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T. Gaskell^a

^a Department of Physics, The University, Sheffield

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A Moment Method Approach to the Viscosities of Simple Liquids

T. GASKELL

Department of Physics,
The University,
Sheffield

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Abstract.—It is shown that the expression for the Fourier components of the density–density correlation function in a fluid obtained from the linearized hydrodynamic equations can also be obtained by adopting a particularly simple form for the associated memory function. The result is used to calculate the longitudinal viscosity of a fluid in terms of the moments of the space and time Fourier transform of the density–density correlation function $S(q, \omega)$.

1. Introduction

A function of great importance in the investigation of the dynamics of atomic motion in fluids is the Fourier transform of the density–density correlation function, $S(q, \omega)$. At long wavelengths it can be determined by measuring the spectral distribution of light scattered by the density fluctuations in a fluid, while for much shorter wavelengths similar information is obtained by inelastic neutron scattering experiments. It may be written in terms of the intermediate scattering function $F(q, t)$ by the equation

$$S(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(q, t) \exp(i\omega t) dt \quad (1.1)$$

where $F(q, t) = (1/N) \langle \rho_{\mathbf{q}}(t) \rho_{-\mathbf{q}}(0) \rangle$, the brackets denoting a canonical ensemble average, N being the number of atoms in the fluid and $\rho_{\mathbf{q}}(t)$ is the density fluctuation given by $\rho_{\mathbf{q}}(t) = \sum_{j=1}^N \exp(-i\mathbf{q} \cdot \mathbf{r}_j(t))$. A calculation of the time-dependent correlation function $F(q, t)$ must necessarily involve a theory of the dynamics of the atoms in the fluid and the experimental accessibility of $F(q, t)$ affords a direct test of the theory.

For small values of q and large t , $F(q, t)$ can be obtained from the linearized hydrodynamic equations (see for example Mountain 1966)⁽⁷⁾ giving the well-known result

$$F(q, t) = F(q, 0)\{(1 - C_v/C_p) \exp(-D_T q^2 t) + C_v/C_p \exp(\Gamma q^2 t) \cos C_s q t\} \quad (1.2)$$

where D_T is related to the thermal conductivity K by

$$D_T = K/\rho m C_p, \quad \Gamma = \frac{1}{2}\left\{\left(\frac{4}{3}\eta + \zeta\right)(\rho m)^{-1} + (C_p/C_v - 1)D_T\right\},$$

η and ζ being the shear and bulk viscosities respectively and C_s is the adiabatic sound velocity. Alternatively from Eq. (1.2) we may obtain $S(q, \omega)$ in the limit of small q and ω . As a point of notation $F(q, 0)$ will be referred to in its usual way as the structure factor $S(q)$.

In order to discuss the viscosities we introduce the spectral function $Z(\omega)$, defined by

$$Z(\omega) = \pi m^2 \rho \beta \lim_{q \rightarrow 0} \frac{\omega^4}{q^4} S(q, \omega) \quad (1.3)$$

in which ρ is the number density, m the atomic mass and $\beta = (k_B T)^{-1}$. In particular it is well-known that the longitudinal viscosity $\frac{4}{3}\eta + \zeta = Z(0)$ (Kadanoff and Martin 1963).⁽⁵⁾ This paper improves and clarifies some work briefly reported earlier (Gaskell 1970,⁽⁴⁾ to be referred to as I) which obtained a result for $Z(0)$ in terms of the moments of $S(q, \omega)$, $\overline{\omega^n}$ given by

$$\overline{\omega^n} = \int_{-\infty}^{\infty} \omega^n S(q, \omega) d\omega / \int_{-\infty}^{\infty} S(q, \omega) d\omega.$$

An unsatisfactory feature of this earlier calculation was that the value of $F(q, t)$ reduced to the hydrodynamic limit given in (1.2) only in the case $C_p/C_v = 1$. This is now corrected so that the hydrodynamic limit is completely obtained and the calculation extended to obtain the spectral function $Z(\omega)$ as well as its zero frequency limit.

The basis of the approach is to describe the time evolution of a correlation function in terms of a memory function, $M(t)$, which one assumes has a simpler structure. It is appropriate to normalize the correlation function to have the value unity at $t = 0$. We shall

denote the normalized intermediate scattering function $\langle \rho_{\mathbf{q}}(t)\rho_{-\mathbf{q}}(0) \rangle / \langle \rho_{\mathbf{q}}(0)\rho_{-\mathbf{q}}(0) \rangle$ by $\psi(t)$ and define the memory function $M(t)$ through the equation

$$\frac{d}{dt} \psi(t) + \int_0^t d\tau M(t-\tau)\psi(\tau) = 0. \tag{1.4}$$

The memory function in this particular problem is closely related to what has been called the time-dependent direct correlation function (Lado 1970).⁽⁶⁾

2. Mathematical Model of the Memory Function

In I, on the basis of an investigation of the concept of a memory function by Berne, Boon and Rice (1966),⁽¹⁾ the ansatz that the memory function decays exponentially at large t was adopted. It was assumed that M could be constructed at large t from the two parameter function $M = \gamma(q) \exp(-\alpha(q)|t|)$. The memory function is shown from the work of Berne, Boon and Rice⁽¹⁾ to be an even function of time and to have zero derivative at $t = 0$, a condition which is not satisfied by the above exponential. It is also well-known that the coefficients of t^n in a small t expansion of $\psi(t)$ may be obtained in terms of the interatomic potential and the equilibrium distribution functions, and since these coefficients are related through Eq. (1.4) to those of $M(t)$ we may choose the parameters in the memory function so that the first few coefficients are given exactly (the coefficients are essentially the moments $\overline{\omega^n}$ mentioned earlier). In order to do this the assumed form for the memory function was modified, to correct the behaviour at small t , by the introduction of a third parameter $\tau(q)$ so that

$$M = \gamma(q) \exp[-\alpha(q)\{(t^2 + \tau^2(q))^{1/2} - \tau(q)\}], \tag{2.1}$$

which at large t means that $M \rightarrow \gamma(q) \exp[-\alpha(q)(t - \tau(q))]$ suggesting that $\tau(q)$ has an interpretation as a relaxation time associated with the complicated small time behaviour of the fluid. This interpretation will be clearer, in the limit $q \rightarrow 0$, when expressions for the viscosities have been derived. The approach may be summarized in the following way. An assumption is made about the form of the memory function which contains a number of parameters chosen so

that the known behaviour of $\psi(t)$ is correctly given, and our firm knowledge of the latter is limited to its hydrodynamic limit and the low order moments $\overline{\omega^n}$. A similar technique has been applied to the transverse part of the current-current correlation function with a view to estimating the shear viscosity (Forster, Martin and Yip 1968)⁽³⁾ but a calculation of the bulk viscosity, which we now attempt, has not to our knowledge been carried out.

It was pointed out earlier that the form of M previously adopted and given in Eq. (2.1) led to a result for $F(q, t)$ which reduced in the hydrodynamic limit to Eq. (1.2) with $C_p/C_v = 1$. This arises in the following way. When the parameters in (2.1) are chosen in the way indicated $\gamma(q) = M(0) = \overline{\omega^2} = q^2/m\beta S(q)$ so that at small q ,

$$\gamma(q) \rightarrow q^2/m\beta S(0) = C_T q^2,$$

where C_T is the isothermal sound velocity and $\alpha(q) \rightarrow aq^2$, a being independent of q . In order to obtain the correlation function, Eq. (1.4) is solved by Laplace transform, subject to the boundary condition $\psi(0) = 1$, to give

$$\tilde{\psi}(p) = (p + \tilde{M}(p))^{-1} \tag{2.2}$$

p being the Laplace variable and $\tilde{\psi}(p)$ and $\tilde{M}(p)$ Laplace transforms. Hence to obtain the hydrodynamic limit we calculate the inverse Laplace transform of

$$\tilde{\psi}(p) = (p + aq^2)/(p^2 + paq^2 + C_T q^2) \tag{2.3}$$

which in the $q \rightarrow 0$ limit is given by $\psi(t) = \exp(-aq^2 t/2) \cos C_T q t$. This has the same form as (1.2) when $C_p/C_v = 1$ and we can identify a as $(\frac{2}{3}\eta + \zeta)/\rho m$, which is the result obtained in I. To describe correctly the hydrodynamic limit we introduce a further parameter $\beta(q)$ which will be related to the heat diffusion coefficient D_T and a third one $\lambda(q)$ to be a measure of the difference $C_p/C_v - 1$.

We shall assume for the memory function the general form

$$M(t) = A \exp(-\delta |t|) + B \exp(-\epsilon |t|),$$

though we choose A, B, ϵ and δ in the following way.

$$M(t) = \gamma(q) \{ \exp(-\delta |t|) + \exp(-\epsilon |t|) \} + \frac{\gamma(q)(\beta(q) - \alpha(q))}{\{(\alpha(q) - \beta(q))^2 - 4\lambda(q)\}^{1/2}} \cdot \{ \exp(-\delta |t|) - \exp(-\epsilon |t|) \}, \tag{2.4}$$

with

$$\begin{aligned}
 2\delta &= \alpha(q) + \beta(q) - \{(\alpha(q) - \beta(q))^2 - 4\lambda(q)\}^{1/2}, \\
 2\epsilon &= \alpha(q) + \beta(q) + \{(\alpha(q) - \beta(q))^2 - 4\lambda(q)\}^{1/2}.
 \end{aligned}
 \tag{2.5}$$

The Laplace transform of M with this choice is easily shown to be

$$\tilde{M}(p) = \gamma(q) \left\{ \frac{2p + 2\beta(q)}{p^2 + p(\alpha(q) + \beta(q)) + \alpha(q)\beta(q) + \lambda(q)} \right\}
 \tag{2.6}$$

and hence

$$\tilde{\psi}(p) = \frac{p^2 + p(\alpha(q) + \beta(q)) + \alpha(q)\beta(q) + \lambda(q)}{p^3 + p^2(\alpha(q) + \beta(q)) + p(\alpha(q)\beta(q) + 2\gamma(q) + \lambda(q)) + 2\gamma(q)\beta(q)}
 \tag{2.7}$$

It will be shown that in this case also as $q \rightarrow 0$,

$$2\gamma(q) \rightarrow \overline{\omega^2} \rightarrow q^2/m\beta S(0).$$

If, when $\alpha(q)$ and $\beta(q)$ are determined in terms of the moments, we can choose that in the small q limit $\alpha(q) \rightarrow aq^2$, $\beta(q) \rightarrow bq^2$ and we select $\lambda(q) = 2\gamma(q) (C_p/C_v - 1)$, Eq. (2.7) is identical in form to the expression for $\tilde{\psi}(p)$ derived from the solution of the hydrodynamic equations (Mountain 1966).⁽⁷⁾ This is

$$\tilde{\psi}(p) = \frac{p^2 + (a+b)pq^2 + abq^4 + (1 - C_v/C_p)C_s^2 q^2}{p^3 + (a+b)p^2q^2 + (C_s^2 q^2 + abq^4)p + bC_s^2 q^4 C_v/C_p}
 \tag{2.8}$$

where C_s is the adiabatic sound velocity given by $C_s^2 = (C_p/C_v)C_T^2$ and we can identify $a = (\frac{2}{3}\eta + \zeta)/\rho m$ and $b = D_T$. The hydrodynamic limit (1.2) follows from this. The relaxation time will be introduced in a slightly different way to that adopted in I. The exponential terms in Eq. (2.4) are modified so that each becomes

$$\gamma(q) \exp [- \delta(q)(t^2 + \tau^2(q))^{1/2}],$$

which at large t have the correct form $\gamma(q) \exp (- \delta(q) |t|)$ rather than $\gamma(q) \exp (\delta(q)\tau(q)) \exp (- \delta(q) |t|)$ mentioned earlier. The additional exponential factor in the latter did not contribute to the hydrodynamic limit in I since in that case $\delta(q)$ was proportional to q^2 in the small q limit. However, in the present situation $\delta(q)$ is proportional to q and there would be additional contributions to Eq. (2.7). By the modification given above we ensure the correct limit as $t \rightarrow \infty$ though this causes a minor adjustment in the calculation of the parameters from the small time expansion.

3. Determination of the Shear and Bulk Viscosities

In the determination of the parameters in the memory function we compare the coefficients of t^n in an expansion of the approximate memory function with the exact values and choose the parameters to give correctly the first few moments $\overline{\omega^n}$. For a classical fluid the coefficients are zero, when n is odd and there is a theorem relating the moments to the coefficients (Singwi 1968)⁽¹⁰⁾ which may be written

$$\overline{\omega^{2n}} = \sum_{m=1}^n (-1)^{m+1} \overline{\omega^{2(n-m)}} \left\{ \frac{d^{2m-2}}{dt^{2m-2}} M(t) \right\}_{t=0} \quad (3.1)$$

The leading terms in a series expansion of the memory function are easily shown to be given by

$$\begin{aligned} M(t) = & \gamma \{ \exp(-\delta\tau) + \exp(-\epsilon\tau) \} \\ & + \frac{\gamma(\beta - \alpha)}{\{(\alpha - \beta)^2 - 4\lambda\}^{1/2}} \{ \exp(-\delta\tau) - \exp(-\epsilon\tau) \} \\ & - \frac{\gamma t^2}{2\tau} \left\{ \delta \exp(-\delta\tau) + \epsilon \exp(-\epsilon\tau) \right. \\ & \left. + \frac{\beta - \alpha}{\{(\alpha - \beta)^2 - 4\lambda\}^{1/2}} (\delta \exp(-\delta\tau) - \epsilon \exp(-\epsilon\tau)) \right\} \\ & + \frac{\gamma t^4}{8} \left\{ \left(\frac{\delta}{\tau^3} + \frac{\delta^2}{\tau^2} \right) \exp(-\delta\tau) + \left(\frac{\epsilon}{\tau^3} + \frac{\epsilon^2}{\tau^2} \right) \exp(-\epsilon\tau) \right. \\ & \left. + \frac{\beta - \alpha}{\{(\alpha - \beta)^2 - 4\lambda\}^{1/2}} \left[\left(\frac{\delta}{\tau^3} + \frac{\delta^2}{\tau^2} \right) \exp(-\delta\tau) \right. \right. \\ & \left. \left. - \left(\frac{\epsilon}{\tau^3} + \frac{\epsilon^2}{\tau^2} \right) \exp(-\epsilon\tau) \right] \right\} + \dots \quad (3.2) \end{aligned}$$

Since the determination of the viscosities is associated with the behaviour of the above expression for small values of q we shall evaluate the coefficient of t^n in the limit $q \rightarrow 0$. Hence from Eq. (3.2)

$$\begin{aligned} M(t) = & \gamma(q)(2 - 2\tau(q)\alpha(q) - \tau^2(q)\lambda(q) + O(q^4)) \\ & - \frac{\gamma(q)t^2}{2\tau(q)} (2\alpha(q) + 2\tau(q)\lambda(q) + O(q^4)) \\ & + \frac{\gamma(q)t^4}{8} \left(\frac{2\alpha(q)}{\tau^3(q)} + O(q^4) \right) \quad (3.3) \end{aligned}$$

It is interesting that the parameter $\beta(q)$ which is associated with the heat diffusion coefficient has not appeared to order t^4 , which means to order t^6 in the intermediate scattering function. Using Eq. (3.1) and the well known expressions for the moments $\overline{\omega^2}$ and $\overline{\omega^4}$ given by

$$\overline{\omega^2} = q^2/m\beta S(q) \tag{3.4}$$

and

$$\overline{\omega^4} = q^4 \left(3 + \rho\beta \int dr g(r) \frac{(1 - \cos qx)}{q^2} \frac{\partial^2 \phi}{\partial x^2} \right) / m^2 \beta^2 S(q)$$

it follows that if we choose the parameters in the following way that the leading terms in a q expansion of the second, fourth and sixth moments of $S(q, \omega)$ constructed from this memory function will be given exactly.

$$2\gamma(q) = \frac{q^2}{m\beta S(0)} + O(q^4)$$

$$\frac{\alpha(q)}{\tau(q)} + \lambda(q) = q^2 \left(3 + \frac{\rho\beta}{2} \int dr g(r) x^2 \frac{\partial^2 \phi}{\partial x^2} - S(0)^{-1} \right) / m\beta + O(q^4)$$

$$\frac{6\gamma(q)\alpha(q)}{\tau^3(q)} = q^4 \lim_{q \rightarrow 0} \frac{\overline{\omega^6}}{q^4} + O(q^6) \tag{3.5}$$

Using the value for $\lambda(q)$ suggested earlier, the parameter $\alpha(q)$ derived from these equations has the type of q dependence in the small q limit to produce the hydrodynamic behaviour correctly, i.e., $\alpha(q) \rightarrow aq^2$, where the coefficient a is given by

$$a = \frac{\frac{4}{3}\eta + \zeta}{\rho m} = \left(3 + \frac{\rho\beta}{2} \int dr g(r) x^2 \frac{\partial^2 \phi}{\partial x^2} - \frac{C_v}{C_s} S(0)^{-1} \right) \tau(0) / m\beta \tag{3.6}$$

We can therefore write $\frac{4}{3}\eta + \zeta = (\frac{4}{3}G + B - B_s)\tau(0)$, where

$$G = \rho k_B T \left(1 + \frac{8\pi\rho\beta}{15} \int dr r^3 \frac{d\phi}{dr} + \frac{2\pi\rho\beta}{15} \int dr r^4 g(r) \frac{d^2\phi}{dr^2} \right)$$

is the rigidity,

$$B = \rho k_B T \left(\frac{5}{3} - \frac{4\pi\rho\beta}{9} \int dr r^3 g(r) \frac{d\phi}{dr} + \frac{2\pi\rho\beta}{9} \int dr r^4 g(r) \frac{d^2\phi}{dr^2} \right)$$

the (instantaneous) bulk modulus and $B_s = \rho k_B T (C_s/C_v) S(0)^{-1}$ the adiabatic bulk modulus. If we infer from this that $\eta = G\tau(0)$ and

$\zeta = (B - B_s)\tau(0)$ we obtain for the ratio of viscosities $\zeta/\eta = (B - B_s)/G$. This result has been derived in a somewhat different fashion by Schofield (1968).⁽⁹⁾ Using the Cauchy relation which is valid for a fluid with two-body central interactions $B = \frac{5}{3}G + 2(P - \rho k_B T)$, where P is the pressure (Zwanzig and Mountain 1965)⁽¹¹⁾ and the above ratio becomes

$$\frac{\zeta}{\eta} = \frac{(B - B_s)}{G} = \rho k_B T \left(\frac{2P}{\rho k_B T} - 2 - \frac{C_p}{C_v} S(0)^{-1} \right) / G \quad (3.7)$$

There is some experimental data available for this ratio in the case of argon (Naugle, Lunsford and Singer 1966)⁽⁸⁾ and a number of values of G and B have been computed for a fluid with a 6–12 interatomic potential (Zwanzig and Mountain 1965,⁽¹¹⁾ Forster, Martin and Yip 1968).⁽²⁾ However the conditions of temperature and density in the experiments do not correspond very closely with those covered by the available calculations and a test of the above equation is not entirely satisfactory. Table 1 gives a sample of the results in which an estimate of the adiabatic bulk modulus has been made where possible from experimental results. Whilst the trend in the observed behaviour of the ratio ζ/η is

TABLE 1

T °K	Density (gm. cm ⁻³)	Observed	$(B - B_s)/G$
142.4	1.068	1.95	
144	1.08		< 1.6
114.8	1.28	1.11	
128.2	1.25		≈ 1
86.3	1.413	0.78	
86.1	1.415		≈ 0.6

followed by the ratio $(B - B_s)/G$ the latter generally seems to be smaller than the ratio of the viscosities. A more satisfactory comparison however would be to evaluate B_s from the computed value of the radial distribution function used in the calculation of G and B , rather than to obtain it from experiment.

To determine absolute values for viscosities we need to be able to

obtain the relaxation time $\tau(0)$ and the final equation in (3.5) provides the means. In order that the sixth moment of $S(q, \omega)$ be given exactly, in the small q limit, we must have

$$\tau^2(0) = \lim_{q \rightarrow 0} 3 \left(\frac{\overline{\omega^4}}{q^4} - \frac{C_p}{C_v} \frac{1}{m^2 \beta^2 S^2(0)} \right) / \frac{\overline{\omega^6}}{q^4} \quad (3.8)$$

An expression for $\overline{\omega^6}$ has been obtained in terms of the equilibrium distribution functions (Forster, Martin and Yip 1968),⁽²⁾ and in addition to $g(r)$ it involves the three atom distribution function g_3 . The latter authors also evaluated $\lim_{q \rightarrow 0} (\overline{\omega^6}/q^4)$, though at the expense of replacing g_3 by its approximate value based on the superposition approximation, in order to carry through the numerical integrations. Since the superposition approximation is quantitatively notoriously unreliable except at very low densities there will therefore be some uncertainty about the accuracy of the values of $\tau(0)$. This is unavoidable at present in the absence of a better theory of g_3 , though there is the possibility of evaluating the integrals using computer experiments. In view of this and the lack of information about the adiabatic compressibility already mentioned, only two values of the viscosities are given. One corresponding closely to conditions at the triple point of argon and the other to somewhat different conditions of temperature and density, to illustrate that the approach is yielding sensible results. These are shown in Table 2.

TABLE 2

T °K	Density (gm cm ⁻³)	η observed (gm cm ⁻¹ sec ⁻¹)	ζ observed (gm cm ⁻¹ sec ⁻¹)	$\tau(0)$ (sec)	$q\tau(0)$ (gm cm ⁻¹ sec ⁻¹)	$(B - B_T)\tau(0)$ (gm cm ⁻¹ sec ⁻¹)
128.2	1.25	1.4×10^{-3}	1.6×10^{-3}	1.47×10^{-13}	1.15×10^{-3}	1.03×10^{-3}
86.1	1.415	2.68×10^{-3}	2.09×10^{-3}	1.68×10^{-13}	1.67×10^{-3}	0.98×10^{-3}

The value of the longitudinal viscosity given by the results in the second row of Table 2 is lower than that obtained in I, which was calculated under the same conditions, because here B , correctly replaces B_T and exceeds the latter by a factor C_p/C_v which at the triple point is ≈ 2.3 . We emphasize that since the numerical results are based on the superposition approximation they are not a convincing test of the method.

4. The Spectral Function $Z(\omega)$

To calculate the Fourier transform of the density-density correlation function, $S(q, \omega)$, we make use of the result

$$\psi(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \psi(t) = \frac{1}{2\pi} (\tilde{\psi}(i\omega) + \tilde{\psi}(-i\omega)).$$

Using Eq. (2.2) this can be written in the form

$$\psi(\omega) = \frac{1}{2\pi} \left(\frac{\tilde{M}(i\omega) + \tilde{M}(-i\omega)}{\omega^2 + i\omega\{\tilde{M}(i\omega) - \tilde{M}(-i\omega)\} + \tilde{M}(i\omega)\tilde{M}(-i\omega)} \right)$$

and hence it is quickly shown that

$$\frac{S(q, \omega)}{S(q)} = \psi(\omega) = \frac{M_c/\pi}{(\omega - M_s)^2 + M_c^2} \tag{4.1}$$

where

$$M_c = \int_0^{\infty} dt M(t) \cos \omega t$$

and

$$M_s = \int_0^{\infty} dt M(t) \sin \omega t.$$

The complete expression that has been adopted for the memory function is

$$\begin{aligned} M(t) = & \gamma(q)\{\exp\{-\delta(q)(t^2 + \tau^2(q))^{1/2}\} + \exp\{-\epsilon(q)(t^2 + \tau^2(q))^{1/2}\}\} \\ & + \frac{\gamma(q)(\beta(q) - \alpha(q))}{\{(\alpha(q) - \beta(q))^2 - 4\lambda(q)\}^{1/2}} \{\exp\{-\delta(q)(t^2 + \tau^2(q))^{1/2}\} \\ & - \exp\{-\epsilon(q)(t^2 + \tau^2(q))^{1/2}\}\} \end{aligned} \tag{4.2}$$

where δ and ϵ are given in (2.5). In deriving the spectral function $Z(\omega)$, defined in (1.3), it is clear that M_s and M_c in the denominator of Eq. (4.1) make no contribution in the limit $q \rightarrow 0$, since both are proportional to q^2 . Only the cosine transform of the memory function is therefore required and for the type of exponential term occurring in the calculations this is given by the result

$$\int_0^{\infty} dt \exp\{-\delta(t^2 + \tau^2)^{1/2}\} \cos \omega t = \frac{\delta\tau K_1\{\tau(\omega^2 + \delta^2)^{1/2}\}}{(\omega^2 + \delta^2)^{1/2}}.$$

K_1 is the Bessel function of the second kind having the following properties; $K_1\{x\} \rightarrow x^{-1}$ as $x \rightarrow 0$ and $K_1\{x\} \rightarrow (\pi/2x)^{1/2} \exp(-x)$ as $x \rightarrow \infty$. The spectral function $Z(\omega)$ then follows readily being given by

$$Z(\omega) = \pi m^2 \rho \beta \lim_{q \rightarrow 0} \frac{\omega^4}{q^4} S(q, \omega) = \rho m a \omega \tau(0) K_1\{\omega \tau(0)\} \quad (4.3)$$

and the result is displayed in Fig. 1. Two points can be made immediately. The first is that since the memory function is known to be correct only at large t the spectral function will be most accurate

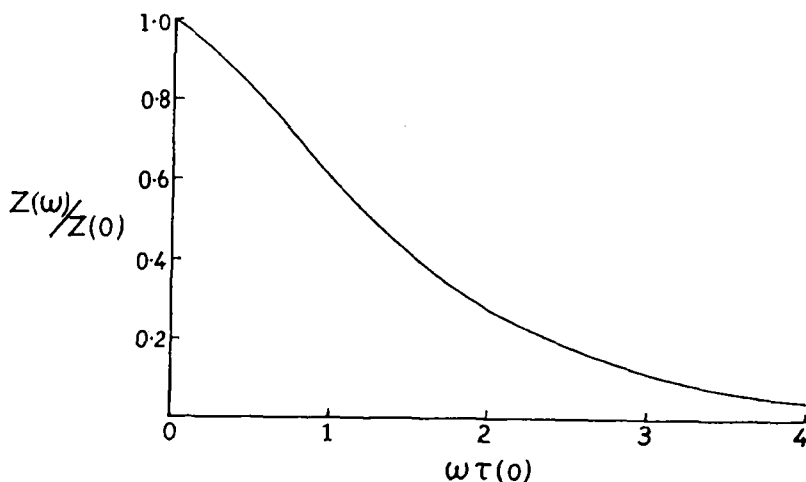


Figure 1. Frequency dependent longitudinal viscosity.

for small values of ω , the behaviour as ω increases is as speculative as the form of the memory function we have adopted to describe the behaviour of the latter as $t \rightarrow 0$. The second concerns the normalization of $Z(\omega)$, which according to (4.3) is

$$\frac{2}{\pi} \int_0^\infty d\omega Z(\omega) = \frac{\rho m a}{\tau(0)} = \frac{4}{3} G + B - B_s,$$

and is in agreement with the exact value given by Schofield (1968).⁽⁹⁾

5. Summary

The usefulness of the memory function approach lies in the fact that a time-dependent correlation function is expressed in terms of a memory function which may be susceptible to approximation or modelling. It has been shown here that the Fourier components of the density-density correlation function which would be obtained from the linearized hydrodynamic equations can also be produced by adopting a particularly simple form for the associated memory function. The latter is in fact the general solution of an equation describing damped harmonic motion, namely

$$\frac{d^2M}{dt^2} + (\alpha(q) + \beta(q)) \frac{dM}{dt} + (\lambda(q) + \alpha(q)\beta(q))M = 0. \quad (5.1)$$

A model for M is then employed which displays correctly both the short and long time behaviour through the introduction of a relaxation time. Expressions for the viscosities follow automatically, of the type which appear in the visco-elastic theory, in which the shear viscosity is given by the product of a rigidity and a relaxation time and the bulk viscosity as the appropriate bulk modulus multiplied by the same relaxation time. An important new feature however is that a prescription for the relaxation time itself is also given.

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