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# Fluidity and diffusion coefficient of simple liquids: a velocity field approach

S F Duffy†, T Gaskell†||, G Jackson†¶, R Vallauri§ and U Balucani§

† Department of Physics, The University, Sheffield S3 7RH, UK

‡ Department of Chemistry, The University, Sheffield S3 7HF, UK

§ Istituto di Elettronica Quantistica CNR, 50127 Firenze, Italy

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**Abstract.** The transverse current autocorrelation function,  $C_T(k, t)$ , can be represented as a sum of a velocity autocorrelation or 'self' term,  $C_T^s(k, t)$ , and a cross-velocity or 'distinct' term,  $C_T^d(k, t)$ . By means of the Langevin equation a generalized (i.e.  $k$ -dependent) fluidity,  $\eta^{-1}(k)$ , may be introduced which is conveniently the sum of the contributions from the two components of the transverse current. We concentrate on  $C_T^s(k, t)$  and for the first time compare a theoretical prediction of this quantity for both liquid Rb and liquid Ar with computer simulation data. The success of the theory suggests a model for the associated fluidity,  $\eta_s^{-1}(k)$ . We show how to use it to predict the diffusion coefficient of a number of simple liquids, with an estimated accuracy of 20 percent or better, given the shear viscosity coefficients as input data. A satisfactory representation of the distinct component,  $\eta_d^{-1}(k)$ , is more difficult to achieve, but we discuss the general features which are revealed by computer simulation studies.

## 1. Introduction

An investigation of aspects of the transverse current autocorrelation function is reported. The emphasis is on achieving a better understanding of the associated generalized fluidity coefficient,  $\eta^{-1}(k)$ . Both theory and computer simulation are employed and the results are used to calculate the self-diffusion coefficient of a liquid, given the hydrodynamic shear viscosity coefficients as input data.

The theoretical framework is presented in the next section and the single-particle components in the transverse current investigated in detail. The conclusions suggest a model for  $\eta_s^{-1}(k)$  which is described in section 3 and its application to the prediction of the diffusion coefficient of liquids is demonstrated.

## 2. Transverse current and generalized fluidity

The momentum current density fluctuation in a simple liquid is defined as

$$j_k^\alpha(t) = \sum_i m v_i^\alpha(t) \exp(ik \cdot r_i(t))$$

|| Deceased.

¶ Author to whom correspondence should be addressed.

where  $\alpha$  signifies a Cartesian component and we may introduce the transverse current autocorrelation function,

$$C_T(k, t) = \langle j_{-k}^\alpha(0) j_k^\alpha(t) \rangle / N \quad (1)$$

in which, with  $k$  along the  $z$  axis,  $\alpha$  denotes  $x$  or  $y$ . Clearly, 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 components as  $C_T^s(k, t)$  and  $C_T^d(k, t)$  respectively.

It is now well known that, by means of the generalized Langevin equation, the Laplace transform of this correlation function,  $\hat{C}_T(k, z)$ , may be usefully expressed in the form

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

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

$$\eta^{-1}(k) = k^2 \hat{C}_T(k, z = 0) / nm C_T(k, t = 0) = \eta_s^{-1}(k) + \eta_d^{-1}(k) \quad (3)$$

and is conveniently the sum of the self and distinct contributions in terms of  $C_T^s(k, t)$  and  $C_T^d(k, t)$ , respectively. The following limits are known exactly (Balucani *et al* 1985):

$$\eta_s^{-1}(k \rightarrow 0) = k^2 D / nk_B T \quad (4)$$

$$\eta^{-1}(k \rightarrow \infty) = k(2mn^2 k_B T / \pi)^{-1/2}. \quad (5)$$

One expects the self-correlation terms in the transverse current to begin to dominate at large enough wavevectors and it has been demonstrated that viscoelastic theory fails to give an adequate account of such terms (Gaskell and Duffy 1989). Now the separate contributions to the transverse current are defined by the equations

$$\begin{aligned} C_T(k, t) &= \langle m v_1^x(0) m v_1^x(t) \exp[ik \cdot (r_1(t) - r_1(0))] \rangle \\ &\quad + \left\langle m v_1^x(0) \sum_{i \neq 1} m v_i^x(t) \exp[ik \cdot (r_i(t) - r_1(0))] \right\rangle \\ &\equiv C_T^s(k, t) + C_T^d(k, t). \end{aligned} \quad (6)$$

We concentrate here on the evaluation of the self term. A quantitatively accurate expression for the velocity autocorrelation function in a dense liquid has been derived by introducing the concept of a velocity field at a microscopic level. This we write as  $V(r, t) = \sum_i v_i(t) f(|r - r_i(t)|)$ . 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  $n \int d^3 R V(r, t) = \sum_i v_i(t)$  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  $\frac{4}{3}\pi a^3 = n^{-1}$  (Gaskell and Miller 1978). Adopting the same technique to the evaluation of  $C_T^s(k, t)$ , we obtain (Gaskell and Duffy 1989)

$$C_T^s(k, t) = \langle m v_1^x(0) m v_1^x(t) \exp[ik \cdot (r_1(t) - r_1(0))] \rangle$$

$$\approx \frac{1}{2\pi^3} \int d^3q \hat{f}(q) [C_L(q, t)(\hat{q} \cdot \hat{x})^2 + C_T(q, t)(1 - (\hat{q} \cdot \hat{x})^2)] F_s(|k - q|, t).$$

(7)

In the above equation  $C_L(q, t)$  is the longitudinal current autocorrelation function and  $F_s(q, t)$  and  $\hat{f}(q)$  are the Fourier transforms of the single-particle probability density and  $f(r)$  respectively.

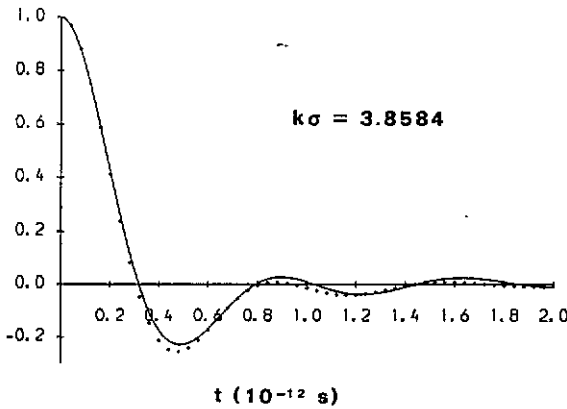


Figure 1. The self term of the transverse current,  $C_T^s(k, t)/m k_B T$ , in liquid rubidium as a function of time in picoseconds. The full curve is the theoretical prediction from (7) and the crosses represent exact MD data.

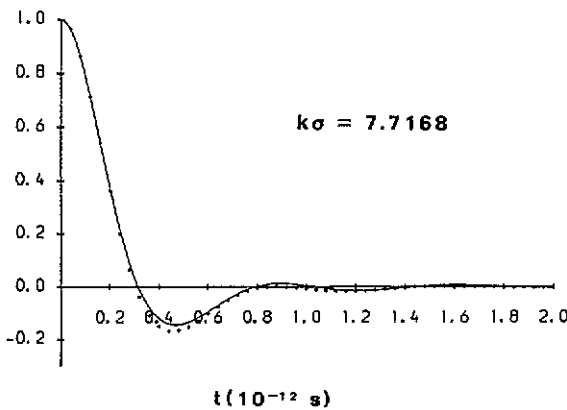


Figure 2. The self term of the transverse current,  $C_T^s(k, t)/m k_B T$ , in liquid rubidium as a function of time in picoseconds. The full curve is the theoretical prediction from (7) and the crosses represent exact MD data.

We have also carried out a molecular dynamics (MD) simulation study of the transverse current autocorrelation function in both liquid rubidium and argon models. The data have been analysed into the self and distinct components so that a direct comparison of the above theoretical expression with MD data is possible. In the rubidium simulation 250 particles interact through the effective pair potential of Price *et al* (1970), which has been tested successfully in the liquid phase (Rahman 1974a, b). The mean temperature of the system is 316.8 K and reduced density  $n\sigma^3 = 0.904$  ( $\sigma = 4.4048 \text{ \AA}$  being the distance at which the potential is first zero). The data and the theoretical expression for  $C_T^s(k, t)$  are compared in figures 1 and 2. Because they are convenient, we use viscoelastic models for  $C_L(q, t)$  and  $C_T(q, t)$  in the evaluation of (7) and the Gaussian approximation for  $F_s(q, t)$  (Gaskell and Duffy 1989). Bearing in mind the limitations of viscoelastic theory the agreement is good, particularly with regard to the phase of the oscillations.

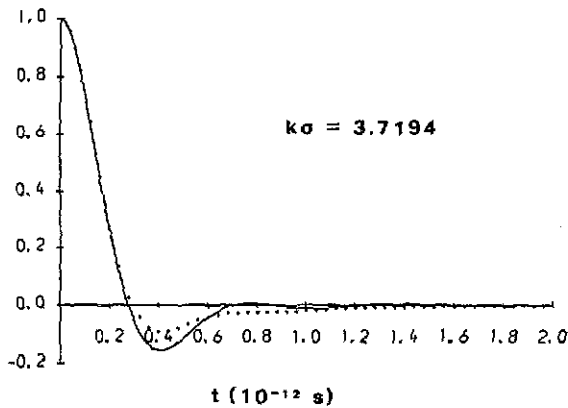


Figure 3. The self term of the transverse current,  $C_T^s(k, t)/mk_B T$ , in liquid argon as a function of time in picoseconds. The full curve is the theoretical prediction from (7) and the crosses represent exact MD data.

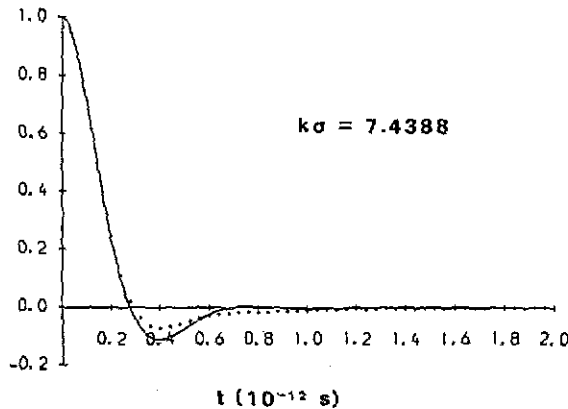


Figure 4. The self term of the transverse current,  $C_T^s(k, t)/mk_B T$ , in liquid argon as a function of time in picoseconds. The full curve is the theoretical prediction from (7) and the crosses represent exact MD data.

In figures 3 and 4 we show equivalent results for a liquid Ar model. The pair potential used in this case in the MD study is of the familiar Lennard-Jones type, the mean temperature being 94.6 K and  $n\sigma^3 = 0.905$  where  $\sigma = 3.405 \text{ \AA}$ . The number of particles used was 864 and the potential was truncated at  $r_c = 2.5\sigma$ . It should be noted, however, that the viscoelastic model for the currents is less satisfactory in argon than in rubidium. As a consequence a rather subtle feature of the details of  $C_T^s(k, t)$  which are revealed by the MD data is not reproduced by the theory. We refer to the 'shoulder' or 'plateau' in the data just beyond the first minimum in  $C_T^s(k, t)$ . This is shown in both figures 3 and 4, in contrast to the results in Rb where further oscillations are discernible beyond the first minimum.

We now discuss a model for the generalized fluidity,  $\eta_s^{-1}(k)$ , arising from the theory and exploit it for the prediction of the self-diffusion coefficient.

### 3. Diffusion model for $\eta_s^{-1}(k)$

The success of the theoretical expression for  $C_T^s(k, t)$  has an implication which suggests a model for  $\eta_s^{-1}(k)$ . The latter may be obtained as

$$\eta_s^{-1}(k) = k^2 \hat{C}_T^s(k, z=0) / nm C_T^s(k, t=0) = \hat{C}_T^s(k, z=0) / nm^2 k_B T \quad (8)$$

where

$$\hat{C}_T^s(k, z=0) = m^2 \int_0^\infty dt \langle v_1^x(0) v_1^x(t) \exp[ik(z_1(t) - z_1(0))] \rangle.$$

With reference to (7), because the time decay of  $C_L$  and  $C_T$  is much more rapid than that of  $F_s$  for the predominant wavevector range in the integral (determined by the width of  $\hat{f}(q)$ ), we may safely ignore the  $q$  dependence in  $F_s$ . In this case the equation becomes

$$C_T^s(k, t) = \frac{1}{3(2\pi)^3} \int d^3 q \hat{f}(q) [C_L(q, t) + 2C_T(q, t)] F_s(k, t).$$

The prefactor of  $F_s(k, t)$  is essentially the velocity-field expression for the velocity autocorrelation function (Balucani *et al* 1985). The implication is that we may usefully decouple the velocity terms in  $C_T^s(k, t)$  and write it as

$$C_T^s(k, t) \approx m^2 \langle v_1^x(0) v_1^x(t) \rangle F_s(k, t) = (k_B T / m) \psi(t) F_s(k, t) \quad (9)$$

where  $\psi(t)$  denotes the velocity autocorrelation function normalized at  $t = 0$ . Hence, within this approximation

$$\eta_s^{-1}(k) = (k^2 / nm) \int_0^\infty dt \psi(t) F_s(k, t). \quad (10)$$

Clearly

$$\eta_s^{-1}(k \rightarrow 0) = (k^2 / nm) \int_0^\infty dt \psi(t) = k^2 D / nk_B T. \quad (11)$$

In the large  $k$  limit,  $F_s(k, t)$  assumes the ideal gas value and decays so rapidly with respect to the velocity autocorrelation function that in the integrand only  $\psi(t \rightarrow 0) = 1$  is significant. The result is that  $\eta_s^{-1}(k \rightarrow \infty) = k(2mn^2k_B T/\pi)^{-1/2}$ . Both these limits are in agreement with exact results given in (4) and (5).

We propose to use the Gaussian approximation for  $F_s(k, t)$ , which is completely specified by a knowledge of  $\psi(t)$ , that is

$$F_s(k, t) = \exp\left(-k^2 k_B T/m \int_0^t ds (t-s)\psi(s)\right). \quad (12)$$

In a normal liquid, non-Gaussian effects are found to be quite small making this expression an excellent approximation for the self-correlation function (Hansen and McDonald 1986). Because the predicted results for  $\eta_s^{-1}(k)$  depend on the integrated value of the velocity autocorrelation function, we may hope that the fine details of the latter's time dependence are not too important. Hence the name diffusion model. We therefore propose to use a relatively simple expression for  $\psi(t)$  derived from an assumed exponential decay of its associated memory function,  $M(t) = \omega_E^2 \exp(-t/\tau)$ ,  $\omega_E$  being the Einstein frequency (see e.g. Hansen and McDonald 1986). The pre-factor guarantees the short-time behaviour of the velocity autocorrelation function, but more importantly, the relaxation time is chosen so that its integrated value correctly reproduces some chosen value for  $D$ . With this choice of memory function both  $\psi(t)$  and the exponent in (12) can be obtained analytically as a function of  $\omega_E$  and  $D$ .

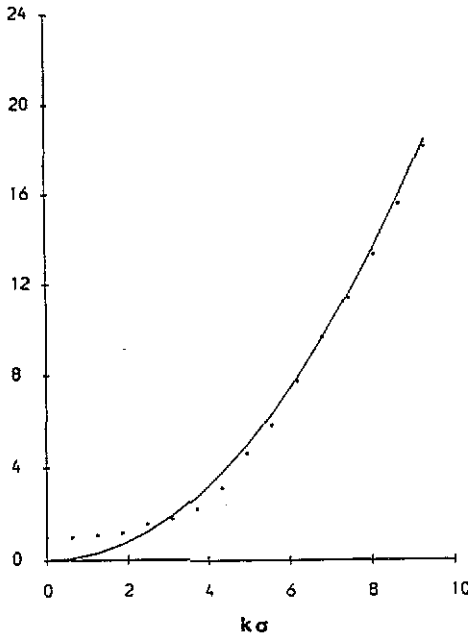


Figure 5. Results obtained using the diffusion model for liquid rubidium for different wavevectors  $k\sigma$ . The smooth curve is the self term of the generalised fluidity  $\eta_s^{-1}(k)$  (10) and the crosses denote the exact MD data for  $\eta_s^{-1}(k)$ .

In figure 5 we demonstrate the applicability of this simple model of  $\psi(t)$  for the liquid Rb system referred to above. Results for  $\eta_s^{-1}(k)$  obtained from (10) using this prescription for  $\psi(t)$  (with a value for  $D$  obtained from MD data) are compared

with exact values of  $\eta_s^{-1}(k)$  obtained from MD data for  $C_T^s(k, t)$  (see equation (8)). The agreement is very good. Therefore, we have an expression for  $\eta_s^{-1}(k)$  which has an explicit dependence on the self-diffusion coefficient. It satisfies both the large and small  $k$  limits and we believe it will give a satisfactory representation for all wavevectors, for the reasons discussed above. In figures 6 and 7 we compare  $\eta_s^{-1}(k)$  for Rb and Ar obtained using the diffusion model with exact computer simulation data for the total generalised fluidity  $\eta^{-1}(k)$  (equation (3)). In this case, the MD Rb study was performed at a temperature of 332 K, all the other state points being the same as those previously discussed. The details clearly establish the predominance of the self term in the generalised fluidity for  $k\sigma \geq 3$ . The contribution from  $\eta_d^{-1}(k)$  dominates at small  $k$  and is, we believe, responsible for the structure observed in the computer data at larger  $k$  which produces the fluctuations in  $\eta(k)$  about the self term.

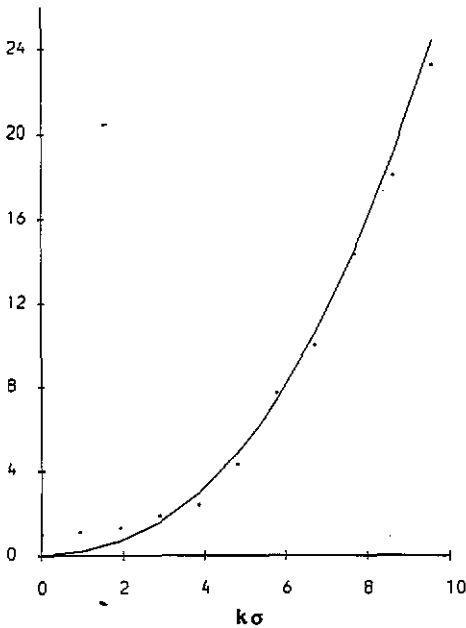


Figure 6. The total generalised fluidity  $\eta^{-1}(k)$  and diffusion model for  $\eta_s^{-1}(k)$  in liquid rubidium as a function of wavevector  $k\sigma$ . The full curve is the self term  $\eta_s^{-1}(k)$  obtained from (10) and the crosses denote the exact MD data for the total generalised fluidity  $\eta^{-1}(k)$ .

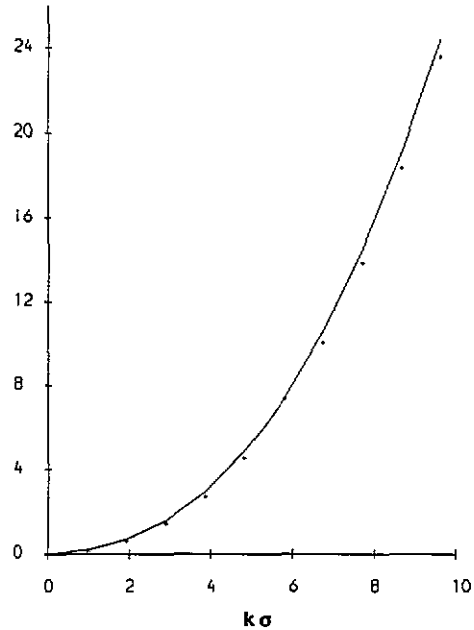


Figure 7. The total generalised fluidity  $\eta^{-1}(k)$  and diffusion model for  $\eta_s^{-1}(k)$  in liquid argon as a function of wavevector  $k\sigma$ . The full curve is the self term  $\eta_s^{-1}(k)$  obtained from (10) and the crosses denote the exact MD data for the total generalised fluidity  $\eta^{-1}(k)$ .

It has been demonstrated before that the velocity-field approach to velocity correlations in liquids leads to a relationship between  $D$  and  $\eta(k)$  (Balucani *et al* 1985). This is essentially a microscopic version of the Stokes-Einstein equation and takes the form

$$D = (nk_B T / 3\pi^2) \int_0^\infty dk \hat{f}(k) \eta^{-1}(k). \quad (13)$$



We now exploit the diffusion model for  $\eta_s^{-1}(k)$  to predict values of the self-diffusion coefficients in liquids, given the shear viscosity coefficients as input data. A relatively simple representation of the distinct component,  $\eta_d^{-1}(k)$ , is much more difficult to obtain. Although  $\eta_d^{-1}(k=0) = \eta^{-1}$  ( $\eta$  being the shear viscosity coefficient), the work of Gaskell and Duffy (1989) shows that it decays rapidly as  $k$  increases. At the same time  $\eta_s^{-1}(k)$  increases quadratically with  $k$ . The combination of the two components makes  $\eta^{-1}(k)$  rather flat at small wavevectors and thereafter the self term is predominant. This suggests the following model for the fluidity of a dense liquid,

$$\eta^{-1}(k) = \eta^{-1}\theta(k_c - k) + \eta_s^{-1}(k)\theta(k - k_c) \quad (14)$$

where  $\theta$  denotes a step function and  $k_c$  is chosen as the wavevector at which  $\eta^{-1} = \eta_s^{-1}(k)$ . When the diffusion model for  $\eta_s^{-1}(k)$  is used in (14) the expression for the generalized fluidity is completely specified in terms of the viscosity and diffusion coefficients. Substitution in (13) leads to an equation for  $D$  which is solved for a given  $n$ ,  $T$  and  $\eta$ . Some results are shown in table 1.

Table 1. Predicted self-diffusion coefficients for some simple liquids. MD or experimental data, where available, are shown for comparison. The Einstein frequency corresponding to the particular system of interest was used in the calculation of  $D$ .

	$T$ (K)	$n \times 10^{-24}$ ( $\text{cm}^{-3}$ )	$\eta$ (mP)	$D \times 10^5$ ( $\text{cm}^2 \text{s}^{-1}$ )	$D \times 10^5$ ( $\text{cm}^2 \text{s}^{-1}$ )
Rb	332	0.010 58	5.5 (MD)	3.04 (theory)	2.66 (MD)
	332	0.010 58	6.0 (expt)	2.78 (theory)	
	319	0.010 58	6.3 (expt)	2.57 (theory)	2.47 (MD)
	312	0.010 38	6.7 (expt)	2.30 (theory)	
Li	453	0.044 02	6.0 (expt)	5.53 (theory)	6.1 (expt)
Na	371	0.024 28	7.0 (expt)	3.33 (theory)	4.2 (expt)
K	337	0.017 32	5.4 (expt)	3.38 (theory)	3.7 (expt)
Ar	84.5	0.021 32	2.9 (expt)	1.76 (theory)	1.53 (expt)

#### 4. Conclusions

This piece of work is part of a continuing investigation of the wavevector-dependent fluidity of a simple liquid and its relationship to the self-diffusion coefficient. We have established an accurate model (the diffusion model) for the self-component,  $\eta_s^{-1}(k)$ , which requires only the Einstein frequency and self-diffusion coefficient to specify it completely. It shows a smooth dependence on  $k$  which is confirmed by computer simulation data on rubidium and argon. The distinct component,  $\eta_d^{-1}(k)$ , is less easy to characterize. It tends to decay rapidly with wavevector but has more structure, which has been demonstrated explicitly and which makes a representation more difficult to achieve. An oversimplified model for the fluidity has, nevertheless, been proposed, enabling the diffusion coefficient to be successfully calculated through a microscopic form of the Stokes-Einstein equation.

## **Acknowledgments**

It is with considerable regret that we note the death of Dr Tom Gaskell in the final stages of this work. This paper is just one example of his many contributions in the area of liquid state physics, and we would like to dedicate it to his memory on behalf of his friends and colleagues.

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