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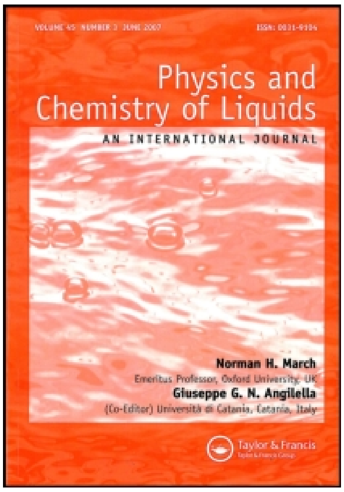

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Microdynamics, Diffusion and Structural Relaxation in Liquids

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Microdynamics, Diffusion and Structural Relaxation in Liquids

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The extensive molecular dynamics data that are available for a liquid aluminium model are used to investigate single particle dynamics. The introduction of structural rearrangements into a theory of the velocity autocorrelation function is carefully examined, and its influence on the self-diffusion coefficient investigated. It is pointed out that structural relaxation becomes particularly significant in supercooled states of the liquid, and provides a dynamical feedback effect that could be a mechanism for the glass transition.

Key words: single particle dynamics, structural relaxation, liquid aluminium model, structural rearrangements.

1 INTRODUCTION

The extensive molecular dynamics data available from a liquid aluminium model[1,2] is used to try to establish the effects of structural relaxation in a theory of the diffusion process in simple liquids. A recent analysis[3] of these data is briefly reviewed, but the emphasis here is on single particle dynamics via the velocity autocorrelation function $\psi(t)$. We attempt to elucidate the effects on $\psi(t)$, and hence the diffusion coefficient, of structural rearrangements in the relaxation of fluctuating shear stresses. Within our theory these produce a slowly decaying component in the velocity autocorrelation function. The magnitude is too small to have a noticeable impact on the appearance of the latter, but its influence on the low frequency behaviour of the frequency spectrum, particularly the predicted self-diffusion coefficient, is emphasised.

Now structural relaxation itself is clearly controlled by atomic diffusion, and in principle our approach leads to a closed equation for the diffusion coefficient including this dynamical feedback effect. The framework for our analysis should be applicable to all simple liquids, even when strongly supercooled. In the latter case structural relaxation becomes more and more important in controlling the diffusion process. It is pointed out that our theory may have some relevance to a better understanding of the frustration of the diffusion mechanism in strongly supercooled states, and perhaps the onset of the glass transition.

2 THEORETICAL FRAMEWORK

The expression we use to interpret the velocity autocorrelation function data is derived by introducing a microscopic velocity field[4]. The result will be quoted here, but we emphasise the following points. Firstly, by means of the velocity field we introduce momentum transfer between a chosen atom and its neighbours and can impose momentum conservation in the theory. Secondly, the essential step in the derivation relies on the assumption that the time scale for momentum transfer is very much shorter than for atomic diffusion. This is clearly justified in a dense liquid. Eventually we obtain

$$\psi(t) = \frac{1}{3mk_BT}\frac{1}{(2\pi)^3}\int d\mathbf{q}\tilde{f}(q)(C_L(q,t) + 2C_T(q,t))F_S(q,t) \tag{1}$$

which allows us to define the components $\psi_L(t)$ and $\psi_T(t)$ such that $\psi(t) = \psi_L(t) + \psi_T(t)$. $C_L(q,t)$ and $C_T(q,t)$ are the longitudinal and transverse momentum current correlation functions, $F_S(q,t)$ is the self-intermediate scattering function and $\tilde{f}(q)$ the Fourier transform of (essentially) a step function introduced through the velocity field.

An analysis was made[3] of molecular dynamics data obtained for a liquid aluminium model. The average temperature of the system is $T = 984$ K and the number density $\rho = 0.05276 \times 10^{24}$ cm^{-3}. Details of the pair potential are given in Ref. 1, where it was shown to give a good description of phonon dispersion curves in solid aluminium. It is known from the data that collective density excitations are supported for wavelengths down to about twice the interparticle separation (r_0). If Eq. (1) is to be usefully applied it is important that the expression we use for $C_L(q,t)$ should be accurate enough to reflect both this behaviour and the appropriate dispersion of the collective modes. This is because $\psi(t)$ is determined by a superposition of two components and the phase of the oscillations in $\psi_L(t)$ are particularly significant. The familiar

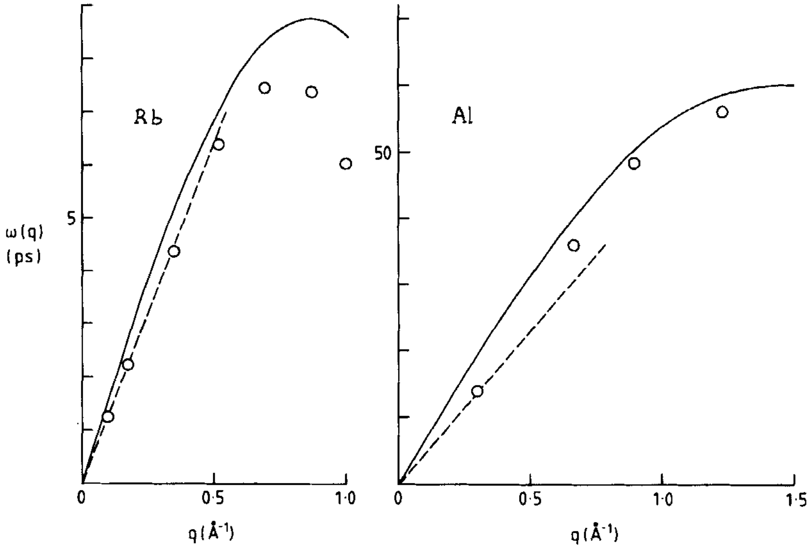

Figure 1 Open circles show dispersion curves, obtained from computer simulation data of the dynamic structure factor, for liquid rubidium and liquid aluminium. The dashed line is the hydrodynamic form $\omega = c_s q$, where c_s is the velocity of sound in the liquid. The full curve is $\omega_l(q)$.

viscoelastic model[5] does not come into this category. This may be connected with the form of dispersion relation derived from the molecular dynamics study. In Figure 1 we illustrate the dispersion relation, $\omega(q)$, for Rb (where the viscoelastic model works quite well) and for Al, both obtained from $S(q, \omega)$ data. Also shown are the respective frequencies, $\omega_l(q)$, defined through the second and fourth moments of $S(q, \omega)$ by $\omega_l^2 = \overline{\omega^4}/\overline{\omega^2}$, where as usual $S(q, \omega)$ is the dynamic structure factor.

The viscoelastic model predicts for the longitudinal current an expression of the form

$$\begin{aligned} C_L(q, t) = {} & A(q)e^{-a(q)t} + B(q)e^{-b(q)t}\cos(\omega_0(q)t) \\ & + C(q)e^{-b(q)t}\sin(\omega_0(q)t) \end{aligned} \tag{2}$$

The frequency of the excitations, $\omega_0(q)$, is normally determined from the solution of a cubic equation, whose coefficients are expressed in terms of $\overline{\omega^2}$ and $\overline{\omega^4}$. In an attempt to adapt this model for Al (following the lead given by Ebbsjo *et al.*'s[1] numerical fit of the intermediate scattering function data) we select $\omega_0(q)$ as $\omega_l(q)$. This can be seen to be not unreasonable from the details in Figure 1. Information about the choice

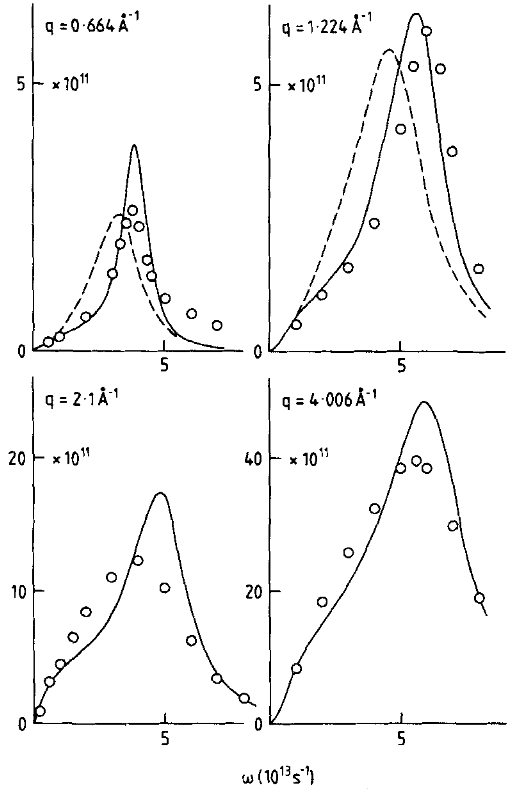

Figure 2 Longitudinal current spectra, $\omega^2 S(q, \omega)(s^{-1})$, for a range of wavevectors in Al. The full curves show modified viscoelastic model[3] results, the broken curves are obtained from the usual viscoelastic model[5] and the open circles represent computer data[1].

of relaxation times, and some limitations of this procedure are contained in Ref. 3. Figure 2 compares computer data of $\omega^2 S(q, \omega) = (q^2/m^2)C_L(q, \omega)$ with model predictions for a range of wavenumbers. The model gives a respectable description of the location of peak frequencies, whereas in the unmodified viscoelastic scheme the peak frequencies are consistently low.

We discuss the transverse current in terms of its Laplace transform

$$\tilde{C}_T(q, s) = \int_0^\infty dt \exp(-st) C_T(q, t)$$

and write, formally

$$\tilde{C}_T(q, s) = mk_B T/(s + (q^2/\rho m)\tilde{\eta}(q, s)) \tag{3}$$

where $\tilde{\eta}(q, s)$ is the memory function or generalized viscosity. In the viscoelastic approximation the time-dependence of $\eta(q, t)$ is described by a single exponential. However, it can be shown that

$$\eta(q = 0, t) = (\rho/k_B T)\langle\sigma_{xy}(0)\sigma_{xy}(t)\rangle \tag{4}$$

with $\sigma_{xy}(t)$ an off-diagonal element of the microscopic stress tensor[6]. Computer studies in dense liquid models show that the decay of the stress autocorrelation function in Eq. (4) is described by two quite different relaxation times. Mode coupling theory suggests that the slowly decaying component may be accounted for in terms of the relaxation of density fluctuations, which in turn involves structural rearrangements. One would expect, at least at small q, that the memory function will also contain two components. Consequently we modify the viscoelastic scheme to try to incorporate these processes in a phenomenological manner by writing

$$\eta(q, t) = G(q)[(1 - \alpha(q))e^{-t/\tau_s(q)} + \alpha(q)e^{-t/\tau_l(q)}] \tag{5}$$

$G(q)$ is the rigidity and $\tau_l \gg \tau_s$. The first term is used, at small t, to describe the rapid decay of the correlation function due to binary collisions. Such a scheme was used by Levesque *et al.*[7] to fit computer simulation data of $C_T(q, t)$ for liquid argon.

There is no transverse current data for Al, and our selection of the parameters in Eq. (5) uses the following ideas:

i) $\tau_s(q = 0)$ and $\tau_l(q = 0)$ are fixed in units of the Enskog mean collision time by appealing respectively to Enskog theory in a rigid sphere fluid, and computer simulation studies in a Lennard-Jones (and rigid sphere) fluid[3]. By representing the liquid metal as a hard sphere system of approximately the same packing fraction their values are transferred to the metal. The relaxation time $\tau_l(q)$ is taken to be independent of q[7], whilst the assumed form of $\tau_s(q)$ is a familiar one from the viscoelastic approximation[8]. We find that $\tau_l \simeq 15\tau_s(q = 0)$, which is not inconsistent with the numerical fit by Levesque *et al.*

ii) $\alpha(q = 0)$ is then fixed by the hydrodynamic requirement

$$(1 - \alpha(0))\tau_s(0) + \alpha(0)\tau_l = \eta/G(q = 0) \tag{6}$$

where η is the shear viscosity coefficient. Since the presence of $\alpha(q)$ is to take account of structural rearrangements, we expect it to decay rapidly for $q \gtrsim 2\pi/2r_0$ and it was assumed[3] that $\alpha(q) = \alpha(0)\exp(-(q/q_c)^2)$ where $q_c = \pi/r_0$.

3 RESULTS AND DISCUSSION

The details of the velocity autocorrelation function, obtained from Eq. (1), are shown in Figure 3 together with the frequency spectrum $\tilde{\psi}(\omega) \equiv \int_0^\infty dt \cos(\omega t)\psi(t)$. It can be seen that $\tilde{\psi}_L(\omega)$ is responsible for the "shoulder" on the high-frequency side of the principle peak in the frequency spectrum. The work of Hahn and Matzke[2] has made it possible to compare the two components $\psi_L(t)$ and $\psi_T(t)$ with their molecular dynamic counterparts. The improvement in the longitudinal component, when compared to that obtained with the usual viscoelastic model for $C_L(q, t)$, is significant. It is also apparent that the transverse component is in overall better accord with the computer data when the

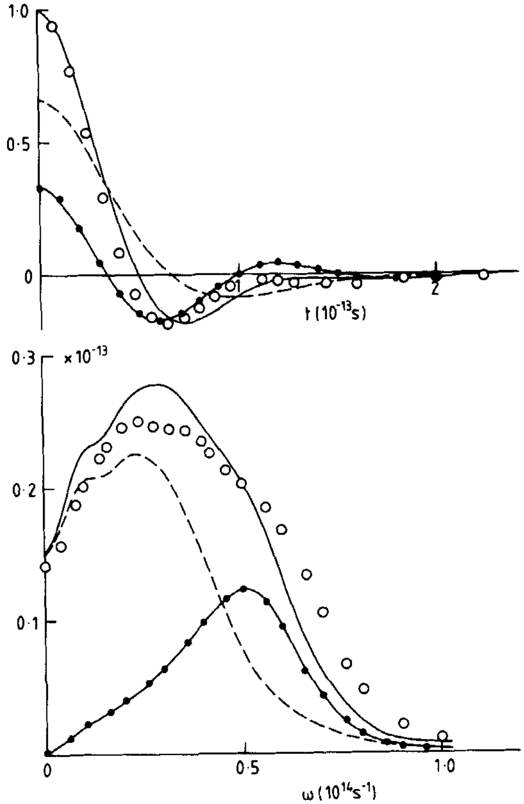

Figure 3 The full, dotted and broken curves in the upper figure represent $\psi(t)$, $\psi_L(t)$ and $\psi_T(t)$ respectively, as defined through Eq. (1), for Al. The corresponding frequency spectra are shown below. The open circles represent computer data of $\psi(t)^1$ and its spectrum $\tilde{\psi}(\omega)(s)$.

two exponential model is used for the memory function of the transverse current[3].

However, we wish to concentrate here on other aspects of the effect of the slowly decaying component in the memory function. The stucture on the low frequency side of the peak in the spectrum in Figure 3 is produced by a weak but extensive negative tail in $\psi_T(t)$, which itself arises from the slow decay of $\eta(q, t)$. Computer data of $\psi(t)$ by Ebbsjo *et al.* (Studsvik Research Laboratory Report NFL-4, 1978) does show evidence of a long-ranged negative tail, but the magnitude is smaller than in our theory. Some of these data are plotted in Figure 3 (although the tail, beyond 2×10^{-13} s, is too small to be seen), along with the frequency spectrum we have calculated from these data. Probably the most important effect of the long-ranged component is on the self-diffusion coefficient D. In our theory D is determined by the coupling of a particles motion to the transverse current. Using Eq. (1) and Eq. (3) it follows that in a dense liquid[9] (where we can, to an excellent approximation, put $F_s(q, t) = 1$ in Eq. (1))

$$D = (k_B T/m) \int_0^\infty dt \psi(t) = (\rho k_B T/3\pi^2) \int_0^\infty dq f(q)/\eta(q) \tag{7}$$

where $\eta(q) \equiv \tilde{\eta}(q, s = 0)$ and $\tilde{\eta}(q = 0) = \eta$. According to the model used here the wavevector-dependent viscosity is given by

$$\eta(q) = G(q)[(1 - \alpha(q))\tau_s(q) + \alpha(q)\tau_l(q)] \tag{8}$$

The inclusion of τ_l reduces the predicted diffusion coefficient by about 20%. In Figure 4 we give details of $\tilde{\eta}(q) \equiv \eta(q)/\eta$. The influence of the term $\alpha(q)\tau_l(q)$ is to tend to flatten the curve at small q. For comparison, computer data obtained recently for a rigid sphere fluid[10] and a Lennard-Jones liquid[11] at approximately the same packing fraction are included. The data and the theoretical curve show a rapid decrease of $\tilde{\eta}(q)$ for $q\sigma < 10$. Although not shown here, this is followed by a slower $1/q$ decay typical of free particle behaviour for $q\sigma > 25$. However, both sets of data show the appearance of a sort of 'shoulder' at $q\sigma \sim 4$. We expect it to be present in Al, but our simple model cannot produce the effect.

We conclude with some comments which attempt to clarify the role of the relaxation time, τ_l, in controlling the diffusion process as the liquid is supercooled. They should be applicable to all simple liquids. The structural relaxation time itself could be interpreted through the leakage of particles from the nearest neighbour shell of a given reference atom. We could conveniently take it to be the time required for 50% of the nearest neighbours to be exchanged. A relaxation time, so defined,

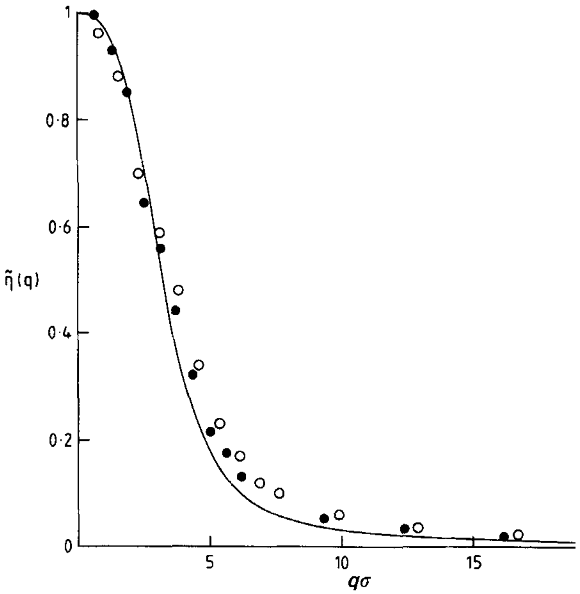

Figure 4 Generalized wavevector-dependent shear viscosity $\tilde{\eta}(q) = \eta(q)/\eta$. The open circles show simulation data for a rigid sphere fluid[10], the dots are data from a Lennard-Jones system[11] and the full curve is the theoretical prediction for Al from Eq. (8).

has been investigated recently in a molecular dynamics study of supercooled states of a liquid Rb model[12]. The movements of about 12 nearest neighbours of a tagged particle, initially within a sphere of appropriately chosen radius, are "observed" in the computer experiment. After the requisite averaging over tagged particles and time origins the number of original atoms within the sphere is calculated as a function of time. As the system was supercooled from the melting point (318.5 K) to 234.4 K the structural relaxation time was found to increase from 12 ps to 30 ps. The self-diffusion coefficient decreased from $2.21 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ to $0.83 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Since structural relaxation depends on diffusive motion, we suggest that the stuctural relaxation time $\sim A(r_0/2)^2/D$, $(r_0/2)$ being the atomic sphere radius, and A is a parameter whose value we would anticipate to be of order unity. This expression gives a very reasonable estimate of the relaxation times obtained by Kinell and Lovesey[12], when $A \approx 0.33$.

Consequently we anticipate that $\tau_l \sim ar_0^2/D$, where a is a numerical factor which could be estimated from computer simulation data of the transverse current. With this expression for τ_l we have

$$D = (\rho k_B T/3\pi^2) \int_0^\infty dq f(q)/\{G(q)[(1-\alpha(q))\tau_s(q) + \alpha(q)ar_0^2/D]\}$$

or

$$D\left[1-(\rho k_B T/3\pi^2)\int_0^\infty dq\, f(q)/\{G(q)[(1-\alpha(q))D\tau_s(q)+\alpha(q)ar_0^2]\}\right]=0 \tag{9}$$

If the explicit dependence of τ_l on D^{-1} can be made more precise, the above equation may give valuable information about the temperature dependence of the self-diffusion coefficient in the supercooled region of the phase diagram. Because of the introduction of a dynamical feedback mechanism into the theory it is also possible that in some regions $D = 0$ is the only solution of Eq. (9), perhaps signalling the onset of the glass transition. Similar ideas have been discussed by Geszti[13] (see also Sjolander and Turski[14]) although in terms of a viscosity feedback mechanism. In this case it was suggested that the feedback mechanism leads to an instability, namely $\eta \to \infty$, at some temperature. It also follows from our work that if $D \to 0$, $\tau_l \to \infty$ and hence that $\eta \equiv \int_0^\infty dt\eta(q=0,t) \to \infty$. The merit of the present derivation is that it is contained within a microscopic framework which can accurately describe the details of atomic dynamics displayed in computer simulation data, as we have demonstrated above.

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