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### Theoretical Approaches to Thermal Conductivity in Liquids

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## *Review*

# THEORETICAL APPROACHES TO THERMAL CONDUCTIVITY IN LIQUIDS

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We first review analytical and computer modelling approaches to heat conduction in insulating liquids. Thermal conductivity  $\lambda$  can be calculated by approximate analytic theory, and also by molecular simulation which solves the many-body problem for molecules interacting through specific interactions. Equilibrium and non-equilibrium molecular dynamics, NEMD, techniques are now available that enable  $\lambda$  to be computed for single-component monatomic and molecular liquids, as well as their mixtures. For mixtures,  $\lambda$  can be determined from the distinct Onsager coefficients, individually computed using equilibrium molecular dynamics. Electronic contributions to the thermal conductivity of liquid metals are then considered, by invoking the Wiedemann-Franz Law relating thermal and electrical transport.

## 1. INTRODUCTION

Of all the transport coefficients in condensed matter, the thermal conductivity has a number of notable features that distinguish it from the others, such as, self-diffusion and viscosity. Unlike these other two, the thermal conductivity does not exhibit any major discontinuity at the liquid solid phase boundary. Also, in contrast, there can be a substantial electronic contribution in the case of metallic systems (see section 4 below). The thermal conductivity is defined (in the linear response limit) by Fourier's law,

$$\underline{J}_Q(\underline{r}, t) = -\underline{\lambda} \cdot \underline{\nabla} T(\underline{r}, t) \quad (1)$$

where  $\underline{J}_Q$  is the local flux  $\underline{J}_Q$  and  $\underline{\nabla}T$  is the corresponding temperature gradient. Strictly,  $\underline{\lambda}$  is a second rank tensor, which is important when considering anisotropic solids and liquids (*e. g.*, liquid crystals). Here however, we will confine our discussion to liquids which over time have no preferred direction for the molecules, so-called 'isotropic' liquids. In this case, the thermal conductivity is a scalar,  $\lambda$ .

Accurate theoretical predictions of transport coefficients are still lacking; no convergent perturbation theory of transport coefficients has emerged, and currently we rely to a large extent on computer simulation methods although the transport coefficients do appear to obey a corresponding states behaviour which correlates reasonably well with the excess entropy of the liquid<sup>1</sup>.) The heat flux, and hence the thermal conductivity, has components that are purely kinetic and those that represent energy transfer by virtue of the interaction forces, and are definable solely in terms of the microscopic details of the molecular coordinates, velocities and the force field between them. Molecular Dynamics, MD, computer simulation solves the many-body problem for a representative region of the liquid by numerical integration of the equations of motion of the interacting molecules, and can be used to calculate the heat flux by employing appropriate microscopic expressions. The MD technique has been used to calculate the thermal conductivity of a range of model molecular systems. This has proved to be more complicated than for other transport coefficients, and for mixtures it is only recently that a consensus is emerging about the correct formulae to employ as microscopic definitions for the relevant fluxes. In this section, the progress that has been made at computing the thermal conductivity of single component and liquid mixtures by Molecular Dynamics computer simulation is reviewed. We will first consider single component monatomic and molecular liquids. Then applications to mixtures of monatomic liquids will be discussed.

## 2. MOLECULAR DYNAMICS

Two classes of Molecular Dynamics, MD, method have been proposed to compute the thermal conductivity for an arbitrary molecular system, specified solely in terms of the pair potentials and imposed

thermodynamic conditions. The approaches that can be adopted are to use either equilibrium Molecular Dynamics, in which the molecules are free to interact in the absence of any perturbing field (*e.g.*, temperature gradient). The other approach is to use a non-equilibrium Molecular Dynamics (NEMD) method, which is closer in spirit to the machine implementation of Fourier's Law. In the infinitesimal applied field limit, the equilibrium Green-Kubo method can be used in which the  $\lambda_x$  is related to the integral of the correlation function of fluctuations in the heat-flux vector:

$$\lambda = \frac{V}{k_B T^2} \lim_{t \rightarrow \infty} \int_{t_0}^{t_0+t} \langle J_{Qx}(\tau) J_{Qx}(0) \rangle d\tau. \quad (2)$$

For an atomic fluid consisting of  $N$  molecules in volume  $V$ , and considering the  $x$ -component of the heat flux, we have

$$J_{Qx} = V^{-1} \left( \sum_i^N e_i v_{xi} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N r_{xij} \phi'_{ij}(r_{ij}) v_i \right) \quad (3)$$

where

$$e_i = \frac{1}{2} m_i v_i^2 + \frac{1}{2} \sum_{j \neq i} \phi_{ij} \quad (4)$$

which is the energy of a molecule index  $i$  in the fluid. The Green-Kubo approach has been applied to Lennard-Jones liquids by a number of groups since the pioneering simulations of Levesque, Verlet and Kurkijarvi,<sup>2</sup> see for another example.<sup>3</sup> This treatment has been generalised for a single component *molecular* fluid consisting of  $N$  molecules containing  $n$  interaction sites,  $\alpha$  on molecule  $i$  and  $\beta$  on molecule  $j$ .

$$J_{Qx} = V^{-1} \left( \sum_i^N e_i^m v_{xi} + \sum_{i=1}^{N-1} \sum_{\alpha=1}^n \sum_{j=i+1}^N \sum_{\beta=1}^n r_{x\alpha j \beta} \phi'_{i\alpha j \beta}(r_{i\alpha j \beta}) v_i \right) \quad (5)$$

where  $v_i$  is the velocity of the centre of mass of the molecule,  $\phi_{i\alpha j \beta}$  is the pair potential between site  $\alpha$  in molecule  $i$  and site  $\beta$  in molecule  $j$

separated by  $r_{i\alpha j\beta}$ . The total energy of molecule  $i$  is  $e_i^m$ ,

$$e_i^m = \frac{1}{2} m_i \underline{v}_i^2 + \frac{1}{2} \sum_{\alpha=1}^n \sum_{j \neq i} \sum_{\beta=1}^n \phi_{i\alpha j\beta} \quad (6)$$

Simulations of the thermal conductivity of compact near-spherical molecules such as  $SF_6$  and  $CF_4$  have been carried out using this formula<sup>4</sup>. Where rigid body motion is integrated by for example quaternions then<sup>5</sup>,

$$\underline{J}_Q = V^{-1} \left( \sum_i^N e_i^m \underline{v}_i - \sum_{i=1}^{N-1} \sum_{j=i+1}^N r_{ij} [\underline{v}_i \cdot \underline{f}_{ij} + \underline{\omega}_{pi} \cdot \underline{\Gamma}_{pi}] \right) \quad (7)$$

where  $i$  and  $j$  refer to centre of mass quantities,  $f_{ij}$  is the force between centres of mass of molecules  $i$  and  $j$ ,  $\underline{\omega}_{pi}$  is the principle angular velocity of molecule  $i$  and  $\underline{\Gamma}_{pi}$  is the corresponding principle torque.

It has proved rather difficult to devise rigorous non-equilibrium Molecular Dynamics equations of motion to compute thermal conductivity. Thermal conductivity is perhaps one of the most straightforward of transport coefficients to measure experimentally, by direct application of Fourier's law. This approach has also been mimicked in molecular simulation, by sandwiching a MD system which is periodic in the  $x$  and  $y$  directions only, and of finite extent in the  $z$  direction, between two 'thermal' walls at different temperature.<sup>6</sup> The problem with this approach, as with all such "wall-based" methods for transport coefficients, is that the liquid becomes spatially inhomogeneous (the molecules form layers against the wall) and very large temperature gradients have to be imposed on the system. The results obtained from such a study are therefore difficult to interpret, as the modelled system exists in different thermodynamic states within the simulation cell. These techniques also tend to be statistically quite poor. Nevertheless, thermal wall Molecular Dynamics techniques have proved useful in investigating other non-equilibrium thermal phenomena of importance such as Rayleigh-Bernard convection rolls<sup>7</sup>.

It is not possible to have a constant temperature gradient across a simulation cell, and *also* be compatible with periodic boundary conditions. The nearest that can be achieved is to impose a profile (*e.g.*, an oscillatory temperature profile) in the cell, with a finite wave vector

compatible with the periodic boundary conditions. (The Lees-Edwards periodic boundary conditions is a striking exception to this rule, in which for shear viscosity, a shear gradient at zero wavevector is introduced to the contents of a MD cell that is compatible with periodic boundary conditions<sup>8</sup>.) One novel procedure that has been applied to Lennard-Jones and ionic systems involves dividing the MD cell into a number of layers (*e.g.*, 32) parallel to one of its faces. One layer at each end of the cell is heated and two layers in the middle are used as heat sinks, both by appropriate velocity scaling. Therefore two heat fluxes in opposite direction are induced towards the centre of the cell.<sup>9</sup> The thermal conductivity can then be obtained by direct application of Fourier's Law in the two regions.

Evans<sup>10</sup> and Gillan<sup>11</sup> devised ingenious synthetic NEMD equations of motion which are free of gradients. (An earlier method, which employed an external field perturbation method invented by Ciccotti, Jacucci and McDonald contains some of the same underlying ideas<sup>12</sup>.) The theory for this approach is described below, using the more recent notation and formalism of Evans and Morriss, who extended the Green-Kubo formula to apply to non-equilibrium systems.<sup>13</sup>

Consider an equilibrium fluid that has a homogeneous field imposed on it at time  $t = 0$ . Therefore at  $t = 0$  the system goes from being in an equilibrium state to a non-equilibrium one. Consider an arbitrary time dependent property of the system,  $B(t)$ . (We will assume that the equilibrium time average,  $\langle B \rangle = 0$ , which is the case for the heat flux, to simplify the formulae; although the more general case of  $\langle B \rangle \neq 0$  can also be treated with minor modifications of the formulae below). If an external field,  $\underline{F}_e$  is imposed at time  $t = 0$ , then the response of  $B(t)$  is given by

$$\langle B(t) \rangle = \langle B(0) \rangle + \frac{1}{k_B T} \int_0^t ds \langle B(s) \dot{H}(0) \rangle \quad (8)$$

where the time derivative of the Hamiltonian ('dissipative heat') is identified with its phenomenological form of a flux time times a perturbing thermodynamic force *i.e.*,  $\dot{H} = -\underline{J}_Q \underline{F}_e$ . Here  $\underline{J}_Q$  is the dissipative flux. In the case of thermal conductivity, the fictitious force or "heat" field,  $\underline{F}_e$ , replaces the temperature gradient but still induces an additional heat flux,  $\Delta \underline{J}_Q(t)$  in the system. Setting  $B = \underline{J}_Q$  and substitu-

ting for  $H$  in Eq. (8) gives the so-called *transient time correlation function* formula for the thermal conductivity at *arbitrary* applied field. We then have,

$$\lambda(\underline{F}_e) = \lim_{t \rightarrow \infty} \frac{\Delta \underline{J}_Q(t)}{F_e} = \frac{V}{3k_B T^2} \int_0^t ds \langle \Delta \underline{J}_Q(s) \cdot \underline{J}_Q(0) \rangle \quad (9)$$

In order to satisfy  $\dot{H} = -\underline{J}_Q \cdot \underline{F}_e$  at the microscopic level, then the equations of motion for a monatomic system are,

$$\begin{aligned} \dot{\underline{r}}_i &= \frac{\dot{\underline{p}}_i}{m} \\ \dot{\underline{p}}_i &= \underline{F}_i + (e_i - \langle e \rangle) \underline{F}_e - \sum_{j=1}^N f_{ij} \underline{r}_{ij} \cdot \underline{F}_e \\ &\quad + \sum_{j=1}^{N-1} \sum_{k=j+1}^N f_{ij} \underline{r}_{ij} \cdot \underline{F}_e / 2N - \alpha \underline{p}_i \end{aligned} \quad (10)$$

where  $\underline{F}_i$  is the instantaneous total force on particle  $i$ ,  $\langle e \rangle$  is the average of the instantaneous  $e_i$  taken over all molecules in the system, and as before  $f_{ij}$  is the pair force between molecules  $i$  and  $j$ . In order to prevent an increasing rise in the temperature of the system arising from the imposed heat force, it is necessary to apply a thermostatic control-in this case in the form a gaussian multiplier applied to the peculiar momentum,  $\dot{\underline{p}}_i$ . The gaussian thermostat multiplier,  $\alpha$ , in the above formula is evaluated each time step to maintain a constant temperature, and is calculated from these equations of motion and setting  $\dot{H} = 0$ .

$$\begin{aligned} \alpha &= \sum_{i=1}^N [\underline{F}_i + (e_i - \langle e \rangle) \underline{F}_e - \sum_{j=1}^N f_{ij} \underline{r}_{ij} \cdot \underline{F}_e \\ &\quad + \sum_{j=1}^{N-1} \sum_{k=j+1}^N f_{ij} \underline{r}_{ij} \cdot \underline{F}_e] \cdot \underline{p}_i / 2N \sum_{i=1}^N \underline{p}_i^2 \end{aligned} \quad (11)$$

These equations of motion conserve momentum of the MD cell and are homogeneous. Through the  $(e_i - \langle e \rangle) \underline{F}_e$  term they introduce a

heat current in the periodic system, as the molecules with greater energy than the mean  $\langle e \rangle$  will be driven in the opposite direction to those molecules which instantaneously have an energy lower than the mean. The thermal conductivity is obtained by extrapolation of the field dependent thermal conductivity,  $\lambda(F_e)$ , to zero  $F_e$ . For most systems considered the extrapolation is quite close to being linear. The major disadvantage of the NEMD approach in general is that, if linear response transport coefficients are of sole interest, several simulations at different applied field strengths need to be carried out in order to perform the desired extrapolation to zero heat field. The simulations carried out at finite heat field,  $F_e$ , have no experimental analogue, as would those states generated from a finite temperature gradient, for example. The homogeneous NEMD thermal conductivity equations of motion have been generalised to apply to rigid molecular liquids [5]. In contrast to the corresponding NEMD procedure for shear viscosity, only the limit of zero applied shear has any physical significance for thermal conductivity. In the case of shear viscosity the finite field corresponds to finite shear rate, which is experimentally realisable, and can lead to the important phenomenon of non-Newtonian flow—an effect very much apparent in real systems.

Away from equilibrium and the linear response regime, the decoupling of transport co-efficients (*e.g.*, shear viscosity and thermal conductivity) no longer holds. Simulations of the thermal conductivity of a strongly sheared Lennard-Jones fluid reveal that the symmetry breaking of the shear field cause (a) the diagonal elements of the thermal conductivity  $3 \times 3$  tensor to start to become unequal at a reduced shear rate of  $\sim 1 \sigma^{-1} \epsilon^{1/2} m^{-1/2}$ , and (b) the appearance of nonzero off-diagonal elements in the thermal conductivity tensor<sup>14</sup>.

### 3. MULTICOMPONENT SYSTEMS

For a multicomponent system a number of interesting so-called ‘thermodiffusion’ effects can occur which have no analogue in the single component systems; and which have a well defined relationship to the thermal conductivity of the mixture. A temperature gradient will cause a relative flow of the different molecules in the mixture in opposite



directions. Consequently it is by no means a trivial exercise to obtain the thermal conductivity of liquid mixtures by Molecular Dynamics, and there are still some unresolved issues pertaining to the definitions of the matter and heat fluxes required in the formulae and relating these to what are actually measured in experiment. A number of additional transport coefficients are required to characterise multi-component fluid systems. For clarity, consider a binary mixture where there are  $N_v$  molecules of species type  $v$  each with a molecular mass  $m_v$ . When a concentration gradient is imposed on an isothermal fluid mixture, a temperature gradient will develop as interdiffusion occurs. This is called the Dufour or diffusion-thermo effect. It is rather hard to measure for liquids, however; but there is more success for the reverse process, known as the Soret or thermal-diffusion effect. Here a temperature gradient creates a species concentration gradient, and can be specified by the following equation,

$$T \underline{\nabla}_{x_1} = -k_T \underline{\nabla} T \quad (12)$$

where  $x_1$  is the mass fraction of species 1, *i.e.*,

$$x_1 = \frac{N_1 m_1}{N_1 m_1 + N_2 m_2} \quad (13)$$

and  $k_T$  is known as the thermal-diffusion coefficient. Let the mass flux of species,  $v$  be  $\underline{J}_v$  then<sup>15,16</sup>

$$V \underline{J}_v = N_v m_v (\underline{u}_v - \underline{u}) \quad (14)$$

where  $\underline{u}$  is the barycentric velocity (the velocity of the centre of mass),

$$N_v \underline{u}_v = \sum_{i=1}^{N_v} \dot{\underline{r}}_i \quad (15)$$

and

$$(N_1 m_1 + N_2 m_2) \underline{u} = \sum_{v=1}^2 m_v \sum_{i=1}^{N_v} \dot{\underline{r}}_i \quad (16)$$

$\underline{u}_v$  is the centre-of-mass velocity of species  $v$ . If  $\rho$  is the total mass density then  $\underline{J}_v = \rho x_v (\underline{u}_v - \underline{u})$ . The Irving and Kirkwood microscopic expression for the heat flux in a multicomponent mixture,  $V\underline{J}_Q$  is,<sup>15</sup>

$$V\underline{J}_Q = \frac{1}{2} \sum_v \sum_{i=1}^{N_v} \left( (\dot{r}_i - \underline{u}) \left( m_v (\dot{r}_i - \underline{u})^2 + \sum_{j=1} \phi_{ij} \right) - (\dot{r}_i - \underline{u}) \cdot \sum_j r_{ij} \underline{f}_{ij} \right) \quad (17)$$

Considering that we have a binary mixture, the mass currents of the two species are related in the Molecular dynamics ensemble, *i.e.*,  $\underline{J}_2 = -\underline{J}_1$  then only one need be considered<sup>17</sup>. Linearised irreversible thermodynamics relates flows to driving forces through the so-called Onsager phenomenological coefficients,  $L_{\alpha\beta}$ ,<sup>18</sup>

$$\begin{aligned} \underline{J}_1 &= L_{11} \underline{X}_1 + L_{1Q} \underline{X}_Q \\ \underline{J}_Q &= L_{Q1} \underline{X}_1 + L_{QQ} \underline{X}_Q \end{aligned} \quad (18)$$

where the gradients  $\underline{X}_\alpha$  are,

$$\begin{aligned} \underline{X}_1 &= -\frac{1}{T} \underline{\nabla}_T (\mu_1 - \mu_2) \\ \underline{X}_Q &= -\frac{1}{T^2} \underline{\nabla} T \end{aligned} \quad (19)$$

where  $\mu_v$  is the chemical potential of species  $v$ . In the absence of a temperature gradient, Fick's Law gives another expression for  $\underline{J}_1$ ,

$$-\underline{J}_1 = \rho D_1 \underline{\nabla}_{x1} \quad (20)$$

where  $D_1$  is the bulk diffusion coefficient of species 1 relative to the barycentric centre (centre-of-mass frame) which using the Gibbs-Duhem equation gives,

$$D_1 = \frac{L_{11}}{\rho x_2 T} \frac{\partial \mu_1}{\partial x_1} \quad (21)$$

In the experimental fixed volume frame  $D_1$  and  $D_2$  are trivially related to the mutual diffusion coefficient  $D$

$$D = \rho v_2 D_1 = \rho v_1 D_2 \quad (22)$$

where  $v_v$  is the partial specific volume of species  $v$ . The above definitions for the mass and heat fluxes are not identical to those measured experimentally; however the evidence from Green-Kubo simulations of the Onsager coefficients performed by MacGowan is that the differences are rather small and can be ignored for practical purposes.<sup>17</sup> The Onsager coefficients  $L_{\alpha\beta}$  can be computed by Molecular Dynamics simulations using the following Green-Kubo relationships,

$$\begin{aligned} L_{11} \underline{I} &= \frac{V}{k_B} \int_0^\infty dt \langle \underline{J}_1(0) \underline{J}_1(t) \rangle \\ L_{1Q} \underline{I} &= \frac{V}{k_B} \int_0^\infty dt \langle \underline{J}_1(0) \underline{J}_Q(t) \rangle \\ L_{QQ} \underline{I} &= \frac{V}{k_B} \int_0^\infty dt \langle \underline{J}_Q(0) \underline{J}_Q(t) \rangle \end{aligned} \quad (23)$$

The cross coefficient,  $L_{1Q}$  characterises the thermal diffusion or Soret effect. Combination of Eq. (12) with Eq. (20) gives for the Soret coefficient,

$$k_T = \frac{L_{1Q}}{\rho T D_1} \quad (24)$$

The thermal conductivity of the mixture, defined using Fourier's Law  $\underline{J}_Q = -\lambda \nabla T$  can be obtained from Eq. (18) using  $L_{1Q} = L_{Q1}$  (Onsager's symmetry reciprocal relationship) and  $\underline{J}_1 = 0$  then,

$$\lambda = \frac{1}{T^2} \left( L_{QQ} - \frac{L_{1Q}^2}{L_{11}} \right) \quad (25)$$

Therefore machine simulation of the  $L$  from Eq. (23) yields the thermal conductivity when substituted in Eq. (25).

The Onsager coefficients can also be computed using NEMD just as for the thermal conductivity of the single-component fluid, using appropriately generalized synthetic homogeneous equations of motion as described in refs 15 and 16.

#### 4. ELECTRONIC CONTRIBUTION TO THERMAL CONDUCTIVITY OF LIQUID METALS

As mentioned in the Introduction, there can be important electronic contributions to thermal conduction in liquid metals such as Na or Cu. These are presently best approached, at least near the freezing point, by calculating first the electrical conductivity  $\sigma$ , and then invoking the Wiedemann-Franz Law relating  $\sigma$  to the (electronic contribution to) thermal conductivity  $\lambda$ : We shall therefore briefly summarize the underlying ideas below.

##### 4.1. Wiedemann-Franz Law

The most elementary approach to the Wiedemann-Franz Law involves three steps (a)-(c). First, one adapts the kinetic theory of heat conduction in gases appropriately: step (a). Then one uses the usual formula for the electrical conductivity  $\sigma$ , namely  $\sigma = ne^2\tau/m$ , with  $n$  the electron number density,  $m$  the electronic mass and  $\tau$  the usual relaxation time. The third essential step (c) is to assume that the two relaxation times entering steps (a) and (b) are equal. Then one finds the relation (see also March<sup>19</sup>)

$$\frac{\lambda}{\sigma T} = L, \quad (26)$$

Here the constant  $L$  is the so-called Lorenz number. A semiclassical treatment leads to the value

$$L = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 \quad (27)$$

which has the numerical magnitude  $2.45 \times 10^{-8} J^2/C^2 K^2$ . Experimentally (see Table 1) the Lorenz number for the liquid alkali metals is between 2.1 and  $2.6 \times 10^{-8}$ .

Combining eqn (26) with a theory of the electrical resistivity  $\rho = 1/\sigma$  leads to a theoretical estimate of the (dominant) electronic contribution to  $\lambda$  in a liquid metal. For instance, for simple s-p liquid metals near freezing, the nearly free electron theory gives the explicit formula<sup>20,21</sup>

$$\rho = \frac{12\pi m^2}{\hbar^3 n e^2 k_F^2} \int_0^1 |V_{ei}(q)|^2 S(q) \left(\frac{q}{2k_F}\right)^3 d\left(\frac{q}{2k_F}\right) \quad (28)$$

with  $k_F$  is the Fermi wave number. The microscopic formula (28) of the nearly free electron (NFE) theory involves knowledge not only of the liquid structure factor  $S(q)$  but also of the electron-ion interaction  $V_{ei}(q)$ . Pastore et al<sup>22</sup> have shown that eqn (28) is in excellent agreement with experiment for the liquid alkali metals near freezing.

Evidently, using their calculations, the thermal conductivity can be calculated from the Wiedemann-Franz Law (26).

March and Tosi<sup>23</sup> have also related the thermal and electrical conductivities of liquid metals near freezing to the shear viscosity  $\eta$ . Their analysis makes use of the earlier work of Tosi<sup>24</sup> who used ion-electron plasma theory to calculate the (longitudinal) viscosity of the alkali metals near the freezing point. The result of March and Tosi<sup>23</sup> is that the thermal conductivity  $\lambda_m$  at the melting temperature  $T_m$  is related to

TABLE I Lorenz numbers  $L \times 10^8$  in units of  $WK^{-2}$  for a variety of liquid metals.

| Metal | $L \times 10^8$ | Metal | $L \times 10^8$ | Metal | $L \times 10^8$ |
|-------|-----------------|-------|-----------------|-------|-----------------|
| $L_i$ | 2.6             | Pb    | 2.4             | Ta    | 2.4             |
| Na    | 2.2             | Sb    | 2.6             | Re    | 1.75            |
| K     | 2.1             | Bi    | 2.5             | Os    | 1.75            |
| Cs    | 2.4             | Ti    | 2.9             | Pt    | 2.3             |
| Cd    | 2.5             | Zr    | 2.25            | In    | 2.7             |
| Hg    | 2.75            | Hf    | 2.7             | La    | 2.65            |
| Zn    | 3.2             | Mo    | 2.6             | Ce    | 2.56            |
| Al    | 2.4             | W     | 2.5             | Pr    | 2.89            |
| Ga    | 2.07            | Ru    | 2.45            | Nd    | 2.27            |
| Tl    | 3.2             | Ir    | 1.95            | Gd    | 1.83            |
| Sn    | 2.9             | Nb    | 2.6             | Dy    | 2.34            |

electrical resistivity  $\rho_m$  and shear viscosity  $\eta_m$  at  $T_m$  by

$$\lambda_m = \frac{L\eta_m^2}{A^2\rho_m M_i n_i^{4/3}} \quad (29)$$

where  $A = 5.1 \times 10^{-4}$ . Here  $M_i$  and  $n_i$  denote the ion mass and ionic number density respectively.

Having invoked the static structure factor  $S(q)$  in the NFE formula (28) for electrical resistivity, we shall below consider its dynamical generalization  $S(q, \omega)$  such that

$$\int_{-\infty}^{\infty} S(q, \omega) d\omega = S(q) \quad (30)$$

in relation to thermal conductivity. Though the work below is posed in terms of liquid metals, the argument in the hydrodynamic limit outlined is immediately relevant also to insulating liquids. Of course, the appropriate thermal conductivity must be used in the two classes of liquids considered in detail above.

## 5. INFLUENCE OF THERMAL CONDUCTION ON NEUTRON DIFFRACTION

Since thermal conduction is a transport property, it enters the equations of hydrodynamics for all liquids, and in particular for a liquid metal. Following the discussion of insulating multicomponent liquids above, it is natural also to refer below to two-component liquid metal alloys.

### 5.1. Dynamical structure factor

As introduced above,  $S(q, \omega)$ , introduced into the theory of liquids by Van Hove<sup>25</sup>, has the physical meaning that it represents the probability that a neutron incident on the liquid will transfer momentum  $\hbar q$  and energy  $\hbar\omega$  to the liquid. One immediate property of the dynamical structure factor  $S(q, \omega)$  is that, when integrated over all energy

transfers, the static structure factor  $S(q)$  is regained, as set out in eqn (30).

We referred above already to the hydrodynamic regime. Then the hydrodynamic equations of a liquid, in linearized form, can be applied to set up the form of  $S(q, \omega)$ , in of course the appropriate regime for which the hydrodynamic equations are valid. These equations, in fact, apply in the long wavelength and low frequency limits, or equivalently, in the Fourier transform variables  $q \rightarrow r, \omega \rightarrow t$ , the limit of large  $r$  and long time  $t$ .

Following the pioneering work of Landau and Placzek,<sup>26</sup> the usual procedure in such a calculation is to use the linearized hydrodynamic equations of irreversible thermodynamics to describe the relaxation in time of relevant fluctuating thermodynamic variables in the liquid: this procedure is described, for instance by Mountain.<sup>27</sup>

Though a little more detail will be recorded below for liquid metal alloys, let us summarize here the main physical content emerging from such an approach. There are basically three peaks evident in  $S(q, \omega)$  as a function of angular frequency  $\omega$ . The central ( $\omega = 0$ ) component (Rayleigh peak) is found to consist of the sum of two Lorentzians, the width of one of these being controlled largely by thermal conduction. There are also two 'Doppler-shifted' peaks, referred to as Brillouin components, centred at frequencies  $\omega = C_0 q$  where  $C_0$  is the adiabatic speed of sound given by

$$C_0 = (\partial p / \partial p)_s^{1/2} \quad (16)$$

where  $S$  is the entropy. These peaks arise from sound propagation in opposite directions (for a given wave vector  $q$ ) and their width, having the form  $\Gamma q^2$ , turns out to be controlled by acoustic attenuation (see also below). It is important to note that the ratio of the integrated intensity ( $I_0$ ) of the Rayleigh components in  $S(q, \omega)$  to that of the doublet Brillouin side peaks ( $2I_1$ ) is quite generally given by

$$\frac{I_0}{2I_1} = (\gamma - 1) \quad (31)$$

The generalization of this result to liquid metal alloys in which there are size differences between the two components will be treated later.

There are also 'non-Lorentzian' "parts" in  $S(q, \omega)$ , though these make no contribution to the integrated intensity and, usually, only a

relatively small contribution to the intensity distribution. However, if  $\Gamma q/C_0$  is not much less than unity, they can markedly affect the position and shape of the Brillouin peaks in  $S(q, \omega)$ .

## 6. BINARY LIQUID METAL ALLOYS

Turning from pure metals to binary liquid alloys, we note first that Bhatia and Thornton<sup>28</sup> (1970) introduced number-concentration ( $N$ - $C$ ) dynamical structure factors  $S_{NN}(q, \omega)$ ,  $S_{NC}(q, \omega)$  and  $S_{CC}(q, \omega)$ , to describe the structural aspects of scattering processes in such alloys.

### 6.1. Role of thermal conduction in neutron scattering

The aim below is to discuss the hydrodynamic limit of long wavelength and low frequency of the  $N$ - $C$  dynamical structure factors of such a liquid alloy. This follows the approach of Bhatia, *et al.*,<sup>29</sup> who made extensive use of the earlier study of Cohen, *et al.*<sup>30</sup> These workers gave results for correlations between mass-density and mass-concentration. Let us first consider  $S_{NN}(q, \omega)$ . If we take the limit of a dilute alloy such that the concentration  $c$  goes to zero, then  $S_{NN}(q, \omega)$  becomes the dynamical structure factor of pure liquid metal discussed above. Paralleling the discussion of  $S(q, \omega)$ , the Rayleigh component in  $S_{NN}(q, \omega)$  is again found to be the sum of two Lorentzians. As before, the width of one Lorentzian is largely controlled by thermal conduction: the other by mutual diffusion. The two Doppler shifted (Brillouin) components are largely as in the one-component case, speaking in general terms (see Bhatia, *et al.*<sup>29</sup> for fuller details of  $S_{NN}(q, \omega)$  in the hydrodynamic regime). It is worth noting that eqn. (31) for the ratio of the ratio of the integrated intensity ( $I_0$ ) of the Rayleigh components in  $S_{NN}(q, \omega)$  to that of the doublet Brillouin side peaks ( $2I_1$ ) is modified from the result of eqn. (31) though still proportional to  $(\gamma - 1)$ , with  $\gamma$  of course, the specific heat ratio at the particular concentration considered in the liquid alloy, there is a multiplying factor of the form  $(1 + \text{constant } \delta^2)$ , where  $\delta$  is the size difference of the two components in the alloy:

$$\delta = \frac{1}{V} \left[ \frac{\partial V}{\partial c} \right]_{P, T; N} = \frac{v_1 - v_2}{v}. \quad (32)$$



Here  $v_x = [\partial V / \partial N]_{P,T,N,\beta}$  ( $\beta \neq x$ ) denotes the partial molar volume per atom of species  $x$ , while  $v$ , the mean molar volume per atom is given by

$$v = \left[ \frac{\partial V}{\partial N} \right]_{P,T,c} = cv_1 + (1-c)v_2 \quad (33)$$

Of course, in the dilute alloy limit  $c$  tends to zero, whereas  $S_{NN}$  tends to the one-component  $S(q, \omega)$ ,  $S_{NC}$  and  $S_{cc}$  tend to zero. These latter two quantities are therefore crucially about the alloy at finite concentration  $c$ . Let us write out shape of  $S_{NC}$ , without going into full details; (for these, see Bhatia *et al.*)<sup>29</sup> It is such that

$$S_{NC}(q, \omega) = \frac{Nk_B T}{2\pi} \left[ \frac{K_1 q^2}{\omega^2 + X^2 q^4} + \frac{K_2 q^2}{\omega^2 + Y^2 q^4} \right. \\ \left. + K_3 q \left[ \frac{\omega + C_0 q}{(\omega + C_0 q)^2 + \Gamma^2 q^4} - \frac{\omega - C_0 q}{(\omega - C_0 q)^2 + \Gamma^2 q^4} \right] \right] \quad (34)$$

In this general expression, the constants are all known in terms of macroscopic constants, both thermodynamic and irreversible transport coefficients being involved. The two Lorentzians (terms involving  $K_1$  and  $K_2$ ) primarily arise in the number-concentration structure factor  $S_{NC}(q, \omega)$  respectively from diffusive processes and the coupling between this type of mode and the thermal conductive mode. If this coupling is zero, then the latter component is no longer present and the width of the remaining Lorentzian is simply  $Dq^2$ , where  $D$  is the coefficient of mutual diffusion.

The concentration-concentration structure factor has a central role in understanding the thermodynamic properties of liquid binary alloys, when integrated over all energy transfers. As to its frequency dependence, this again follows from the linearized hydrodynamic equations and has the form of the sum of two Lorentzians:

$$S_{cc}(q, \omega) = \frac{Nk_B T}{2\pi Z} \left[ \frac{K_3 q^2}{\omega^2 + X^2 q^4} + \frac{K_4 q^2}{\omega^2 + Y^2 q^4} \right] \quad (35)$$

These two components behave in a similar manner to the Lorentzians in  $S_{NC}(q, \omega)$ . The quantity  $Z$  appearing in eqn (35) is connected with the Gibbs free energy  $G$  of the liquid alloy by

$$Z = \left( \frac{\partial^2 G}{\partial c^2} \right)_{P,T,N} \tag{36}$$

**6.2. Thermal conduction and ultrasonic absorption**

The way in which thermal conduction affects sound wave attenuation in liquid metal alloys will now be considered briefly. Specifically, the width,  $\Gamma q^2$ , of the Brillouin components in the number-number dynamical structure factor  $S_{NN}(q, \omega)$  is related to the acoustic attenuation in the liquid. In particular, the amplitude attenuation per wavelength,  $\alpha$ , is given by

$$\frac{\alpha}{\omega} = \frac{\pi(\zeta + 4/3\eta)}{\rho C_0^2} + \frac{\pi(\gamma - 1)\lambda M}{\rho C_0^2 C_p} + \left[ \frac{\alpha}{\omega} \right]_D \tag{37}$$

where

$$(\alpha/\omega)_D = (\pi MD/Z)[(\delta - \delta_m) + Zk_T \alpha_T / C_p]^2. \tag{38}$$

The three terms appearing in the last part of eqn (37) come from (i) bulk ( $\zeta$ ) and shear ( $\eta$ ) viscosities, (ii) attenuation caused by thermal conductivity, out main interest here, while the last term gives the contribution due to diffusion. Bhatia *et al*<sup>29</sup> treat the limiting case of eqn. (24) for an ideal gas mixture. Here there is no size effect, so  $\delta = 0$ , the coefficient of thermal expansion  $\alpha_T = 1/T$  while the isothermal compressibility  $K_T = 1/P$ , as follows from the ideal gas equation of state  $PV = Nk_B T$ . From the Gibbs free energy in this ideal gas model, it is readily, shown that  $Z$  is given by

$$Z = Nk_B T / c(1 - c). \tag{39}$$

Hence, for the last term one readily finds

$$(\alpha/\omega)_D = \pi D c(1 - c) \frac{\rho}{P} \left[ \frac{(m_2 - m_1)}{m} + \frac{(\gamma - 1)\beta}{\gamma} \right] \tag{40}$$

where  $\beta = k_T/c(1 - c)$ , the thermal diffusion factor, has been introduced. This formula has been derived previously from kinetic theory calculations and has been verified experimentally for noble gas mixtures of various compositions. For a fuller discussion of ultrasonic absorption, and in particular the role of thermal conduction, the reader may consult the book by Bhatia.<sup>30</sup>

## 6. SUMMARY

To summarize the part of this review on insulating liquids, the molecular simulation of thermal conductivity of arbitrary mixtures of molecular liquids interacting via pair interactions is by now a routine procedure. It is appropriate therefore to ask at this stage as to the benefits of these simulations. As yet, these techniques have not been applied to very many chemical systems. Nevertheless, the simulations carried out to date have verified that the Green-Kubo ('equilibrium') and homogeneous heat field non-equilibrium MD techniques do give the same results within the statistical uncertainty of the simulations. These methods will undoubtedly be used in the future to study the dependence of thermal conductivity on molecular structure and state point for many different classes of system.

Turning to liquid metals, it has been emphasized here that, to date, the dominant electronic contribution to thermal conduction has been approached largely via electrical conductivity calculations, plus the Wiedemann-Franz Law. However, it has to be stressed that this Law is approximate, and at times large deviations from it can occur. Therefore most work to date has focussed on simple s-p metals near freezing. But we already know that even supposedly simple metals like the liquid alkalis behave very differently from the NFE theory as they are taken up the liquid-vapour coexistence curve towards the critical point. There is therefore a wide area here, both in pure liquid metals and also in liquid metal alloys in which further work is called for, both analytic theory and computer modelling. But we should also stress the need for further experiments, both macroscopic transport measurements and also neutron diffraction studies.

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### *References*

- [1] Hoover, W. G., Glover, R. and Moran, B. (1985). *J. Chem. Phys.*, 83:1255.
- [2] Verlet, L., Levesque, D. and Kurkijarvi, J. (1973). *Phys. Rev. A*, 7:1690.
- [3] Hoheisel, C., Vogelsang, R. and Luckas, M. (1988). *Mol. Phys.*, 64:1203.
- [4] Hohcisl, C. (1988). *J. Chem. Phys.*, 89:3195
- [5] Evans, D. J. and Murad, S. (1989). *Mol. Phys.*, 68:1219
- [6] Ashurst, W. T. and Hoover, W. G. (1974). *Phys. Rev. A*, 11:658
- [7] Given, J. A. and Clementi, E. (1989). *J. Chem. Phys.*, 90:7376.
- [8] Evans, D. J. and Morriss, G. P. (1990). *Statistical Mechanics of Nonequilibrium Liquids*. Academic Press, London, 1st edition.
- [9] Hafskjold, B., Bresme, F. and Wold, I. (1996). *J. Phys. Chem.*, 100:1879.
- [10] Evans, D. J. (1982). *Phys. Lett. A*, 91:457.
- [11] Gillan, M. J. and Dixon, M. (1983). *J. Phys. C*, 16:869.
- [12] Jacucci, G., Ciccotti, G. and McDonald, I. R. (1978) *J. Phys. C*, 11:L509.
- [13] Morriss, G. P. and Evans, D. J. (1988) *Phys. Rev. A*, 38:4142
- [14] Daivis, P. J. and Evans, D. J. (1983). *Phys. Rev. E*, 1058:48
- [15] MacGowan, D. and Evans, D. J. (1986). *Phys. Rev. A*, 34:2133
- [16] MacGowan, D. and Evans, D. J. (1987) *Phys. Rev. A*, 36:948.
- [17] MacGowan, D. (1986). *Molec. Phys.*, 59:1017.
- [18] MacGowan, D. and Evans, D. J. (1986). *Phys. Lett. A*, 117:414.
- [19] March, N. H. (1990). *Liquid metals, Concepts and theory* (Cambridge: University Press)
- [20] Krishnan K. S. and Bhatia, A. B. (1945). *Nature*, **156**, 503
- [21] Ziman, J. M. (1961). *Phil. Mag.* **6**, 1013.
- [22] Pastore, G., Senatore, G. and Tosi, M. P. (1981), *Physics*, **111B**, 283
- [23] March, N. H. and Tosi, M. P. *J. Plasma Phys.*, in press.
- [24] Tosi, M. P. (1992). *Nuovo Cimento* **14D**, 559.
- [25] Van Hove, L. (1954). *Phys. Rev.*, **95**, 249.
- [26] Landau, L. and Placzek, G. (1934). *Physik Z. Sowjetunion* **5**, 172
- [27] Mountain, R. D. (1970). *Critical Rev. in Solid State Science*, **1**, 5.
- [28] Bhatia, A. B. and Thornton, D. E. (1970). *Phys. Rev. Phys.*, **B2**, 3004.
- [29] Bhatia, A. B., Thornton, D. E. and March, N. H. *Phys. Chem. Liquids*
- [30] Bhatia, A. B. (1967). *Ultrasonic absorption* (Oxford: University Press).