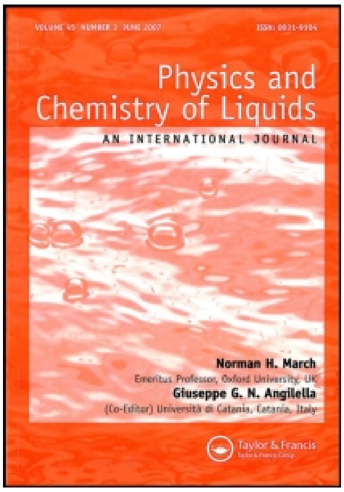

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INVERSE SHEAR VISCOSITY (FLUIDITY) SCALED WITH MELTING POINT PROPERTIES: ALMOST 'UNIVERSAL' BEHAVIOUR OF HEAVIER ALKALIS

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Some numerical considerations relating to the potential of mean force at the melting point of Rb metal are first presented, which argue against the existence of a well defined activation energy for the shear viscosity of this liquid.

Therefore, a scaling approach is developed, based on a well established formula for the viscosity η_m of sp liquid metals at their melting points T_m. This approach is shown to lead to an 'almost' universal plot of scaled fluidity $\eta^{-1}\eta_m$ against $(T/T_m)^{1/2}$ for the liquid alkali metals, excluding Li. This metal is anomalous because it is a strong scattering liquid, in marked contrast to the other alkali metals.

Keywords: Viscosity; melting temperature; scaling

1. BACKGROUND

There has been a lot of attention, from both experiment and theory, given to the problem of the temperature dependence of the shear viscosity η for, say, the sp liquid metals such as the alkalis. A survey of early work is presented, for example in the book by Faber [1].

At the melting temperature T_m, a formula has emerged which embodies all the trends of $\eta(T_m)$ through a variety of simple metals. This formula expresses $\eta(T_m)$ as

$$\eta(T_m) = \text{const}\ T_m^{1/2} M^{1/2} V_m^{-2/3}, \tag{1.1}$$

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*Corresponding author.

where M is the ionic mass and V_m is the atomic volume at the melting temperature. Provided the constant in equation (1.1) is fixed, say for Sn, then Table I below shows that equation (1.1) has all the trends of $\eta(T_m)$ through a variety of simple metals, including the closed d shell noble metals. A brief summary of the argument due to Brown and March [2] leading to equation (1.1) is presented in the Appendix, starting from the Green-Kubo formula for the longitudinal viscosity η_l, defined by

$$\eta_l = \frac{4}{3}\eta + \xi, \tag{1.2}$$

where ξ is the bulk viscosity. Little is known from experiment about the bulk viscosity of liquid metals, but current theoretical arguments indicate that it is contributing very little to η_l in equation (1.2) compared with $(4/3)\eta$. Needless to say, this point needs testing in the future by careful experimental studies.

The aim of the present work is to embed the formula (1.1) into a treatment of the temperature dependence of the shear viscosity η. This we shall attempt to do by scaling, for the liquid alkali metals specifically, over a wide temperature range. However, before doing so, we shall consider, rather briefly for liquid Rb near T_m, whether there is any evidence for a 'natural' activation energy to appear in η, from known features of the liquid structure factor $S(q)$, or what is essentially its Fourier transform, the pair distribution function $g(r)$.

2. IS THERE A NATURAL ACTIVATION ENERGY FROM THE POTENTIAL OF MEAN FORCE?: EXAMPLE OF LIQUID Rb NEAR MELTING

Since the ions in liquid metals near melting can be treated classically, let us write the Boltzmann form for $g(r)$ as

$$g(r) = \exp(-\beta U(r, \beta)); \quad \beta = (k_B T)^{-1} \tag{2.1}$$

where $U(r, \beta)$ is the potential of mean force. Some early workers suggested, by relating shear viscosity to static structure (plus pair potential, say), that an activated behaviour might therefore arise from the form (2.1) at some specific characteristic value of r (say the hard core diameter).

To explore this, we have been motivated to examine, in the light of equation (1.1) involving $T_m^{1/2}$, the Verlet rule for freezing, which states that liquids will freeze when the maximum of structure factor $S(q_{\max})$ reaches a value ≈ 2.7. Thus in Figure 1, we have plotted for suitable data on liquid Rb near melting [3] the integrand $I(r)$ in

$$S(q_{\max}, T_m) = 1 + \int_0^{\infty} I(r)\,dr \tag{2.2}$$

Precisely, $I(r)$ is given by

$$I(r) = 4\pi n\,(g(r) - 1)\,r^2\,\frac{\sin(q_{\max} r)}{q_{\max} r} \tag{2.3}$$

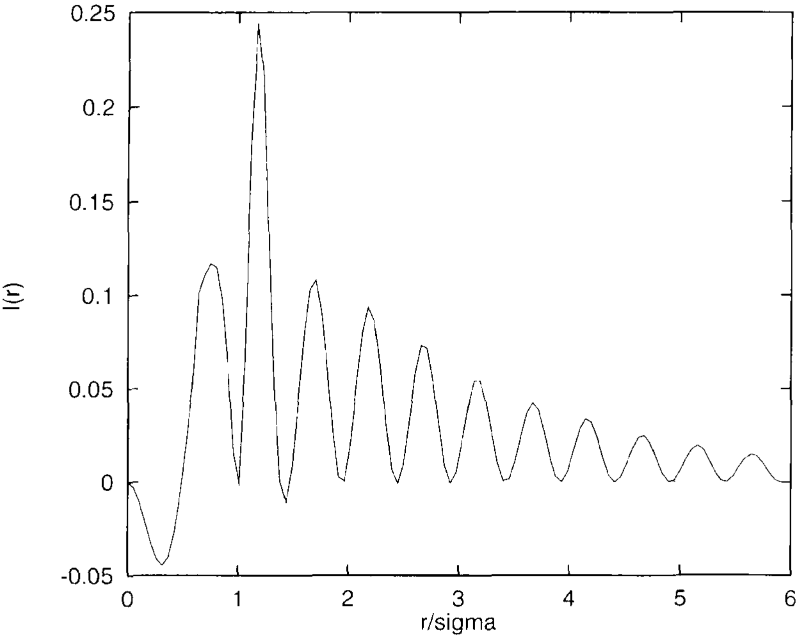

FIGURE 1 Integrand $I(r)$ of r space formula (2.2) for $S(q_{\max})$ for liquid Rb near melting. "sigma" represents the position of first zero of the potential with its value equal to 4.19786 Angstrom.

It is clear that, though $S(q_{\max}, T_m) \approx 2.7$ determines the melting temperature T_m, no particular value of r is especially significant and this point is pressed in Figure 2, where essentially $1 + \int_0^{r_{\max}} I(r)\,dr$ is plotted as a function of $r_{\max}$. The convergence towards the 'Verlet limit' is evidently slow in this r-space representation.

In the light of Figures 1 and 2, there seems to us no evidence to suppose that any well defined activation energy exists for Rb near melting (and presumably not for the other alkalis under similar thermodynamic conditions). Therefore, we turn immediately below to a quite different approach, based on scaling, in which we seek to embed the successful formula (1.1) for the shear viscosity η_m at the melting temperature T_m into a representation of the fluidity η^{-1} as a function of temperature.

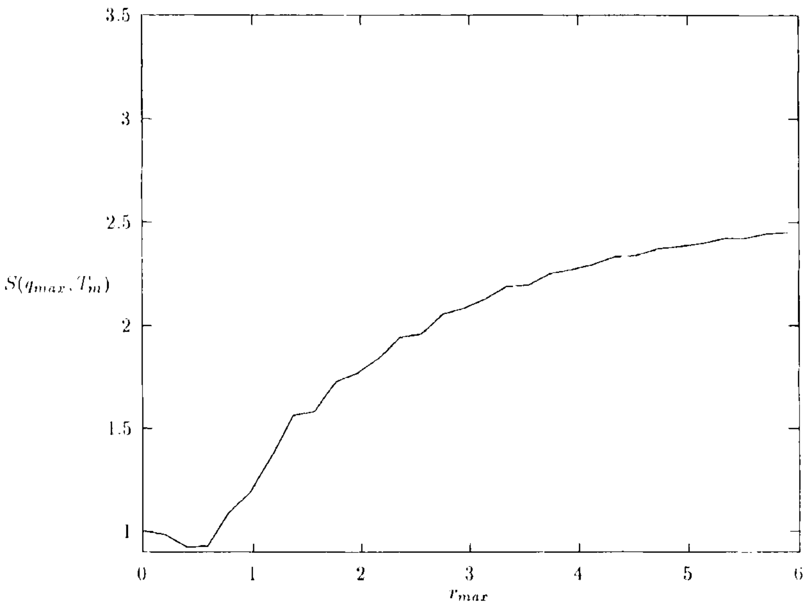

FIGURE 2 Approach to Verlet limit (approximately) as a function of maximum range $r_{\max}$ of integration $r = 0$ to $r_{\max}$ using integrand of Figure 1 for liquid Rb near melting.

3. SCALED FLUIDITY IN TERMS OF SCALED THERMAL IONIC MOMENTUM, WITH SPECIFIC REFERENCE TO LIQUID ALKALIS

It will be useful below, motivated by the appearance in equation (1.1) of the quantity $(T_m M)^{(1/2)}$, with M the ionic mass, to work with the thermal ionic momentum, p_t, as the independent variable. Specifically we will define p_t precisely for the present purposes as

$$p_t = (Mk_BT)^{1/2}, \tag{3.1}$$

with the value p_{tm} corresponding to the melting temperature T_m.

We now define scaled quantities from 'fluidity' η^{-1} and temperature as

$$F = \eta^{-1} M^{1/2} T_m^{1/2} V_m^{-2/3} \tag{3.2}$$

and reduced thermal ionic momentum s by

$$s = \frac{p_t}{p_{tm}} = \left(\frac{T}{T_m}\right)^{1/2}, \tag{3.3}$$

where in the final part of equation (3.3) we have utilized the definition (3.1).

3.1. Taylor Expansion of Scaled Fluidity $F(s)$ Around Reduced Melting Temperature $s = 1$

We now utilize equations (1.1), (3.2) and (3.3) to develop $F(s)$ by Taylor expanding around $s = 1$, which from equation (3.3) corresponds to $T = T_m$. We have then

$$F(s) = F(1) + (s-1)\left(\frac{dF}{ds}\right)_{s=1} + \ldots \tag{3.4}$$

From equation (3.2), $F(1)$ is simply the constant appearing in equation (1.1). The interest then is evidently in the range of applicability of equation (3.4), and within that range the form of $(dF/ds)_{s=1}$.

To address these issues, we consider in the following section the experimental data for five liquid alkali metals Li-Cs.

4. CONFRONTATION OF EQUATION (3.4) WITH EXPERIMENTS ON LIQUID ALKALI METALS

Since s in equation (3.4) is simply $(T/T_m)^{1/2}$ from equation (3.3), we have used this latter quantity as the independent variable in Figure 3. The experimental data is plotted in the form of scaled fluidity $F(s)$ defined explicitly in equation (3.2) versus s for alkali metals.

The two remarkable features of this plot are (i) the linearity in s over a wide range of temperature and (ii) the 'almost universal' curve for the three heaviest alkalis K, Rb and Cs. For these 3 metals the slope

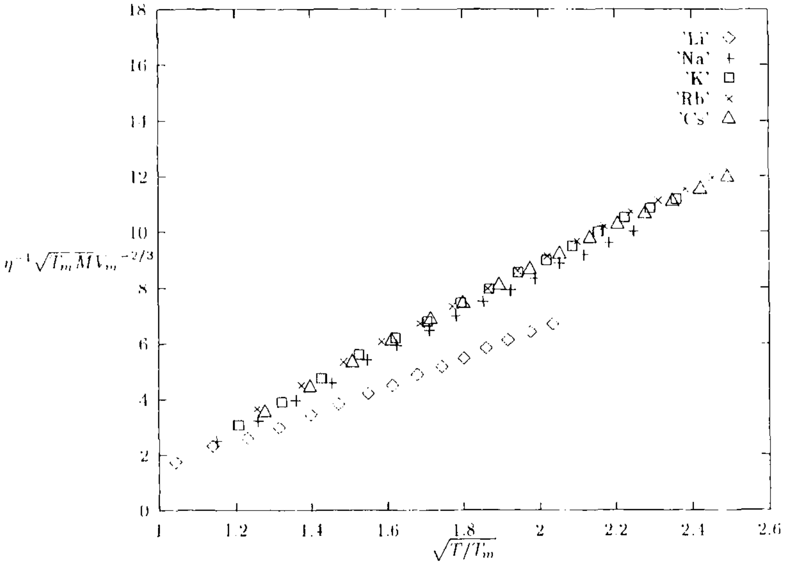

FIGURE 3 Scaled fluidity $F \propto \eta^{-1}(T)\eta(T_m)$ vs (T/T_m) where $\eta(T_m)$ is replaced by equation (1.1), from experiment for the five alkali metals at saturated vapour pressure. η in m poise, V_m in cm^{3}gm/atom, M is atomic mass and T in Kelvin. Li, however has an appreciably lower slope than the other alkali metals. This is connected with the nearly-free electron like character of heavier alkalis whereas Li liquid metal is characterized by strong electron-ion interaction. Nevertheless the linearity of the scaled fluidity plot vs $(T/T_m)^{1/2}$ still remains.

$(dF/ds)_{s=1}$ in equation (3.4) has the numerical value

$$F(1)^{-1}\,(dF/ds)_{s=1} = 4.42 \tag{4.1}$$

For Na, while equation (4.1) is already useful, the best slope to fit the data is reduced to 4.35 from the value in equation (4.1). But for Li, the value (4.1) is not appropriate, the slope being reduced by a factor ≈ 2/3.

It is clear that Li is the salient exception from the 'almost universal' behaviour exhibited in the upper pencil of the curves in Figure 3. Our present interpretation of the exceptional behaviour of liquid Li is that while the heavier alkali metals are characterised by weak electron-ion interaction, the absence of p electrons in Li core is responsible for strong scattering of itinerant electrons in the sp conduction band. More speculatively, it is also possible, drawing on the experiments of shear viscosity on isotopes of Li by Ban *et al.* [4], that quantal effects are important in liquid Li. However, we do not expect such effects to explain more than a small fraction of the large difference in slope $(dF/ds)_{s=1}$ of the plots in Figure 3 between liquid Li and the heavier liquid alkali metals.

5. SUMMARY AND FUTURE DIRECTIONS

The main achievements of the present study are summarised in the 'scaled fluidity' plot of Figure 3. This plot embodies the melting point formula (1.1) for shear viscosity on the ordinate $F(s)$ and a reduced thermal ionic momentum $s = (p_t/p_{tm})^{1/2} = (T/T_m)^{1/2}$ along the abcissa. We note here that in their review on atomic transport in liquids, Gaskell *et al.* [5] plot in their Figure 2.2 $\eta^{-1}(T)$ *vs* $T^{1/2}$. The 5 alkalis have clearly different slopes, whereas after scaling the present Figure 3 shows that experimental data for the heavier alkalis lies on an 'almost universal' curve. The plot made here was in fact, motivated by the Taylor expansion in the reduced thermal ionic momentum, though it remains to explain why the slopes for the heavier alkalis are almost the same. The scaling of self-diffusion coefficients for expanded Rb and Cs has already been noted [6] along the liquid vapour co-existence curve.

We want to caution that the present work is about liquid alkalis. It must not be assumed that in general for sp metals a similar plot to that in Figure 3 will necessarily represent the experimental fluidity data. For example previous workers have noted for liquid Pb that there is experimental evidence in favour of an activated process. This may suggest that the type of analysis made of static structure factor for liquid Rb in section 2 above will have to be generalised for Pb. This point needs further study.

The present work also needs generalizing to treat binary alloys of simple sp liquid metals. Here, three partial structure factors are involved, and these are now known for a very limited number of systems using neutron studies with isotopic enrichment. There is a whole area here that seems ripe now for further studies of the mechanism of atomic transport in metallic mixtures.

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APPENDIX

Green Kubo formulae and Moment Arguments Applied to Longitudinal Viscosity

Let us first summarise the nature of the argument by which Brown and March [2] obtained equation (1.1) from the so- called Green-Kubo formula for the longitudinal viscosity η_l defined in equation (1.2). This formula reads

$$\eta_l = \frac{\pi M^2 \rho}{k_B T} \lim_{\omega \to 0} \omega^4 \lim_{k \to 0} \frac{S(k,\omega)}{k^4}, \tag{A1}$$

where ρ is the ionic number density and $S(k, \omega)$ is the liquid dynamical structure factor, such that

$$S(k) = \int_{-\infty}^{\infty} S(k,\omega)\, d\omega. \tag{A2}$$

Brown and March define the frequency function

$$s_\eta(\omega) = \omega^4 \lim_{k \to 0} \frac{S(k,\omega)}{k^4} \tag{A3}$$

and it then follows directly from (A1) and (A3) that

$$s_\eta(o) = k_B T \eta_l / \pi M^2 \rho \tag{A4}$$

A1. Melting Point Consideration for Liquid Metals

Brown and March argued that at the melting temperature T_m, $s_\eta(\omega)$ is non zero essentially in the range between $-\omega_d$ and ω_d, where ω_d denotes the Debye frequency. Assuming further that the frequency spectrum $s_\eta(\omega)$ is usefully approximated by a rectangle, then

$$\int_{-\infty}^{\infty} s_\eta(\omega)\, d\omega \approx \frac{2\omega_d k_B T_m \eta_l (T_m)}{\pi M^2 \rho_m}, \tag{A5}$$

which relates $\eta_l(T_m)$ to the 4th moment

$$< \omega^4 > = \int_{-\infty}^{\infty} \omega^4 S(k,\omega)\, d\omega \tag{A6}$$

in the long wavelength $k \to 0$ limit. Evaluating this $k \to 0$ limit of $<\omega^4>$ by approximate methods led Brown and March [2] to the result

$$\eta_l \approx \frac{\rho_m k_B T_m}{10\omega_d S_{T_m}(0)} \tag{A7}$$

where ρ_m is the ionic density at melting temperature T_m and $S_{T_m}(0)$ is long wavelength limit of the liquid structure factor $S(k)$ at T_m. Using the Lindemann relation

$$\omega_d = \frac{\text{constant } T_m^{1/2}}{M^{1/2} V_m^{1/3}} \tag{A8}$$

plus the constancy of $S_{T_m}(0)$ for liquid metals at T_m (see also Bhatia and March [7]) equation (1.1) for η_m is recovered, provided the bulk viscosity ξ_m is small compared to $(4/3)\eta_m$. Equation. (1.1) is compared with experiment in Table I.

Brown and March [2] also noted that provided frequency spectra scale with Debye frequency ω_d, equation (1.1) can be recovered from the Green-Kubo formalism without further assumptions. Andrade [8] earlier obtained the form (1.1) by kinetic theory arguments which Faber [1] in his book terms unconvincing.

A2. Possible Generalization of Viscosity Arguments Away from the Melting Temperature

It is tempting to assume some parts of the above arguments will continue to apply for $T \geq T_m$. The Feynman collective mode model, known to be semiquantitative for liquid Rb (see Matthai and March [9]) near the melting point, allows one to compute (A6), since

$$S(k,\omega) = S(k)\,\frac{1}{2}\,[\delta(\omega - \omega(k)) + \delta(\omega + \omega(k))], \tag{A9}$$

TABLE I Experimental data for shear viscosity (poise) at melting temperature T_m for variety of sp liquid metals plus noble metals

	Li	*Na*	*K*	*Rb*	*Cs*	*Cu*	*Ag*	*Au*	*In*	*Sn*
Expt.	0.0060	0.0069	0.0054	0.0067	0.0069	0.041	0.039	0.054	0.019	0.021
Eqn. (1.1)	0.0056	0.0062	0.0050	0.0062	0.0066	0.042	0.041	0.058	0.020	0.021

N.B. Constant in equation (1.1) is determined by fitting to value of shear viscosity at melting temperature for Sn. All the trends in the experimental values are then reproduced correctly by the formula (1.1).

with

$$\omega^2(k) = \frac{k^2 k_B T}{MS(k)}. \tag{A10}$$

Equation (A6) and (A9) provide

$$< \omega^4 > = \omega^4(k)\, S(k) = \frac{k^4}{S(k)} \left(\frac{k_B T}{M} \right)^2. \tag{A11}$$

Utilizing equations (A3) and (A11) and assuming some frequency cut-off for the spectra say $\omega_{\max}$ which is now temperature dependent we obtain

$$s_l(0) = \frac{1}{2\omega_{\max} S(0)} \left(\frac{k_B T}{M} \right)^2 \tag{A12}$$

Using the above equation and (A4) we find

$$\eta_l = \frac{\rho k_B T}{S(0)\, \omega_{\max}} \tag{A13}$$

Taking this result at T_m and using $S_{T_m}(0) \approx \text{const.}, \omega_{\max} = \omega_D$, we recover equation (1.1). For $T > T_m$ one finds from equation (A10) for small value of 'k' $\sim k_{\max}$ that ω will be maximum when $S(k)$ is proportional to k^2. This sets

$$\eta_l = \text{const.}\rho \frac{(k_B T)^{1/2}}{S(0)} \tag{A14}$$

Knowing that $S(0) = \rho k_B T K_T$; K_T being the isothermal compressibility, one finds for a given density that the longitudinal viscosity varies inversely as the square root of temperature, in accord with the experimental data shown in Figure 3.