression for the coefficient Λ in (11) for free electrons is

$$\Lambda=\tfrac{4}{15}v_F\,l_e, \tag{12}$$

where v_F is the Fermi velocity.

In the appropriate regime of long wavelength and low frequency, the density response function of the OCP is (Postogna and Tosi 1980)

$$\chi_0(k,\omega)=\frac{nk^2}{M}\left[\omega^2-\Omega^2\left(1+\frac{k^2}{k_i^2}\right)+i\omega k^2 f_i\right]^{-1}. \tag{13}$$

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Here, as usual, n is the number density, $\Omega = (4\pi ne^2/M)^{1/2}$ is the ionic plasma frequency, k_i is the inverse screening length of the OCP and f_i is a friction coefficient characteristic of the OCP model. The Green–Kubo limit then yields for the longitudinal viscosity η_l

$$\eta_l = -M^2 \lim_{\omega\to 0}\left[\omega^3 \lim_{k\to 0} k^{-4}\,\mathrm{Im}\,\chi(k,\omega)\right]$$
$$= nMf_i + \tfrac{4}{15}nmv_F\, l_e, \tag{14}$$

this result being appropriate for the monovalent liquid alkali metals. Tosi points out that the electronic contribution represents a small correction only to the ionic (first) term on the right-hand side of (14). If one scales ωk^2 multiplying f_i in (13) by Ω/a^2, with a the mean interparticle separation, then $f_i\,\Omega/a^2$ is a function of the coupling parameter Γ in (1).

From (14), with $\eta_l = \frac{4}{3}\eta + \zeta$ and $\zeta \ll \frac{4}{3}\eta$, $\eta \approx \eta_l$ and Tosi's values for η near the freezing points of the five liquid alkali metals are recorded in the third row of Table 1. In essence, they lend support to the formula (8) as an (of course) approximate consequence of an ion–electron plasma model. Equation (8), as already noted, gives a quantitative account of the experimental data.

Thus we can proceed with some confidence to utilize (8) in the approximate formula (6), valid near the freezing temperature T_m, to find

$$\rho(T) = A^2 M n^{4/3}\frac{\rho_m}{\eta_m^2}\,T. \tag{15}$$

Returning to the Wiedemann–Franz law (3), we find for the thermal conductivity κ the approximate form

$$\kappa_m = \frac{L\eta_m^2}{A^2\rho_m M n^{4/3}}, \tag{16}$$

which, in particular, relates the three transport coefficients κ_m, ρ_m and η_m at the freezing temperature T_m to the ionic mass and number density, the constants L and A in (16) being known.

5. Summary and future directions

For strongly coupled plasmas, and especially for the liquid alkali metals, (5) should yield directly the order of magnitude of the thermal conductivity κ. However, as it stands, any temperature dependence (very small over the current range of experiments on the liquid alkali metals) would arise from the increase of the mean interparticle separation a with increasing temperature. But experiments show that the temperature dependence of κ is positive for liquid Na (and also for liquid Ga), and this has been related to the temperature dependence of ρ/T following at constant density from the NFE microscopic formula (7) for the alkali metals evident in Fig. 1.

As to the relation of κ and the shear viscosity η for liquid alkali metals, near the freezing temperature T_m one has the formula (16), which relates the three transport coefficients κ, ρ and η at $T = T_m$. Of course, η is more strongly dependent on temperature than either κ or ρ, so it must not be expected that (16) will apply away from T_m.

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Further experiments over a wider range of thermodynamic states than presently available would clearly be of interest, and should point the way in which refinements of the present semi-empirical approach can be effected.

Acknowledgements

One of us (N.H.M.) wishes to thank the Scuola Normale Superiore for its generous hospitality during his visit, in which his contribution to this work was brought to fruition. He also acknowledges partial financial support from the EC Network on 'High energy density matter', coordinated by Professor J. M. Martinez-Val (Madrid).

References

Andrade, E. N. da C. 1934 *Phil. Mag.* **17**, 497.

Ascough, J. A., Chapman, R. G. and March, N. H. 1988 *Phys. Chem. Liq.* **18**, 253.

Barasoni, M., Williams, R. K. and McElroy, D. L. 1968 *Proc. 7th Conference on Thermal Conductivity* (ed. B. A.Peary and R. Flynn), p. 279. NBS Spec. Publ. 302, Gaithersburg, MD.

Brown, R. C. and March, N. H. 1968 *Phys. Chem. Liq.* **1**, 141.

Collins, F. C. and Raffel, H. 1954 *J. Chem. Phys.* **22**, 1728.

DeSilva, A. W. and Kunze, H.-J. 1994 *Phys. Rev.* **E49**, 4448.

Endo, H. 1963 *Phil. Mag.* **8**, 1403.

Faber, T. E. 1972 *An Introduction to the Theory of Liquid Metals*. Cambridge University Press.

Krishnan, K. S. and Bhatia, A. B. 1945 *Nature* **156**, 503.

Lien, S. Y. and Sivertsen, J. M. 1969 *Phil. Mag.* **20**, 759.

Longuet-Higgins, H. C. and Pople, J. A. 1956 *J. Chem. Phys.* **25**, 884.

March, N. H. 1990 *Liquid Metals: Concepts and Theory*. Cambridge University Press.

March, N. H. and Tosi, M. P. 1976 *Atomic Dynamics in Liquids*. Macmillan, London.

March, N. H. and Tosi, M. P. 1994 *Phys. Chem. Liq.* **29**, 273.

Montgomery, D. 1969 *Phys. Fluids* **12**, 804.

Montgomery, D. 1971*a* *Phys. Fluids* **14**, 2088.

Montgomery, D. 1971*b* *Phys. Rev. Lett.* **27**, 419.

Montgomery, D. and Tappert, F. 1972 *Phys. Fluids* **15**, 815.

Pastore, G., Senatore, G. and Tosi, M. P. 1981 *Physica* **111B**, 283.

Postogna, F. and Tosi, M. P. 1980 *Nuovo Cim.* **55B**, 399.

Sittig, M. 1956 *Sodium: Its Manufacture, Properties and Uses*. American Chemical Society Monograph Series, Reinhold, New York.

Tosi, M. P. 1992 *Nuovo Cim.* **14D**, 559.

Winter, R., Pilgrim, W. C. and Hensel, F. 1994 *J. Phys.: Condens. Matter* **6**, A245.

Ziman, J. M. 1961 *Phil. Mag.* **6**, 1013.

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