Transverse current modes and the wavevector-dependent fluidity of simple liquids

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Abstract. The transverse current correlation function, $C_T(k, t)$, is re-examined and some of the limitations of the familiar viscoelastic model, particularly for wavelengths less than a few interatomic spacings, emphasised. An alternative theory, which stresses the role of the velocity autocorrelation components in $C_T(k, t)$, is proposed, with momentum transfer effects to the surrounding atomic shells of a given atom calculated separately. When applied to a liquid rubidium model, the results are in good agreement with computer simulation data. The theory is also used to investigate the generalised wavevector-dependent fluidity, $\eta^{-1}(k)$, and gives new insight into the detailed structure which has been revealed by computer simulation data. A model for $\eta^{-1}(k)$ is proposed, and the relationship of the self-diffusion coefficient of the liquid to the fluidity investigated.

1. Introduction

The transverse current autocorrelation function, denoted as usual by $C_T(k, t)$, is of interest in its own right, since it gives information about the wavevector range for which the liquid will support propagating shear-wave modes. It also appears in a subsidiary role in theories of other time-dependent correlation functions, for example the velocity autocorrelation function, when such theories exploit mode-coupling ideas to describe the details of correlation effects at intermediate or long times. The familiar viscoelastic model provides a useful description of $C_T(k, t)$, especially at small wavevectors i.e. $k \leq n^{1/3}$, where n is the number density. This is not too surprising since this model is an extension of the hydrodynamic form of the correlation function to finite k and ω. It does, however, have significant defects at larger k where the velocity autocorrelation terms in $C_T(k, t)$ start to become more important.

   Through the framework of the generalised Langevin equation and the introduction of the associated memory function, we may define a wavevector- and frequency-dependent shear viscosity coefficient. Some details of the latter are now available from computer simulation studies of rigid sphere, Lennard-Jones and liquid-metal-like systems. The purpose of this work is to present a means of calculating $C_T(k, t)$, and hence the generalised viscosity, by a method which focuses attention on the single-particle components, but can be extended to include momentum transfer effects to neighbouring atomic shells. The theory complements the viscoelastic approach to this problem by concentrating on the higher end of the k-range. Nevertheless, it appears to be applicable at small enough wavevectors to extend into the viscoelastic regime. This is valuable because we are particularly interested in the crossover from single-particle to collective behaviour.

The theoretical framework is presented in the next section and the importance of the single-particle components in the transverse current autocorrelation function demonstrated for a liquid-rubidium model. In § 3, theoretical results for $C_T(k, t)$ are compared with molecular dynamics (MD) data, and then details of the wavevector dependence of the generalised viscosity for rubidium are reported and discussed.

2. Transverse current and generalised fluidity

The momentum current density fluctuation in a liquid is defined as

$$j_k^\alpha(t) = \sum_j m v_j^\alpha(t) \exp(i\mathbf{k} \cdot \mathbf{r}_j(t))$$

where α signifies a Cartesian component. Through this expression we may introduce the transverse current autocorrelation function

$$C_T(k, t) \equiv \langle j_k^\alpha(0) j_{-k}^\alpha(t) \rangle / N \tag{2.1}$$

in which, with $\mathbf{k}$ along the z axis, α denotes x or y. It is now well known that by means of the generalised Langevin equation, the Laplace transform of this correlation function, $\tilde{C}_T(k, z)$, may be usefully expressed in the form

$$\tilde{C}_T(k, z) = C_T(k, t = 0) / [z + (k^2/nm)\tilde{\eta}(k, z)] \tag{2.2}$$

n being the number density (see, for example, Hansen and McDonald 1986). In an obvious extension of the hydrodynamic limit of this expression, $\tilde{\eta}(k, z = i\omega)$ is interpreted as a wavevector- and frequency-dependent shear viscosity. We shall be interested in the generalised viscosity, $\eta(k) \equiv \tilde{\eta}(k, z = 0)$, although from the point of view of this paper it is more convenient to think in terms of the generalised fluidity, $\eta^{-1}(k)$. This can be obtained from $\tilde{C}_T(k, z = 0)$ through the equation

$$\eta^{-1}(k) = k^2 \tilde{C}_T(k, z = 0) / nm C_T(k, t = 0). \tag{2.3}$$

The transverse current will consist of velocity autocorrelation or 'self' terms and contributions from the correlation of the velocities of different or 'distinct' atoms which arise from momentum transfer. We refer to these as $C_T^s(k, t)$ and $C_T^d(k, t)$ respectively, and propose to investigate these contributions to the transverse current separately. The fluidity (rather than the viscosity) is conveniently the sum of the separate terms. Apart from any intrinsic interest in the generalised transport coefficient, the latter has been shown to play an important role in understanding the relationship between the self-diffusion coefficient, D, and the shear viscosity coefficient, $\eta \equiv \eta(k = 0)$, at a microscopic level (Balucani *et al* 1985). The following limits are known exactly:

$$\eta_s^{-1}(k \to 0) = k^2 D / nk_B T \qquad \eta^{-1}(k \to \infty) = \eta_s^{-1}(k \to \infty) = k(2mn^2 k_B T/\pi)^{-1/2}.$$

Molecular dynamics data of the fluidity in a liquid rubidium model (Balucani *et al* 1987) are shown in figure 1, for the state point $T = 332$ K and $n = 0.01058 \times 10^{24}$ cm^{-3}. The computed value of the shear viscosity coefficient in the hydrodynamic limit is 5.5 mP. Also included in the figure is a theoretical result based on a simple viscoelastic model for $\tilde{\eta}(k, z)$. This predicts that $\tilde{\eta}(k, z) = G(k)/(z + \tau^{-1}(k))$, from which

$$\eta^{-1}(k) = \left(G(k)\tau(k)\right)^{-1}. \tag{2.4}$$

The rigidity $G(k)$ is given by

$$G(k) = nk_B T + (n/k)^2 \int d\mathbf{r} \frac{\partial^2 \varphi(r)}{\partial x^2} (1 - \exp(-i\mathbf{k} \cdot \mathbf{r})) g(r)$$

$\varphi(r)$ being the pair potential, and $g(r)$ the radial distribution function. The relaxation
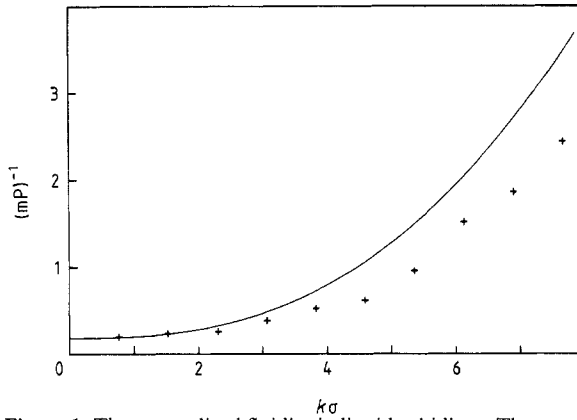
Figure 1. The generalised fluidity in liquid rubidium. The crosses refer to MD data, the full curve the viscoelastic model prediction (equation (2.4)) and $\sigma = 4.405$ Å is the usual pair-potential parameter.

time, $\tau(k)$, has the frequently used form suggested by Akcasu and Daniels (1970). This reflects an interpolation procedure for $C_T(k, t)$ between the known hydrodynamic and ideal gas behaviour in the low- and high-k limits respectively. Clearly, the theory is not satisfactory for $k\sigma \geq 3$. In particular, it fails to explain the structure in $\eta^{-1}(k)$ which is evident in the MD data. Similar, although less obvious, effects can be seen in the generalised viscosity data from computer simulation studies of the rigid sphere and Lennard-Jones systems (Alley and Alder 1983, Gaskell *et al* 1987).

One expects the self-correlation terms in the transverse current to begin to dominate at large enough wavevectors, and figure 1 demonstrates that the viscoelastic model fails to give an adequate account of such terms. Consequently, we concentrate on an approach to transverse current correlations which gives a more appropriate description of the single-particle contributions. It is convenient to write

$$C_T(k, t) = \langle mv_1^x(0)mv_1^x(t) \exp[i\mathbf{k} \cdot (\mathbf{r}_1(0) - \mathbf{r}_1(t))] \rangle$$

$$+ \left\langle mv_1^x(0) \sum_{j \neq 1} mv_j^x(t) \exp[i\mathbf{k} \cdot (\mathbf{r}_1(0) - \mathbf{r}_j(t))] \right\rangle$$

$$\equiv C_T^s(k, t) + C_T^d(k, t) \tag{2.5}$$

and to evaluate the terms separately by introducing the idea of a velocity field at a microscopic level, which we write as

$$v(r, t) = \sum_i v_i(t)f(|\mathbf{r} - \mathbf{r}_i(t)|).$$

The 'form factor', $f(r)$, is constructed so that (i) the velocity field is essentially constant across an atomic diameter and (ii) the macroscopic sum rule

$$n \int dr\, v(r, t) = \sum_i v_i(t)$$

is satisfied. For all practical purposes, both requirements are met by choosing a step function form for $f(r)$, whose width, a, is obtained through the condition $\frac{4}{3}\pi a^3 = n^{-1}$.

2.1. Autocorrelation contribution to $C_T(k, t)$

The velocity field approach has been used before to investigate the velocity auto-correlation function in liquids, and leads to the result (Gaskell and Miller 1978)

$$m^2 \langle v_1^x(0) v_1^x(t) \rangle = [1/3(2\pi)^3] \int \mathrm{d}\boldsymbol{q}\, \tilde{f}(q) [C_\mathrm{L}(q, t) + 2C_\mathrm{T}(q, t)] F_\mathrm{s}(q, t). \tag{2.6}$$

$C_\mathrm{L}(q, t)$ is the longitudinal current autocorrelation function, $F_\mathrm{s}(q, t)$ the self-inter-mediate scattering function and $\tilde{f}(q)$ the Fourier transform of the form factor. Using viscoelastic models for C_L and C_T, and the Gaussian approximation for F_s, this expression has been shown to account remarkably well for some of the details revealed by computer simulation. However, when calculating the self-diffusion coefficient through the Green–Kubo formula

$$D = \int_0^\infty \mathrm{d}t \langle v_1^x(0) v_1^x(t) \rangle$$

the deficiencies of the viscoelastic approximation for C_T, particularly those demonstrated in figure 1, are reflected in an overestimate of D near the melting point by approximately 35% in Rb (Balucani *et al* 1987).

Adopting the same technique to the evaluation of $C_\mathrm{T}^\mathrm{s}(k, t)$, we have

$$m^2 \langle v_1^x(0) v_1^x(t) \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r}_1(0) - \boldsymbol{r}_1(t))] \rangle$$

$$= \int \mathrm{d}\boldsymbol{R} \langle v_1^x(0) v^x(\boldsymbol{r}_1(0) + \boldsymbol{R}, t) \delta(\boldsymbol{R} + \boldsymbol{r}_1(0) - \boldsymbol{r}_1(t))\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}} \rangle$$

$$\simeq \int \mathrm{d}\boldsymbol{R} \langle v_1^x(0) v^x(\boldsymbol{r}_1(0) + \boldsymbol{R}, t) \rangle \langle \delta(\boldsymbol{R} + \boldsymbol{r}_1(0) - \boldsymbol{r}_1(t)) \rangle\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}}$$

$$= \int \mathrm{d}\boldsymbol{R} \langle v_1^x(0) v^x(\boldsymbol{r}_1(0) + \boldsymbol{R}, t) \rangle G_\mathrm{s}(R, t)\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}}. \tag{2.7}$$

The justification for the decoupling of the ensemble average rests on the observation that at liquid densities the timescale for momentum transfer is very much shorter than that for atomic diffusion. By Fourier transforming the velocity field it is easy to show that the momentum transfer component in (2.7) becomes

$$\langle v_1^x(0) v^x(\boldsymbol{r}_1(0) + \boldsymbol{R}, t) \rangle$$

$$= [1/(2\pi)^3] \int \mathrm{d}\boldsymbol{q}\, \tilde{f}(q) \{C_\mathrm{L}(q, t)(\hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2 + C_\mathrm{T}(q, t)[1 - (\hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2]\}\, \mathrm{e}^{\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{R}}$$

and hence we obtain

$$C_\mathrm{T}^\mathrm{s}(k, t) = m^2 \langle v_1^x(0) v_1^x(t) \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{r}_1(0) - \boldsymbol{r}_1(t))] \rangle \simeq [1/(2\pi)^3] \int \mathrm{d}\boldsymbol{q} \tilde{f}(q)$$

$$\times \{C_\mathrm{L}(q, t)(\hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2 + C_\mathrm{T}(q, t)[1 - (\hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2]\} F_\mathrm{s}(|\boldsymbol{q} - \boldsymbol{k}|, t). \tag{2.8}$$

In the limit $k = 0$, this equation reduces to (2.6).

Because they are convenient, we again use viscoelastic models for the currents in (2.8) and the results from this expression are compared in figure 2 with both MD data and viscoelastic theory for the *full* transverse current. It appears that (i) at the chosen wavevectors (which represent wavelengths of the order of the interparticle spacing) the self terms in the transverse current are predominant, and (ii) the present treatment of velocity correlations represent a significant improvement on the viscoelastic approximation, particularly with regard to the phase of the oscillations. Nevertheless, it has to be appreciated that the results are achieved within the limitations imposed by using the viscoelastic models for the currents. This will be noticeable when we use the theory to
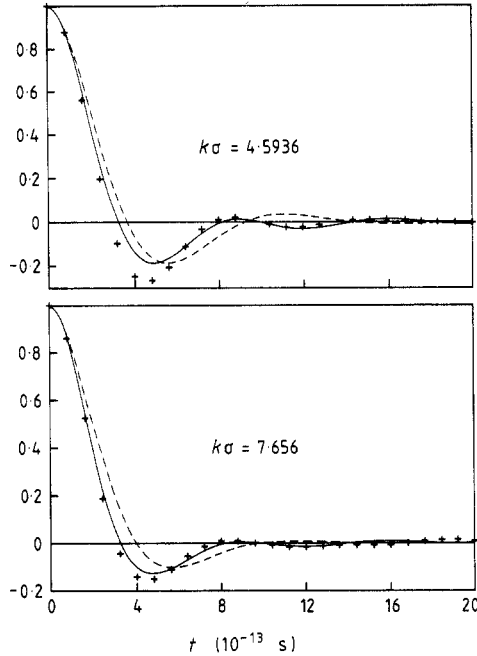
Figure 2. Transverse current correlations in liquid rubidium. The crosses and broken curve show MD data and viscoelastic model results respectively for $C_T(k, t)/mk_BT$. The full curve is the prediction for $C_T^s(k, t)/mk_BT$ from equation (2.8). MD data was from Balucani *et al* (1987).

evaluate the contribution of the self term to the generalised fluidity, $\eta_s^{-1}(k)$, because the deficiencies which produced the overestimate of the diffusion coefficient will also intervene here. With this in mind, we mention another point of interest which emerges from the calculation.

It has been pointed out before that the influence of single-particle diffusion on the velocity autocorrelation function is small. Putting $F_s(q, t) = 1$, its initial value, in (2.6) has no significant effect on the results (Gaskell 1984). This is because the C_T and C_L decay much more rapidly than F_s for the predominant wavevector range, and means that the result for $C_T^s(k, t)$ in the last equation may be replaced by

$$C_T^s(k, t) = [1/(2\pi)^3] \int d\mathbf{q}\, \tilde{f}(q)\{C_L(q, t)(\hat{\mathbf{q}} \cdot \hat{\mathbf{x}})^2 + C_T(q, t)[1 - (\hat{\mathbf{q}} \cdot \hat{\mathbf{x}})^2]\}F_s(k, t)$$

$$= [1/3(2\pi)^3] \int d\mathbf{q}\, \tilde{f}(q)[C_L(q, t) + 2C_T(q, t)]F_s(k, t)$$

without any serious consequences. We have indeed verified that this simplified expression gives essentially the same results for $C_T^s(k, t)$ as (2.8), when evaluated with viscoelastic models for the currents. However, it also implies that we may usefully write the self term as

$$C_T^s(k, t) \simeq m^2 \langle v_1^x(0)v_1^x(t)\rangle\langle \exp[i\mathbf{k} \cdot (\mathbf{r}_1(0) - \mathbf{r}_1(t))]\rangle = m^2 \langle v_1^x(0)v_1^x(t)\rangle F_s(k, t) \qquad (2.9)$$

If we invoke the Gaussian approximation for $F_s(k, t)$ it has the simple form

$$F_s(k, t) = \exp[-k^2\langle [\mathbf{r}_1(0) - \mathbf{r}_1(t)]^2\rangle/6] \qquad (2.10)$$

where $\langle [\mathbf{r}_1(0) - \mathbf{r}_1(t)]^2\rangle$ is the mean square displacement of a particle in the liquid. This
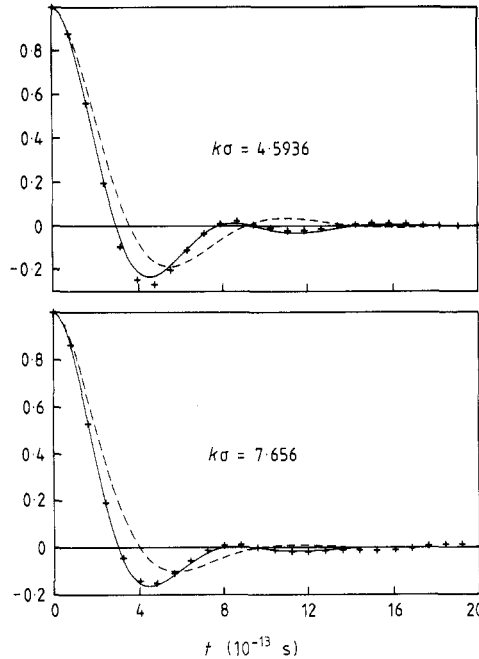
Figure 3. The same as for figure 2, except that the full curve shows $C_T^s(k, t)/mk_BT$ as obtained from equations (2.9) and (2.10), using MD data for the velocity autocorrelation function and mean square displacement.

is useful, because (2.9) and (2.10) allow us to avoid the use of viscoelastic models. In figure 3 we show the results for $C_T^s(k, t)$, obtained from (2.9), *using computer data for both the velocity autocorrelation function and the mean square displacement* (Balucani *et al* 1984). For $t \lesssim 2$ ps the self terms almost reproduce the computed transverse current data. There are some residual oscillations in $C_T(k, t)$ for longer times, although beyond 2 ps the velocity autocorrelation function data is 'noisy' and further comparison not very meaningful. It may be possible to make a more accurate assessment of $\eta_s^{-1}(k)$ by this means, a point we return to in Section 3.

2.2. Cross-velocity contribution to $C_T(k, t)$

Now, however, the cross-velocity terms, designated $C_T^d(k, t)$, have to be included. The velocity field is again employed so that we write

$$\left\langle mv_1^x(0) \sum_{j \neq 1} mv_j^x(t) \exp[i\mathbf{k} \cdot (\mathbf{r}_1(0) - \mathbf{r}_j(t))] \right\rangle$$

$$= \int d\mathbf{R} \left\langle mv_1^x(0) \sum_{j \neq 1} mv^x(\mathbf{r}_1(0) + \mathbf{R}, t) \delta(\mathbf{R} + \mathbf{r}_1(0) - \mathbf{r}_j(t)) e^{-i\mathbf{k} \cdot \mathbf{R}} \right\rangle. \quad (2.11)$$

Once again we decouple the momentum transfer and configurational relaxation components, and express this equation as

$$\left\langle mv_1^x(0) \sum_{j \neq 1} mv_j^x(t) \exp[i\mathbf{k} \cdot (\mathbf{r}_1(0) - \mathbf{r}_j(t))] \right\rangle$$

$$\simeq \int d\mathbf{R} \left\langle mv_1^x(0) mv^x(\mathbf{r}_1(0) + \mathbf{R}, t) \right\rangle \left\langle \sum_{j \neq 1} \delta(\mathbf{R} + \mathbf{r}_1(0) - \mathbf{r}_j(t)) \right\rangle e^{-i\mathbf{k} \cdot \mathbf{R}}$$

$$= [1/(2\pi)^3] \int d\boldsymbol{q} \, \tilde{f}(q) \int d\boldsymbol{R} \, [C_L(q, t)(\hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2$$

$$+ C_T(q, t)(1 - \hat{\boldsymbol{q}} \cdot \hat{\boldsymbol{x}})^2)] G_d(R, t) \, e^{i(\boldsymbol{q}-\boldsymbol{k}) \cdot \boldsymbol{R}}. \tag{2.12}$$

$G_d(R, t) \equiv \langle \Sigma_{j \neq 1} \delta(\boldsymbol{R} + \boldsymbol{r}_1(0) - \boldsymbol{r}_j(t)) \rangle$ is the distinct part of the well known van Hove correlation function, $G(R, t)$. The x direction indicated above refers to a reference frame in which $\boldsymbol{k}$ defines the z axis. With $C_L(q, t = 0) = C_T(q, t = 0) = mk_B T$, it follows that

$$C_T^d(k, t = 0) = 4\pi nmk_B T \int_0^\infty dR \, R^2 g(R) f(R) j_0(kR)$$

where we have used the result $G_d(R, t = 0) = ng(R)$, and j_0 denotes a spherical Bessel function. The width, a, of $f(R)$ is determined by the number density. For dense liquids, bearing in mind the exclusion effect in $g(R)$ at small R, it is small enough to make the product $f(R)g(R)$ zero for all practical purposes. This guarantees that $C_T(k, t)$ has the correct initial value. Now, in general we may represent $G_d(r, t)$ in the form

$$G_d(R, t) = n + [1/(2\pi)^3] \int d\boldsymbol{p} \, [F(p, t) - F_s(p, t)] \, e^{i\boldsymbol{p} \cdot \boldsymbol{R}}$$

$F(p, t)$ being the intermediate scattering function. With reference to (2.12)

$$\int d\boldsymbol{R} \, G_d(R, t) \, e^{i(\boldsymbol{k}-\boldsymbol{q}) \cdot \boldsymbol{R}} = (2\pi)^3 n\delta(\boldsymbol{k} - \boldsymbol{q}) + F(|\boldsymbol{k} - \boldsymbol{q}|, t) - F_s(|\boldsymbol{k} - \boldsymbol{q}|, t).$$

For the reason just mentioned, it is important that the excluded volume effect is properly taken into account in the evaluation of $C_T^d(k, t)$, and this is not a trivial achievement. Although we may choose, for example, a viscoelastic model for $F(|\boldsymbol{k} - \boldsymbol{q}|, t)$, the inevitable termination effects in the wavevector ($\boldsymbol{q}$) integral will distort the behaviour of $G_d(R, t)$ at small r. To avoid this problem we have made the following simplification. using the Vineyard approximation (Vineyard 1958) for the intermediate scattering function, we have

$$F(|\boldsymbol{k} - \boldsymbol{q}|, t) - F_s(|\boldsymbol{k} - \boldsymbol{q}|, t) \simeq [S(|\boldsymbol{k} - \boldsymbol{q}|) - 1]F_s(|\boldsymbol{k} - \boldsymbol{q}|, t).$$

Within the context of (2.12) the q-dependence of $F_s(|\boldsymbol{k} - \boldsymbol{q}|, t)$ may be safely neglected, for the reason given earlier in the arguments leading to the result in (2.9). Hence, we propose

$$\int d\boldsymbol{R} \, G_d(R, t) \, e^{i(\boldsymbol{k}-\boldsymbol{q}) \cdot \boldsymbol{R}} \simeq (2\pi)^3 n\delta(\boldsymbol{k} - \boldsymbol{q}) + F_s(k, t) n \int d\boldsymbol{R} \, h(R) \, e^{i(\boldsymbol{k}-\boldsymbol{q}) \cdot \boldsymbol{R}}$$

with $h(R) \equiv g(R) - 1$, and that in the evaluation of the integrals molecular dynamics data for $g(R)$ be used. This also ensures that the local structure around atom 1 is correctly described, which is important when considering momentum transfer between this atom and the neighbouring atomic shells.

On carrying out the angular integrations we eventually obtain from (2.12)

$$C_T^d(k, t) = n\tilde{f}(k)C_T(k, t)$$
$$+ (2n/3\pi) \int_0^\infty dq \, q^2 \tilde{f}(q) \int_0^\infty dR \, R^2 h(R) [C_L(q, t)(j_0(kR)j_0(qR)$$
$$- j_2(kR)j_2(qR)) + C_T(q, t)(2j_0(kR)j_0(qR)$$
$$+ j_2(kR)j_2(qR))]F_s(k, t) \tag{2.13}$$

where once again, j_0 and j_2 represent spherical Bessel functions. As with the auto-
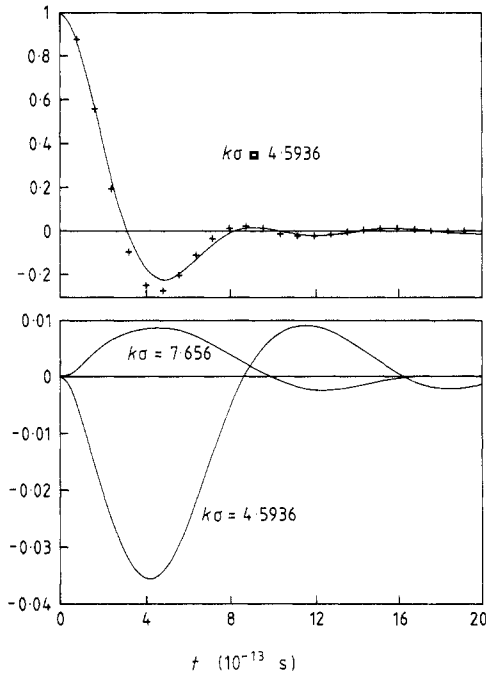
Figure 4. The upper diagram compares a theoretical result for the $C_T(k, t)/mk_BT$, obtained from equations (2.8) and (2.13) (full curve) with MD data (crosses). The lower diagram shows $C_T^d(k, t)/mk_BT$, as predicted by equation (2.13), for two different wavevectors.

correlation contribution, this expression is evaluated by using viscoelastic models for the currents. The equation explicitly introduces a Fourier component of the 'form factor' of the velocity field. Given the conditions attached to $f(r)$, there is little flexibility in $\tilde{f}(k)$. To test any differences the above expression has been evaluated with two different choices for $f(r)$, namely $f(r) = \exp[-(r/a)^{12}]$ and the step function $\theta(a - r)$. There was no significant change in the two results.

3. Results and conclusions

In figures 4 and 5 details of the theoretical results for $C_T(k, t)$ are presented, together with information about the separate components. In contrast to the earlier results, for the wavevector chosen in figure 5, $C_T^d(k, t)$ plays at least as equally important role as $C_T^s(k, t)$. Nevertheless, the overall agreement with the computer data is satisfactory, although probably because of the use of the Vineyard convolution approximation, the theory tends to underestimate $C_T(k, t)$ at small t. Whilst the Vineyard approxmation is intuitively quite appealing, it does have defects which become apparent when its prediction for the intermediate scattering function is analysed. However, it is convenient to use here, for the reasons already given. For the smallest wavevector we investigated, $k\sigma = 0.7656$, the results obtained for the transverse current are not significantly different from the viscoelastic model prediction. Indeed, at small k and large t, the dominant term arises from $C_T^d(k, t)$, namely $n\tilde{f}(k \to 0)C_T(k, t) \to C_T(k, t)$. So in this limit we reproduce the viscoelastic model. The advantage is that we gain some insight into the momentum transfer effects.
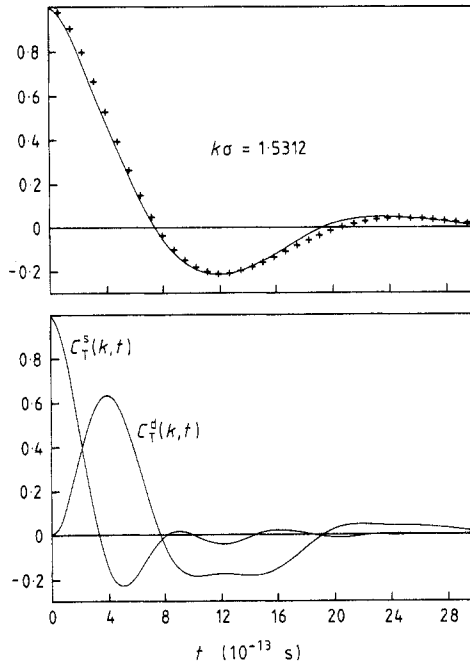
Figure 5. The upper diagram has the same caption as figure 4. The lower one shows the theoretical predictions for the 'self' and 'distinct' contributions to $C_T(k, t)/mk_BT$, using equations (2.8) and (2.13) respectively.

Table 1. The generalised fluidity results for liquid Rb.

$k\sigma$	$\bar{C}_T^s(k, z = 0)$ $(10^{-13}\,\text{s})$†	$\bar{C}_T^d(k, z = 0)$ $(10^{-13}\,\text{s})$†	$\bar{C}_T(k, z = 0)$ $(10^{-13}\,\text{s})$†	$\eta\,(\text{mP})^{-1}$ (Theory)†	$\eta\,(\text{mP})^{-1}$ (Viscoelastic model)	$\eta\,(\text{mP})^{-1}$ (MD data)
0.7656	1.163 (0.822)	7.987	9.150	0.184	0.1897	0.192 ± 0.014
1.5312	1.172 (0.838)	1.402	2.574	0.207	0.2281	0.232
2.2968	1.186 (0.865)	0.342	1.528	0.277	0.3233	0.255
3.0624	1.205 (0.900)	0.034	1.239	0.399	0.4882	0.380
3.8280	1.227 (0.942)	−0.088	1.139	0.573	0.7296	0.525
4.5936	1.253 (0.988)	−0.140	1.113	0.806	1.0586	0.618 ± 0.06
5.3592	1.280 (1.037)	−0.091	1.189	1.172	1.4907	0.952
6.1248	1.307 (1.085)	0.000	1.307	1.682	2.0400	1.515
6.8904	1.333 (1.133)	0.058	1.391	2.266	2.7073	1.850
7.6560	1.355 (1.177)	0.043	1.398	2.812	3.4744	2.427

† These values are obtained from (2.8) and (2.13) with $C_T(k, t = 0) = 1$. The numbers in brackets were derived from (2.9) and (2.10), using MD data for the velocity autocorrelation function and mean square displacement.

The results for the generalised transport coefficient are reported in table 1. The relative insensitivity of $\bar{C}_T^s(k, z = 0)$ to the size of the wavevector is quite striking, and in contrast to the behaviour of $\bar{C}_T^d(k, z = 0)$. The combination of the two terms produces a quite well defined minimum in $\bar{C}_T(k, z = 0)$ (for the viscoelastic model this feature is somewhat flatter). The effect appears to be more sharply defined when $\bar{C}_T(k, z = 0)$ is obtained by integrating computer simulation data of Balucani *et al* (1987) for the
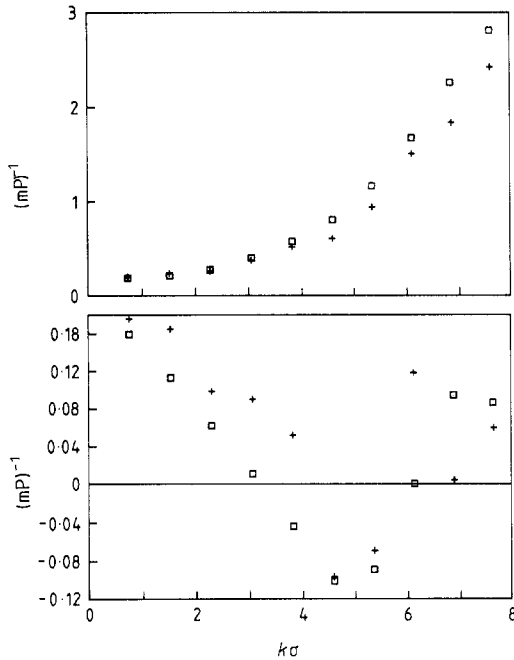
Figure 6. The upper diagram gives details of the generalised fluidity in liquid rubidium. The crosses represent MD data and the squares are theoretical results derived from equations (2.8) and (2.13). The lower one shows the fluctuations in $\eta_d^{-1}(k)$. The computed values are derived by subtracting $\eta_s^{-1}(k)$, as obtained from the second column in table 1 (brackets), from the MD data for $\eta^{-1}(k)$.

transverse current autocorrelation function. It is also clear that $\eta_d^{-1}(k)$ largely determines the value of the fluidity at small k, emphasising that in this limit the viscosity is a property of the collective behaviour of the liquid. For $k\sigma \simeq 3$, however, $\eta_s^{-1}(k)$ plays an equal role, and as k increases further rapidly becomes the dominant component.

The relationship between D and $\eta(k)$, which we referred to at the beginning of § 2, may be derived from the time integral of the velocity autocorrelation function given in (2.5). It is made more transparent by putting $F_s(k, t) = 1$, a well justified procedure in a dense liquid (Balucani *et al* 1985). There is no contribution from $C_L(q, t) = -(m^2/q^2)\ddot{F}(q, t)$, so it leads to

$$D = (nk_BT/3\pi^2) \int_0^\infty dk \, \tilde{f}(k)\eta^{-1}(k). \tag{3.1}$$

The fluidity tends to be significantly exaggerated by the viscoelastic model, leading to an overestimate of the diffusion coefficient. Table 1 shows clearly that our treatment of the different components in $C_T(k, t)$ lead to a much improved prediction of the generalised transport coefficient. The remaining discrepancy in magnitude arises from $\eta_s^{-1}(k)$. If we circumvent the use of the viscoelastic models in the theory, by using the numbers in brackets in table 1, it is largely removed. Theory and MD data are displayed in figure 6. The theoretical results do not show structure to the same degree as in the MD data. It is particularly evident in the latter for $3 \leqslant k\sigma \leqslant 6$, where there appears to be a quite well defined change in the gradient of $\eta^{-1}(k)$ (bear in mind that the size of the effect is subject to error bars, some of which are indicated in the table). Nevertheless, our work does provide some insight into its origin, which is the fluctuations in the distinct

term about a rather smoothly varying self-contribution, and reflects the momentum exchange effects with the surrounding atomic shells. This is demonstrated in the lower diagram in figure 6, which also represents a quite stringent test of the theory.

Some comments about the application of (3.1) are relevant in the light of the above calculations. It has been pointed out before that if we neglect the k-dependence of the fluidity completely and replace $\eta^{-1}(k)$ by its hydrodynamic limit, η^{-1}, this equation predicts (Gaskell 1984)

$$D \equiv D_{\mathrm{H}} = k_{\mathrm{B}}T/4\pi\eta a \tag{3.2}$$

with a playing the role of an effective particle radius in a Stokes–Einstein relation between D and η. We may use the result to estimate the self-diffusion coefficient of some simple liquids (e.g. argon), given the viscosity, over most of the liquid region of the phase diagram with an accuracy of about 25% or better. This can be useful since experimental information of the viscosity is far more readily available. For liquid metals however, this simple formula can underestimate D substantially near the melting point, according to the available experimental data. This is in sharp contrast with equivalent details for liquid argon. If we assume the validity of a Stokes–Einstein relation between D and η, for the purpose of defining an effective particle radius, R, the latter statements imply that a/R is significantly closer to unity for argon than for the alkali metals. The reason is not understood, though we suggest that a smaller effective radius for the diffusion process could be linked to the softer core of the pair potential in the metals.

Although the fine details of $\eta^{-1}(k)$ are not easily calculated, our work suggests a simple but realistic model for the fluidity which should allow a more accurate calculation of D. We exploit the details revealed by the calculations. These are (i) that $\eta^{-1}(k)$ is initially rather flat and (ii) that as k increases $\eta_{\mathrm{d}}^{-1}(k)$ decays rapidly and the fluidity is thereafter predominantly determined by $\eta_{\mathrm{s}}^{-1}(k)$. On the basis of these observations we propose the following model for the fluidity of a dense liquid. It is that

$$\eta^{-1}(k) = \eta^{-1}\theta(k_{\mathrm{c}} - k) + \eta_{\mathrm{s}}^{-1}(k)\theta(k - k_{\mathrm{c}}) \tag{3.3}$$

where θ denotes a step function. The self-term is zero at $k = 0$ then increases as k increases, and k_{c} is chosen as the wavevector at which the two components become equal, i.e. $\eta^{-1} = \eta_{\mathrm{s}}^{-1}(k_{\mathrm{c}})$. Unfortunately, we do not have a convincing model for $\eta_{\mathrm{s}}^{-1}(k)$ either, to fully exploit this suggestion. Nevertheless, we have the advantage of knowing that it has a parabolic dependence on k at small k, as pointed out in § 2, given by $k^2 D/nk_{\mathrm{B}}T$. As a first approximation, we use it to replace the self-term in (3.3). From our experience in the rubidium application this is still a reasonable procedure for a limited range of wavevectors beyond k_{c}, but then significantly underestimates $\eta_{\mathrm{s}}^{-1}(k)$ (except at large enough wavevectors for the ideal gas value to be relevant). Since it contains the unknown D, we further suggest replacing D by D_{H}. That is, (3.3) has become

$$\eta^{-1}(k) = \eta^{-1}\theta(k_{\mathrm{c}} - k) + [k^2 D_{\mathrm{H}}/nk_{\mathrm{B}}T]\theta(k - k_{\mathrm{c}}). \tag{3.4}$$

This should, at the very least, give a useful guide to the effect of including the wavevector dependence of $\eta(k)$. In table 2 we show predictions of the self-diffusion coefficient for some liquid metals near their melting points, and in table 3 the corresponding details for a wide range of thermodynamic states of a liquid argon model.

We conclude with the following remarks. From our work it is clear that a theory of the transverse current autocorrelation function must include a correct treatment of the self-component $C_{\mathrm{T}}^{\mathrm{s}}(k, t)$. The viscoelastic model assumes an exponential memory function, and whilst acceptable at small enough k, it fails for wavevectors where $C_{\mathrm{T}}^{\mathrm{s}}(k, t)$

Table 2. Theoretical predictions of the self-diffusion coefficient of some liquid metals at the melting point, using (3.1) and (3.4).

	T (K)	$10^{24}\, n$ (cm^{-3})	η(mP) Expt.	$10^5\, D$ (cm^2 s^{-1}) Expt.	$10^5\, D_H$ (cm^2 s^{-1}) From (3.2)	$10^5\, D$ (cm^2 s^{-1}) Theory
Li	453	0.04402	6.0	6.1	4.72	5.33
Na	371	0.02428	7.0	4.2	2.72	3.07
K	337	0.01732	5.4	3.7	2.58	3.10
Rb	312	0.01038	6.7	2.7	1.80	2.03
In	429	0.03710	19.0	1.6	1.34	1.51
Sn	505	0.03536	21.0	2.0	1.40	1.58

Table 3. Theoretical predictions of the self-diffusion coefficients for a liquid argon model, using (3.1) and (3.4). The MD data are from Hoheisel *et al* (1987).

T (K)	$10^{24}\, n$ (cm^{-3})	η(mP) MD data	$10^5\, D$ (cm^2 s^{-1}) MD data	$10^5\, D_H$ (cm^2 s^{-1}) From (3.2)	$10^5\, D$ (cm^2 s^{-1}) Theory
81.8	0.02161	3.08	1.5	1.31	1.48
85.5	0.02138	2.97	1.72	1.42	1.60
116.5	0.02029	1.97	3.7	2.86	3.23
120.3	0.01824	1.09	4.8	5.147	5.81
139.7	0.01583	0.77	8.2	8.07	9.11
150	0.01061	0.34	16	17.17	19.38
219.6	0.01519	0.73	14	13.2	14.90
221.3	0.02593	6.09	2.3	1.91	2.15
225.4	0.02029	1.75	6.4	6.22	7.02
303.4	0.02634	4.78	3.5	3.35	3.78
309.1	0.01882	1.33	11.7	10.95	12.36

becomes significant. With hindsight this is not surprising because the self-component depends crucially on the velocity autocorrelation function for which an exponential memory function is known to be inadequate. Despite the criticism of the viscoelastic approximation, our use of it through the concept of a microscopic velocity field leads to a much improved description of $C_T(k, t)$ over an important wavevector range. We use viscoelastic models for the currents because of their relatively simple k and ω dependence, which considerably reduces the amount of computation. However, our approach involves the determination of the transverse current through the Fourier components of the velocity field, which themselves contain the current density fluctuations. This, in principle, offers the possibility of a self-consistent determination of the transverse current autocorrelation function and the associated transport coefficient, although the computational effort will be quite heavy, and it has not been attempted. The existing results, we believe, already give new insight into both these quantities.

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