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### Hydrodynamic Modes, Density Fluctuations and Transport Coefficients in Liquid Metals

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# HYDRODYNAMIC MODES, DENSITY FLUCTUATIONS AND TRANSPORT COEFFICIENTS IN LIQUID METALS

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From the theory of long-time tails in the velocity autocorrelation function, a definition of hydrodynamic modes is proposed in the frequency spectrum  $g(\omega) = \omega^2 \lim_{k \rightarrow 0} S_s(k, \omega)/k^2$  where  $S_s$  is the self function, accessible by incoherent neutron scattering. Consequences for the relation between self-diffusion coefficient  $D$  and shear viscosity  $\eta$  are presented.

KEY WORDS: Shear viscosity, self diffusion, long-time tail.

That the self-diffusion coefficient  $D$  and shear viscosity  $\eta$  are intimately related in dense liquids has been known for a long time. A recent contribution in this area, due to Zwanzig,<sup>1</sup> yields the relation

$$\left(\frac{D\eta}{k_B T}\right)\rho^{-1/3} = 0.0658\left(2 + \frac{\eta}{\eta_l}\right) = C' \quad (1)$$

where  $\rho$  is the atomic number density while  $\eta_l$  is the longitudinal viscosity. Unfortunately the actual value of  $C'$  defined in Eq. (1) clearly depends on the ratio of  $\eta$  to  $\eta_l$ , which is often not known quantitatively. In spite of this, Zwanzig pointed out that  $C'$  as defined above can vary only between 0.13 and 0.18.

One of us<sup>2</sup> drew attention to the fact that in liquid metals at their melting temperature  $T_m$  one has the approximate relations:

$$DM^{1/2}\rho^{1/3}/T_m^{1/2} = \text{constant} \quad (2)$$

and

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

Brown and March<sup>3</sup> used arguments based on Green-Kubo formulae to obtain Eqs (2) and (3). They noted that Eq. (3), which was first given by Andrade<sup>4</sup> using a kinetic argument which would not find ready acceptance today,<sup>5</sup> was of considerably higher quality than Eq. (2).

We have therefore examined again the Green-Kubo route to transport, adding to the argument of Brown and March the knowledge that has come from the long-time

tails of the velocity autocorrelation function. This yields the low-frequency expansion of the frequency spectrum  $g(\omega)$ , defined from the self function  $S_s(k, \omega)$  by

$$g(\omega) = \omega^2 \lim_{k \rightarrow 0} \frac{S_s(k, \omega)}{k^2} \quad (4)$$

as<sup>6</sup>

$$g(\omega) = \frac{D}{\pi} - A\omega^{1/2} + O(\omega) \quad (5)$$

where

$$A = (2\pi)^{1/2} \frac{2}{3\rho} \left[ 4\pi \left( D + \frac{\eta}{\rho M} \right) \right]^{-3/2} \frac{k_B T}{M\pi}. \quad (6)$$

Since the coefficients  $g(0)$  and  $A$  involve quantities entering the hydrodynamic equations, we shall now make a division of  $g(\omega)$  into two parts:

$$g(\omega) = g_{\text{hyd}}(\omega) + g_{\text{df}}(\omega) \quad (7)$$

where  $g_{\text{hyd}}$  is evidently the contribution of hydrodynamic modes to the total frequency spectrum, while the remaining contribution, denoted by  $g_{\text{df}}$ , is labelled to indicate that it arises from the density fluctuations. In simple liquid metals, these are known to oscillate more or less harmonically, near the melting temperature  $T_m$ , leading to  $\gamma = c_p/c_v$  near to 1 and  $c_v > 3R$ , with  $R$  the gas constant.

In the absence of a more fundamental approach, we here adopt the definition

$$\begin{aligned} g_{\text{hyd}}(\omega) &= \frac{D}{\pi} - A\omega^{1/2}, & \omega \leq \omega_c \\ &= 0 & \omega > \omega_c \end{aligned} \quad (8)$$

where  $\omega_c$  is chosen to make  $g_{\text{hyd}}(\omega)$  continuous at  $\omega = \omega_c$ :

$$\omega_c = \left( \frac{D}{\pi A} \right)^2. \quad (9)$$

The main point to be stressed is that the fraction  $f$  of the total modes in the hydrodynamic part of the spectrum is presumably a small fraction of the total<sup>3</sup>:

$$\int_0^\infty g(\omega) d\omega = \frac{k_B T}{2M} \quad (10)$$

where  $M$  denotes throughout the ionic mass. Since, with the definition (8):

$$\begin{aligned} \int_0^\infty g_{\text{hyd}}(\omega) d\omega &= \frac{D}{\pi} \omega_c - \frac{2A}{3} \omega_c^{3/2} \\ &= \omega_c \frac{D}{3\pi}, \end{aligned} \quad (11)$$

where the second step in Eq. (11) follows from Eq. (9), we readily find

$$f = \frac{2M}{k_B T} \frac{D^3}{3\pi^3 A^2} \tag{12}$$

for the fraction of hydrodynamic modes. Hence we can write

$$\frac{D}{(\pi A)^{2/3}} = \left(\frac{3\pi}{2}\right)^{1/3} \left(\frac{k_B T}{M}\right)^{1/3} f^{1/3}. \tag{13}$$

Using Eq. (6), this is readily rewritten as

$$D \left[ D + \frac{\eta}{\rho M} \right] = \frac{1}{(48\pi)^{1/3}} \left( \frac{k_B T}{M \rho^{2/3}} \right) f^{1/3}. \tag{14}$$

Equations (2) and (3) suggest the use of the reduced quantities

$$d = \frac{DM^{1/2}\rho^{1/3}}{(k_B T)^{1/2}} \tag{15}$$

and

$$h = \frac{\eta}{\rho M} \frac{M^{1/2}\rho^{1/3}}{(k_B T)^{1/2}}. \tag{16}$$

From Eq. (14) we then obtain

$$d(d + h) = \frac{1}{(12)^{1/3}} \frac{1}{(4\pi)^{1/3}} f^{1/3} \tag{17}$$

which demonstrates that

$$d^2 \text{ or } dh < \frac{1}{(12)^{1/3}} \frac{1}{(4\pi)^{1/3}} f^{1/3}; f < 1. \tag{18}$$

Utilizing now the Zwanzig result (1) to remove the  $dh$  term from Eq. (17), we find  $dh = C'$ . Table 1 shows empirical values of  $d$ ,  $h$  and  $C'$  for the liquid alkali metals and for mercury at the melting temperature  $T_m$ . Though the same situation may, of course, not necessarily obtain at other very different thermodynamic states, it can be seen

**Table 1** Empirical values of  $d$  and  $h$  defined in Eqs (15) and (16) respectively, at the melting temperature  $T_m$  for the alkali metals and for mercury.

Element	$d_m \times 10^2$	$h_m$	$d_m h_m = C'_m$
Li	2.9	5.6	0.16
Na	2.7	5.6	0.15
K	3.3	5.6	0.18
Rb	3.4	4.9	0.17
Cs	3.2	5.4	0.17
Hg	4.8	5.0	0.24

from Table 1 that, at the melting temperature  $T_m$ ,  $d^2 \ll dh$ , and hence Eq. (17) shows that  $dh$  determines  $f$  in essence. Since  $dh = C'$ , this points to the fact that  $f$  depends on  $\eta/\eta_l$  for this important thermodynamic state of liquid metals.

In summary, the Zwanzig relation (1), when combined with an argument enumerating the number of hydrodynamic modes as a fraction  $f$  of the total number of modes in the frequency spectrum  $g(\omega)$  leads to

$$d^2 + C' = \frac{1}{(48\pi)^{1/3}} f^{1/3}. \quad (19)$$

Table 1 shows that, at the melting temperature of liquid metals,  $d^2 \ll C'$  and this suggests at this thermodynamic state that  $f$  is primarily determined by the ratio  $\eta/\eta_l$ . Clearly, it would be of interest to have data over a wide range of thermodynamic states to study further Eq. (17).

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## APPENDIX AN ALTERNATIVE MODEL FOR HYDRODYNAMIC MODES

In writing Eq. (7), one should always choose  $g_{\text{hyd}}$  so that it is everywhere less than  $g(\omega)$ . Should any model violate that, then there is no assurance that  $f < 1$ , and the utility of the present approach is not clear under such circumstances. Therefore, in this Appendix, we propose an alternative model for the hydrodynamic modes. This is motivated again by Eq. (5): and we shall write

$$g(\omega) = g(0) \exp\left(-\frac{A}{g(0)} \omega^{1/2}\right) \quad (A1)$$

which evidently expands to reproduce Eq. (5) at small  $\omega$ .

We have again

$$\int_0^\infty g(\omega) d\omega = g(0) \int_0^\infty \exp(-\alpha s) 2s ds: s = \omega^{1/2} \quad (A2)$$

where  $\alpha = A/g(0) = \pi A/D$ . Using the identity

$$\int_0^{\infty} x^n \exp(-\xi x) = n! \xi^{-(n+1)}$$

we find the results of the main text are recovered, with different, calculable numerical constants. We shall not therefore pursue the details.