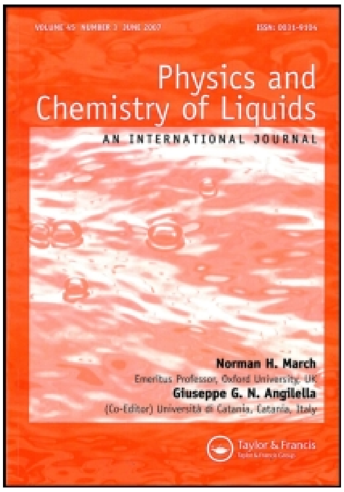

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Atomic Transport and Isotopic Mass Effects in Classical Liquids

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Abstract—In classical liquids differing only in their isotopic mass M, with a total potential energy function independent of mass, the van Hove function $S(k, \omega, M, T)$ is shown to have the form $M^{1/2}f(k, \omega M^{1/2}, T)$, where f is the same function for different isotopes. This result applies also to the self part $S_s(k\omega)$ and, combined with the Kubo formula for the coefficient of self-diffusion D, it follows that D is rigorously proportional to $M^{-1/2}$ in this theory. From the corresponding correlation function expressions for the shear and bulk viscosities, η and ζ respectively, it is found that these are both proportional to $M^{1/2}$, a result obtained earlier on dimensional grounds by Rowlinson.

It is argued in liquid metals, from the machine calculations of Paskin and Rahman, that the frequency spectrum has a rather well defined range, essentially up to the Debye frequency ω_d. First-order formulae, consistent with the isotopic mass dependence discussed above, are then obtained for diffusion and viscosity of liquid metals at the melting point. An interesting feature of the formula for viscosity is its explicit dependence on the long wavelength limit of the liquid structure factor. A more general argument is also presented, which leads to similar results for diffusion and viscosity even when the Debye edge is badly blurred, as in argon.

Shear viscosity measurements for Li^6 and Li^7 deviate appreciably from the predictions of the classical theory. Measurements of the frequency spectra of light isotopes may help in clarifying the situation. Another possibility might be to study neutron scattering from a binary isotopic mixture, the theory of which is discussed in an appendix.

1. Introduction

This work had its origin in the measurements available on the shear viscosity η of Li^6 and Li^7 (Ban, Randall and Montgomery, 1962). This seemed a particularly simple system, for Rowlinson (1953) had earlier pointed out that the relation between the viscosity of different isotopes could be obtained on essentially dimensional grounds. Our work leads to the same result as his for the viscosity, but shows in classical theory how the time-dependent correlation functions transform with mass. This is dealt with in Sections 2 and 3 and then, in Section 4, we develop approximate theories for diffusion D and shear viscosity η in liquid metals at the melting point, which are consistent with the above theory. In Section 5 an approximate relation between D and η is proposed while Section 6 deals with the puzzling discrepancies which remain for Li^6 and Li^7 and suggests experiments on other light isotopes which might clarify the situation.

2. Mass Dependence of Self-part of van Hove Correlation Function

The probability that an atom, at $\mathbf{r} = 0$ at $t = 0$, will be found at $\mathbf{r}$ at time t is defined as $G_s(rt)$. Then the self-part of the van Hove correlation function is given by

$$S_s(k\omega) = \frac{1}{2\pi}\int dt \int d\mathbf{r}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}G_s(rt). \tag{2.1}$$

We shall find it convenient to use the so-called intermediate scattering function, defined by

$$F_s(kt) = \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}G_s(rt) \tag{2.2}$$

and we then find the standard result

$$F_s(kt) = \langle e^{-i\mathbf{k}\cdot(\mathbf{r}_1(0)-\mathbf{r}_1(t))}\rangle \tag{2.3}$$

where the brackets denote the ensemble average. If we choose the x axis along the direction of $\mathbf{k}$, then we may write,

$$F_s(kt) = \langle e^{-ik(x_1(0)-x_1(t))}\rangle. \tag{2.4}$$

We now Taylor expand $x_1(t)$ as

$$x_1(t) = x_1(0)+tx_1^{(1)}(0)+\frac{t^2}{2!}x_1^{(2)}(0)+\ldots+\frac{t^n}{n!}x_1^{(n)}(0)+\ldots \tag{2.5}$$

$$F_s(kt) = \langle \prod_{n=1,2,\text{etc}} e^{[(ikt^n)/n!]x_1^{(n)}(0)}\rangle. \tag{2.6}$$

Clearly, the two sources of mass dependence in (2.6) are the derivatives $x_1^{(n)}(0)$ and the Maxwell-Boltzmann factor $e^{-p^2/2mk_BT}$ in the ensemble average.

It is evident that we can formally remove the mass dependence from the Maxwell-Boltzmann factor by transforming the momentum $\mathbf{p}_i$ of the ith particle into a quantity $\mathbf{q}_i$ defined by

$$\mathbf{q}_i = \frac{\mathbf{p}_i}{M^{1/2}}. \tag{2.7}$$

To deal with the dependence of $x_1^{(n)}(0)$ on mass, we proceed as follows:

We have, for $n = 1$,

$$x_1^{(1)}(0) = \left.\frac{dx_1}{dt}\right|_{t=0} = \frac{p_{x_1}(0)}{M} = \frac{q_{x_1}(0)}{M^{1/2}}, \tag{2.8}$$

while, from Newton's Law,

$$x_1^{(2)}(0) = -\frac{1}{M}\left.\frac{\partial \Phi_N}{\partial x_1}\right|_{t=0}. \tag{2.9}$$

Also

$$x_1^{(3)}(0) = -\frac{1}{M}\left\{\frac{d}{dt}\frac{\partial \Phi_N}{\partial x_1}\right\}_{t=0} = -\frac{1}{M}\sum_i\left\{\frac{dx_i}{dt}\frac{\partial^2 \Phi_N}{\partial x_1\,\partial x_i}\right\}_{t=0} ‡$$

$$= -\frac{1}{M^{3/2}}\sum_i\left\{q_{x_i}\frac{\partial^2 \Phi_N}{\partial x_1\,\partial x_i}\right\}_{t=0}. \tag{2.10}$$

Going back to (2.6), we see that $tx_1^{(1)}(0) \propto M^{-1/2}$, $t^2x_1^{(2)}(0) \propto M^{-1}$, $t^3x_1^{(3)}(0) \propto M^{-3/2}$, and clearly, since we are integrating over the q's and x's, no further mass dependence arises, at least at this order in the $x_1^{(n)}$'s. Similarly,

$$x_1^{(4)}(0) = -\frac{1}{M^{3/2}}\frac{d}{dt}\left.\left\{\sum_i q_{x_i}\frac{\partial^2 \Phi_N}{\partial x_1\,\partial x_i}\right\}\right|_{t=0}$$

$$= -\frac{1}{M^{3/2}}\sum_i\left.\frac{dq_{x_i}}{dt}\frac{\partial^2 \Phi_N}{\partial x_1\,\partial x_i}\right|_{t=0} - \frac{1}{M^{3/2}}\sum_i\left.\frac{q_{x_i}q_{x_j}}{M^{1/2}}\frac{\partial^2 \Phi_N}{\partial x_1\,\partial x_i\,\partial x_j}\right|_{t=0}. \tag{2.11}$$

Now

$$\frac{dq_x}{dt} = \frac{1}{M^{1/2}}\frac{dp_x}{dt} = -\frac{1}{M^{1/2}}\frac{\partial \Phi_N}{\partial x} \tag{2.12}$$

and hence $M^{1/2}(dq_x/dt) = -\partial\Phi_N/\partial x$, the latter quantity being mass independent on our assumptions. Putting $s = t/M^{1/2}$ we have $d/ds = M^{1/2}(d/dt)$ and then

$$\frac{dq_{x_1}}{ds} = -\frac{\partial \Phi_N}{dx_1}. \tag{2.13}$$

---

‡ Sums over i indicate summation over x, z and y.

Hence $dx/dt = p_x/M = q_x/M^{1/2}$, and $M^{1/2}(dx/dt) = q_x$, which introduces no mass dependence on integration. Generalizing the above argument to the nth time derivative we find

$$x_1^{(n)}(0) = -\frac{1}{M}\left(\frac{d}{dt}\right)^{n-2}\frac{\partial\Phi_N}{\partial x_1}\bigg|_{t=0} = -\frac{1}{M^{n/2}}\left(\frac{d}{ds}\right)^{n-2}\frac{\partial\Phi_N}{\partial x_1}\bigg|_{t=0}. \qquad (2.14)$$

Thus we have, that $x_1^{(n)}(0)$ always introduces a factor $M^{-n/2}$, which is the desired generalization of the previous results for $n \leqq 3$. But from (2.6) we see that the basic quantity appearing is $t^n x_1^{(n)}(0)$, and hence the combination $t^n M^{-n/2}$ appears in the general term. The integrals over the q's and x's lead to no mass dependent terms and hence it follows that $F_s(kt)$ is dependent simply on the variable $tM^{-1/2} = s$.

As an obvious check of our general result, we notice that a small t expansion of the exponentials in (2.6) would lead to the usual moment results, and from de Gennes work the second ω moment of $S_s(k\omega)$ is $\propto M^{-1}$, the fourth is $\propto M^{-2}$. This again confirms our result (the sixth moment is given by Nijboer and Rahman (1966), with the proportionality factor M^{-3}) as expected. Thus, our essential result may be summarized as

$$F_s(k, t, M, T) \equiv F_s(k, t/M^{1/2}, T). \qquad (2.15)$$

From (2.1) and (2.2) we have

$$S_s(k\omega) = \frac{1}{2\pi}\int e^{-i\omega t}\,F_s(k, t/m^{1/2}, T)\,dt = \frac{M^{1/2}}{2\pi}\int e^{-i\omega m M^{1/2}}\,F_s(k, s, T)\,ds \qquad (2.16)$$

where $s = t/M^{1/2}$. Hence

$$S_s(k\omega) = M^{1/2}f_s(k, \omega M^{1/2}, T) \qquad (2.17)$$

where f is a function defined by (2.13).

Finally, we note that the coefficient of self-diffusion D is given by

$$D = \operatorname*{Lt}_{\omega\to 0}\,\omega^2 \operatorname*{Lt}_{k\to 0}\frac{S_s(k\omega)}{k^2}. \qquad (2.18)$$

Substituting from (2.14) into (2.15) we find

$$D = \pi \operatorname*{Lt}_{\omega\to 0}\,\omega^2 M^{1/2} g(\omega M^{1/2}, T) \qquad (2.19)$$

where

$$g = \operatorname*{Lt}_{\omega\to 0}\frac{f(k, \omega M^{1/2}, T)}{k^2}.$$

Putting $\omega M^{1/2} = w$, we have finally

$$D = \pi \operatorname*{Lt}_{\omega \to 0} \frac{w^2}{M^{1/2}} g(w, T) = \frac{1}{M^{1/2}} h(T) \tag{2.20}$$

where this equation defines h in terms of g. While $h(T)$ depends, of course, on the specific force law, the mass dependence is exhibited explicitly in (2.20).

The argument, of course, is valid whatever the density ρ. The special cases treated by Enskog‡ for low density and by Longuet-Higgins and Pople (1956) for high density agree with the general result (2.20).

3. Generalization to Viscosity

The exact correlation function expression for the quantity $\frac{4}{3}\eta + \zeta$, where η and ζ are the shear and bulk viscosities respectively, is well known, and has the form

$$\frac{4}{3}\eta + \zeta = \frac{\pi M^2 \rho}{k_B T} \operatorname*{Lt}_{\omega \to 0} \omega^4 \operatorname*{Lt}_{k \to 0} \frac{S(k\omega)}{k^4} \tag{3.1}$$

where $S(k\omega)$ is the sum of the 'self' and 'distinct' correlation functions and ρ is the number density. Again, a generalization of the method of moments shows that $F(k, t, M, T)$, related to S through a transform which is the same as (2.16), has the form

$$F(k, t, m, T) = F(k, t/M^{1/2}, T). \tag{3.2}$$

This follows from noticing that

$$\begin{aligned} F(kt) &= \sum_i \langle \exp [ik\{x_i(t) - x_1(0)\}] \rangle \\ &= \sum_i \langle \exp [ik\{x_i(0) - x_1(0)\}] \exp [ik\{x_i(t) - x_i(0)\}] \rangle \\ &= \sum_i \left\langle \exp [ik\{x_i(0) - x_1(0)\}] \prod_j \exp \left\{ \frac{ikx_i^{(j)}(0)t^j}{j!} \right\} \right\rangle . \end{aligned} \tag{3.3}$$

The argument proceeds exactly as before and using (3.2) in (3.1) we find

$$\tfrac{4}{3}\eta + \zeta \propto M^{1/2} \tag{3.4}$$

---

‡ See, for example, Chapman and Cowling (1960).

This result, in fact, was obtained by Rowlinson (1953) from dimensional arguments. We see that its basic origin resides in the dependence on M of the intermediate scattering function shown in Eq. (3.2). Again, the approximate theory of Green (1952) satisfies the desired relation (3.4).

Similarly, we can show from the relevant correlation function expression for η that we expect the same $M^{1/2}$ dependence for the separate viscosity coefficients.

4. Frequency Spectra and Atomic Transport Coefficients in Liquid Metals

We wish now to consider how the previous theory relates to explicit results for D, η and ζ. Equation (2.18) focusses attention on the quantity

$$z(\omega) = \omega^2 \operatorname*{Lt}_{\omega\to 0} \frac{S_s(k\omega)}{k^2},$$

the so-called frequency spectrum. Rahman has calculated $z(\omega)$ for argon at 94°K and his results are shown in curve 1 of Fig. 1. Assuming these apply to A^{40}, curve 2 shows the explicit modifications which the present theory gives for A^{36}. The differences are significant and may be detectable experimentally.

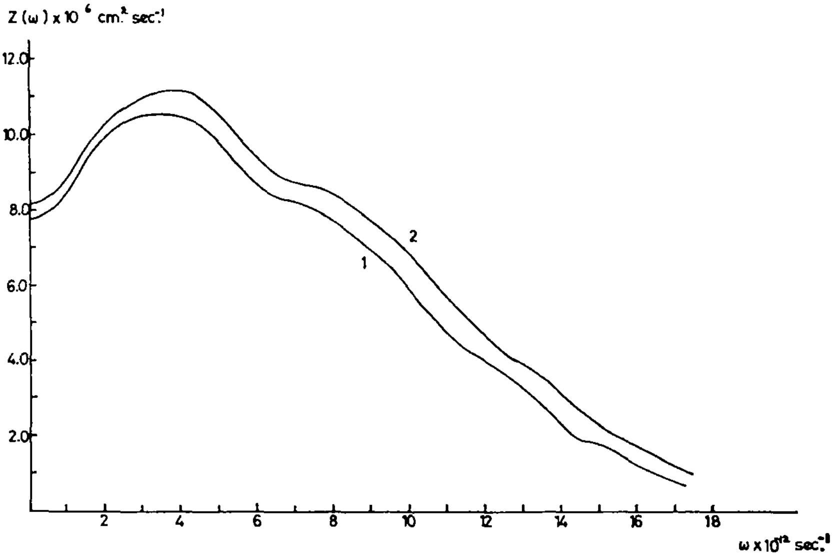

Figure 1. Frequency spectrum $z(\omega)$ for liquid argon at 94°K.
Curve 1 Rahman's result for A^{40}.
Curve 2 Result obtained for A^{36}.

4.1. *Debye frequency and diffusion in liquid metals*

We next contrast the above results for A with the frequency spectrum of liquid sodium at its melting point, as calculated by Paskin and Rahman (see Paskin, 1967). Figure 2 shows that this spectrum has a rather well defined frequency range and in fact, from Fig. 2, this essentially extends as far as the Debye frequency ω_d. From the well known sum rule

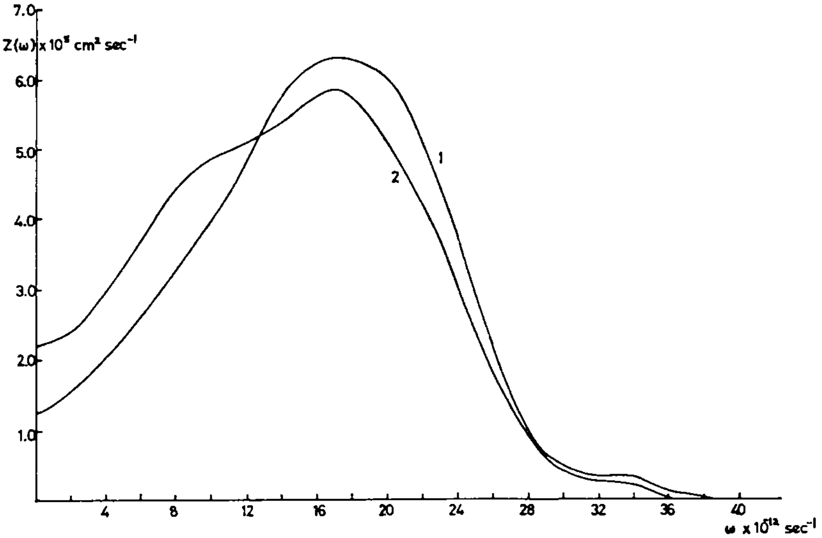

Figure 2. Frequency spectra $z(\omega)$ for liquid Na at the melting point. Curves 1 and 2 refer to two different (oscillatory) pairs potentials. Potential leading to curve 1 is twice as deep at the first minimum as potential generating curve 2. We have scaled curve 2 to have the same Debye frequency as curve 1.
[Note Added in Proof: The ordinates should be multiplied by 0.58]

$$\int_{-\infty}^{\infty} z(\omega)\,d\omega = \frac{k_B T}{M} \tag{4.1}$$

we see that the diffusion constant $D\ (=\pi z(0))$ at T_m will be, in order of magnitude, area/range, that is

$$D \sim \frac{k_B T_m}{M\omega_d}. \tag{4.2}$$

This formula is similar to one proposed recently by Nachtrieb (1967) using a quite different argument. Also, a recent discussion of Ascarelli and Paskin (1967), which does not make explicit mention of the role of the

Debye frequency, can be compared with (4.2) if we use the Lindemann relation that

$$\omega_d = \frac{\text{const}\, T_m^{1/2}}{M^{1/2}\Omega^{1/3}} \tag{4.3}$$

where Ω is the atomic volume. Then (4.2) shows that $DM^{1/2}/T_m^{1/2}\Omega^{1/3}$ is a constant and this is the result Ascarelli and Paskin also obtain. Their theory gives an estimate of the constant which is quantitative, whereas our result (4.2), as Table 1 shows, is at best semiquantitative.

TABLE 1 Diffusion constants at melting temperature

Liquid	$D_{\text{expt}} \times 10^5\,\text{cm}^2\,\text{sec}^{-1}$	$k_B T_m/M\omega_d \equiv D_{\text{calc}} \times 10^5$	$D_{\text{calc}}/D_{\text{expt}}$
Li	6.5	12.3	1.89
Na	4.05	6.4	1.58
K	3.90	5.5	1.41
Cu	3.96	4.0	1.01
Ag	2.55	3.4	1.33
Zn	2.02	1.98	0.98
Mg	1.17	1.04	0.89
In	1.66	2.13	1.28
Sn	2.05	1.04	0.51
Pb	2.19	2.07	0.94
A	1.53	1.71	1.12

However we believe the assumptions of their theory are best suited to liquid argon and ours to liquid metals (see, however, Appendix 1). We want to stress that (4.2) is consistent with D scaling as $M^{-1/2}$. This is because $\omega_d \propto M^{-1/2}$ and the melting temperature T_m is the same for different isotopes if the potential energy function is independent of M.

4.2. *Viscosities of liquid metals*

The above crude discussion, based on the Debye-like nature of the Paskin–Rahman frequency sqectrum for Na, is more interesting when applied to relate the viscosities of a variety of liquid metals at the melting point, as we shall now show. Returning to the formula (3.1), we see by analogy with the discussion of diffusion that the frequency function

$$s(\omega) = \omega^4 \operatorname*{Lt}_{k\to 0} \frac{S(k\omega)}{k^4}$$

plays a fundamental role in theories of viscosity. Unlike the frequency spectrum $z(\omega)$, we appear to have no quantitative knowledge of $s(\omega)$ for any liquid to date.

However, the argument given above for D depended only on the range of $z(\omega)$. Now the most primitive theory of $S(k\omega)$ builds from the structure factor $S(k)$ and the self-correlation function $S_s(k\omega)$. According to Vineyard (1958), we have as a first approximation to the complete correlation function

$$S(k\omega) \fallingdotseq S(k)S_s(k\omega) \tag{4.4}$$

If we examine (4.4) in detail, it does not have the correct behavior for $S(k\omega)$ for small k and ω, and hence cannot be used directly to evaluate the viscosity. However, it tells us that the frequency dependence of $S_s(k\omega)$ ought to be closely reflected in $S(k\omega)$ and, in particular, we infer that $s(\omega)$ extends in frequency out to the Debye value ω_d. We now have the sum rule

$$\int_{-\infty}^{\infty} s(\omega)\,d\omega = 3\left(\frac{k_B T}{M}\right)^2 + \frac{\rho k_B T}{2M^2}\int d\mathbf{r}\, g(r) x^2 \frac{\partial^2 \phi}{\partial x^2} \tag{4.5}$$

where $g(r)$ is the radial distribution function, $\phi(r)$ is the pair potential and ρ is the number density of atoms. Approximating the left-hand-side by $2s(0)\omega_d$ as before, we nevertheless appear to be left with a structure-dependent result.

4.2.1. Relation of structure dependence to $S(0)$

The Vineyard result (4.4) suggests strongly that the structure factor $S(k)$ ought to enter the viscosity rather directly. Since we are dealing with macroscopic properties, it can only be the long-wavelength limit $S(0)$ which can affect the theory.

We shall now show that, near the melting point, the second term on the right-hand-side of (4.5) is indeed intimately related to $S(0)$. From elastic constant arguments (see, for example, Egelstaff (1967)), we have

$$\frac{1}{9}\int d\mathbf{r}\, g(r) r^2 \frac{\partial^2 \phi}{\partial r^2} - \left\{\frac{2}{9}\int d\mathbf{r}\, g(r) r \frac{\partial \phi}{\partial r} - \frac{10 k_B T}{3\rho}\right\} \geqq \frac{2}{\rho^2 K_s} \tag{4.6}$$

where K_s is the adiabatic compressibility. The error involved in replacing the inequality by an equality is, we estimate, of the order of 15% at the melting point, from rough calculations. Furthermore, the integral involving $\partial\phi/\partial x$ can be estimated from the fluid pressure and is only a few % of the integral involving $\partial^2\phi/\partial x^2$.

Finally, the ratio of the specific heats γ is near to unity for liquid metals at the melting point (for example, for Zn, $\gamma \doteqdot 1.25$) and, within the overall accuracy of the present argument, we can replace K_s by the isothermal compressibility K_T. Then we have from (4.6)

$$\frac{5}{9}\int d\mathbf{r}\, g(r) x^2 \frac{\partial^2\phi}{\partial x^2} \approx \frac{2}{\rho^2 K_T}. \tag{4.7}$$

But from well known density fluctuation theory

$$S(0) = \rho k_B T K_T \tag{4.8}$$

and hence from (4.7)

$$\frac{1}{2}\int d\mathbf{r}\, g(r) x^2 \frac{\partial^2\phi}{\partial x^2} \approx \frac{9 k_B T}{5\rho S(0)}. \tag{4.9}$$

This establishes the intimate connection between the viscosities and $S(0)$ which we had anticipated qualitatively from the Vineyard result (4.3). Using (3.1), (4.4) and (4.8), and noting that $S(0)$ at the melting point T_m for liquid metals lies in the range 0.01 to 0.03, we find, at T_m

$$\left.\frac{4}{3}\eta + \zeta\right|_{T_m} \approx \frac{9\pi}{10}\frac{\rho k_B T_m}{\omega_d S_{T_m}(0)}, \tag{4.10}$$

where we have neglected the first term in (4.5) as $\frac{1}{30}-\frac{1}{100}$ times the second term. Experimental results for the bulk viscosity are not very reliable, and we choose therefore to make the comparison with experiment via the shear viscosity. This is related to the stress correlation function, and using the fact again that this has a frequency range equal to the Debye frequency, an identical argument to the above leads to

$$\eta \approx \frac{3\pi}{10}\frac{\rho k_B T_m}{\omega_d S_{T_m}(0)}. \tag{4.11}$$

This formula for η appears to be new and, in particular, the dependence on $S(0)$ has not been derived previously. However, if we neglect the spread in $S_{T_m}(0)$ by using Lindemann's law in (4.11)‡, then we find

$$\eta = \text{const}\,\frac{T^{1/2} M^{1/2}}{\Omega^{2/3}} \tag{4.12}$$

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‡ A derivation of Lindemann's law for metals which leads to an approximate formula for Lindemann's constant has been given recently by Enderby and March (1966).

and this formula was in fact given earlier by Andrade (1934), from a kinetic theory argument. His constant is adopted in comparing the formula with experiment in Table 2. Our constant is an underestimate by a factor between 2 and 3, and tells us that the frequency function determining the shear viscosity, in contrast to $z(\omega)$ of Fig. 2, probably has quite a pronounced maximum at the origin, before falling to zero around ω_d.

TABLE 2 Shear viscosities of liquids at melting point

Liquid	Expt (poise)	Theory $\propto (MT_m)^{1/2}\Omega^{-2/3}$
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	0.041	0.042
Ag	0.039	0.041
Au	0.054	0.058
In	0.019	0.020
Sn	0.021	0.021
Ne	0.0016	0.0019
A	0.0025	0.0036
Kr	0.0039	0.0055
Xe	0.0052	0.0068

There is quite remarkable correlation for the metals.

One final comment on the existence of a rather well-defined Debye frequency in liquid metals seems worth making. It is that the velocity auto-correlation function for A is different in character from that in Na, as can be seen directly from the work of Rahman (1964) and Paskin (1967). The results of these workers show that there are oscillations in the case of Na, whereas there are none following the first node in A. The oscillations in Na come from the well-defined 'edge' on $z(\omega)$, the oscillations being damped with a damping factor like $e^{-\Delta\omega t}$ where $\Delta\omega$ is a measure of the "blurring" of the Debye edge. For A, in contrast, the oscillations are not present because the edge is completely smeared out. The wavelength of the oscillations in Na gives a rough measure of ω_d.

5. Relation between D and η

If we combine formulae (4.2) and (4.11), we find

$$\frac{\eta}{\rho} \sim \frac{MD}{S_{T_m}(0)}\,. \tag{5.1}$$

It is well known that, for a dilute hard sphere gas,

$$\frac{\eta}{\rho} = MD \tag{5.2}$$

and it would seem at first sight that (5.1) is a natural generalization of (5.2), since the structure factor $S(k) \rightarrow 1$ for a dilute gas. This argument is too naive, and until the temperature dependence of $z(\omega)$ and $s(\omega)$ has been studied well above the melting point, the present arguments should be restricted to T_m. However, the quantity $MD\rho/\eta$ is tabulated for liquid metals in Table 3, and is quite constant, consistent with Lindemann's law for the constancy of $S_{T_m}(0)$.

TABLE 3 Experimental results for $MD\rho/\eta$ at melting point

Metal	$D \times 10^5\,\mathrm{cm^2 sec^{-1}}$	η poise	$MD\rho/\eta$
Li	6.5	0.0060	0.0056
Na	4.05	0.0069	0.0056
K	3.90	0.0054	0.0061
Cu	3.96	0.041	0.0082
Ag	2.55	0.039	0.0065
In	1.66	0.019	0.0064
Sn	2.05	0.021	0.0071
Pb	2.19	0.022	0.0112

Quantitative agreement with (5.1) cannot be expected, because of the lack of knowledge of the precise constants to take in (4.2) and (4.11).

All this has prompted us to enquire just how the detailed structure dependence to be expected from one metal to the next will affect the theory. A general argument, depending though on the mass scaling of the Debye frequency, is given in Appendix 1. This makes it more clear why, though there is no Debye-like frequency spectrum for liquid argon, the formulae for D and η still work tolerably well.‡

6. Viscosity of Li^6 and Li^7

As discussed in Section 1, experimental results for η are available for Li^6 and Li^7. The ratio of the viscosities is more like the ratio of the masses to the power $\frac{5}{2}$ at the melting point, reducing to something like a power $\frac{3}{2}$ at about 100°C above the melting point. This is in contrast to the present theory, which would give simply a temperature independent factor equal to the ratio of the masses to the power $\frac{1}{2}$. This is the more worrying because the melting temperatures of Li^6 and Li^7 are the same to within a degree or so. The Michigan group who made the measurements suggested the existence of quantal effects, but these are hard to understand in terms of the ratio of the Debye temperature to the melting temperature of Li.

It would clearly be interesting now if methods could be devised to measure the frequency spectrum $z(\omega)$ for the two isotopes, to see if substantial deviations from our theory exist also away from $\omega = 0$. However, Li^6 absorbs neutrons very strongly and a direct attack on this problem seems precluded with present fluxes. Experiments on other light isotopes to measure frequency spectra would be of considerable interest.

In connection with the puzzle over these isotopes, we have thought it also worthwhile to give a discussion of neutron scattering to be expected from a binary isotopic mixture on the present theory, from a knowledge of the scattering function for a pure isotope. Details are recorded in Appendix 2, where the incoherent scattering from a mixture of two isotopes A and B is calculated to first-order in an expansion in M_A-M_B.

7. Conclusion

The present paper shows that the results on the viscosities of Li^6 and Li^7 cannot be explained without giving up one of three basic assumptions:

(i) Classical equations of motion.
(ii) Kubo formulae for transport coefficients.
(iii) Potential energy function independent of atomic mass.

‡ The ratio of specific heats γ must be retained for argon, however.

The correlation of the first-order formula (4.11) for the shear viscosity at the melting point with experiment suggests that the frequency dependent function determining η as the zero-frequency limit, should scale with the Debye frequency quite accurately within a group. Furthermore, the same should be true, though less precisely, for the frequency spectrum $z(\omega)$. Experiments are suggested using isotopes which might help to clarify the situation regarding Li^6 and Li^7 as well as to test some of the other predictions in the present paper.

Appendix 1

Scaling of frequency spectrum with Debye frequency

The fact that a formula such as (4.2) for D has some success suggested to us that a more general argument might exist. This would have to be consistent with the isotopic mass scaling, the frequency ω always appearing with $M^{1/2}$. Now the Debye frequency $\omega_d \propto M^{-1/2}$ and this suggests that the basic variable in the frequency spectrum $z(\omega)$ should be ω/ω_d. Furthermore, we might argue that, within a group, the major dependence of $z(\omega)$ on the force law is accounted for via ω_d and then we can write

$$z(\omega)/z(0) = Z\left(\frac{\omega}{\omega_d}\right) \Big/ Z(0). \qquad \text{(A1.1)}$$

We then find immediately that

$$\int_{-\infty}^{\infty} \frac{z(\omega)}{z(0)} d\omega = \omega_d \int_{-\infty}^{\infty} \frac{Z(x)}{Z(0)} dx \qquad \text{(A1.2)}$$

and if, as assumed above, $Z(x)$ has approximately the same form throughout a group, then

$$\int_{-\infty}^{\infty} Z(x) \frac{dx}{Z(0)}$$

is clearly a numerical constant and the form (4.2) is regained. The constant varies somewhat from one group to another, as Table 2 shows, and can only be obtained from a knowledge of the frequency spectrum within a group. The above argument holds also for the frequency function involved in the shear viscosity, which, pragmatically, appears to scale more systematically with the Debye frequency than $z(\omega)$.

We stress that the above argument synthesises the apparently very different approaches adopted by Ascarelli and Paskin (1968) and by us. Notwithstanding the very different forms of $z(\omega)$ for A and Na, a scaling law with ω_d within a group gives back the essential results. In one sense, this is disappointing, because it gives us little check on the physical validity of a particular model. We reiterate though that a reasonably sharp edge on the frequency spectrum appears likely for metals, whereas a very blurred edge occurs in A, and presumably the other rare gases.

Appendix 2

Neutron scattering from an isotopic mixture (or binary alloy)

As shown by van Hove (1954), the differential scattering cross-section for neutrons is given by

$$\frac{d^2\sigma}{d\Omega\, d\omega} = N\frac{k}{k_0}\frac{1}{2\pi}\int e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\,\Gamma(\mathbf{r}t)\,d\mathbf{r}\,dt \tag{A2.1}$$

where, in classical theory,

$$\Gamma(\mathbf{r}t) = N^{-1}\left\langle\sum_{ij}^{N} a_i a_j\,\delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}_j(t))\right\rangle \tag{A2.2}$$

with the a's as scattering lengths.

For a binary A–B alloy, we may write (A2.2) in the form

$$\Gamma(\mathbf{r}t) = \sum_{pq}^{AB}\Gamma_{pq}(\mathbf{r}t) \tag{A2.3}$$

where we have explicitly

$$\Gamma_{AA}(\mathbf{r}t) = N^{-1}\left\langle\sum_{i}^{N_A}\sum_{j}^{N_A} a_A^2\,\delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}_j(t))\right\rangle$$

$$\Gamma_{AB}(\mathbf{r}t) = N^{-1}\left\langle\sum_{i}^{N_A}\sum_{j}^{N_B} a_A a_B\,\delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}_j(t))\right\rangle \tag{A2.4}$$

with similar expression for $\Gamma_{BA}(\mathbf{r}t)$ and $\Gamma_{BB}(\mathbf{r}t)$, where $\sum_{i}^{N_A}$ implies summation over atoms of species A only, etc.

It will prove convenient to write

$$\left.\begin{aligned}\Gamma_{AA}(\mathbf{r}t) &= a_A^2\,G_{AA}(\mathbf{r}t)\\ \Gamma_{AB}(\mathbf{r}t) &= a_A a_B\,G_{AB}(\mathbf{r}t)\text{ etc.}\end{aligned}\right\}, \tag{A2.5}$$

and to define the self-correlation functions G_{AAS} and G_{BBS} by

$$\begin{aligned}G_{AAS}(\mathbf{r}t) &= N^{-1}\left\langle\sum_{i}^{N_A}\delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}_i(t))\right\rangle\\ G_{BBS}(\mathbf{r}t) &= N^{-1}\left\langle\sum_{i}^{N_B}\delta(\mathbf{r}+\mathbf{r}_i(0)-\mathbf{r}_i(t))\right\rangle\end{aligned} \tag{A2.6}$$

A2.1 Partial intermediate scattering functions

As in the monatomic case, it is convenient to introduce intermediate scattering functions. This we do through the result

$$F_{AA}(\mathbf{k}t) = \int e^{i\mathbf{k}\cdot\mathbf{r}} G_{AA}(\mathbf{r}t)\, d\mathbf{r} \tag{A2.7}$$

and hence we obtain

$$F_{AA}(\mathbf{k}t) = \frac{N_A}{N}\left\langle \sum_{j=1}^{N_A} \exp[i\mathbf{k}\cdot\{\mathbf{r}_j(t) - \mathbf{r}_A(0)\}]\right\rangle \tag{A2.8}$$

Similarly

$$F_{AB}(\mathbf{k}t) = \frac{N_A}{N}\left\langle \sum_{j=1}^{N_B} \exp[i\mathbf{k}\cdot\{\mathbf{r}_j(t) - \mathbf{r}_A(0)\}]\right\rangle \tag{A2.9}$$

and

$$F_{AAS}(\mathbf{k}t) = \frac{N_A}{N}\langle \exp[i\mathbf{k}\cdot\{\mathbf{r}_A(t) - \mathbf{r}_A(0)\}]\rangle . \tag{A2.10}$$

The van Hove functions may be defined by

$$S_{AA}(\mathbf{k}\omega) = \frac{1}{2\pi}\int e^{-i\omega t} F_{AA}(kt)\, dt, \tag{A2.11}$$

etc.

A.22 Mean mass approximation for isotopic mixture

At this stage we introduce a mean mass $\overline{M}$, given by

$$\overline{M} = c_A M_A + c_B M_B \tag{A2.12}$$

where c_A and c_B are the concentrations of masses M_A and M_B respectively. An expansion parameter δ is then used,‡ given by

$$\delta = \frac{M_A - M_B}{\overline{M}} . \tag{A2.13}$$

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‡ The use of $\overline{M}$ and δ was suggested to us by Dr. P. Schofield.

Developing F_{AAS} in (A2.10) in terms of $\overline{M}$ and δ, and correspondingly for the B atoms, $\Gamma(\mathbf{r}t)$ in (A2.3) can be obtained. Hence, from (A2.1) the differential cross-section for incoherent scattering can then be written in the form, using an obvious notation,

$$\left[\frac{d^2\sigma}{d\Omega\, d\omega}\right]_{\text{inc}} = \frac{Nk}{k_0}\cdot\frac{1}{2\pi}[c_A a_A^2 + c_B a_B^2]\, S_{S\overline{M}}(k, \omega) + G(\overline{M}) c_A c_B [a_A^2 - a_B^2]\,\delta + O(\delta^2). \tag{A2.14}$$

$G(\overline{M})$ depends on the mean mass and cannot be calculated explicitly without appeal to a specific model. It would be of obvious interest to test the validity of the "mean mass" approximation, because the theory of this paper gives $S_{S\overline{M}}$ immediately in terms of S_{SM_A} or S_{SM_B}. If one chooses an isotopic mixture so as to minimize the coherent scattering, it might be possible to test (A2.14). However, to estimate the $O(\delta)$ term, a possible procedure might be to do an experiment with three isotopes in pairs, such that $\overline{M}$ remained constant and hence to eliminate $G(\overline{M})$. But the magnitude of the coherent scattering might then constitute a problem.

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