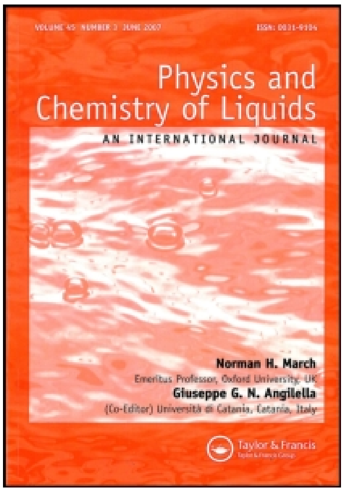

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A RELATION BETWEEN DIFFUSION AND VISCOSITY IN BINARY FLUID MIXTURES

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Starting from the expressions for the mutual diffusion coefficient D_{12} and the longitudinal viscosity $\frac{4}{3}\eta + \zeta$, where η and ζ are respectively the shear and bulk contributions, in terms of partial dynamical structure factors, $S_{ij}(q, \omega)$, $i, j = 1, 2$, a linear combination is formed to eliminate the cross-term $S_{12}(q, \omega)$. In the course of this development, Vineyard's approximation is invoked to relate $S_{ii}(q, \omega)$ to the self-functions $S_{ii}^{(s)}(q, \omega)$. This reduces then the above linear combination of D_{12} and $(\frac{4}{3}\eta + \zeta)$ to an expression in terms of the self-diffusion coefficients D_1 and D_2 in the mixture, and quantities that can be calculated from thermodynamic data. The result should be most accurate for small mass differences. Some possible experimental tests of the proposed relation are finally referred to.

KEY WORDS: Longitudinal and bulk viscosity. Dynamical structure.

1. INTRODUCTION

Though some progress has been made on the theory of transport coefficients in binary fluid mixtures, this has, to date, either invoked simplified models such as hard spheres[1] or conformal solution theory;[2] or computer simulation studies, say with Lennard-Jones potential.[3]

Analytic progress, leading to transport coefficients in such mixtures, without direct appeal to the nature of the interatomic interactions, has so far been slow. However, in the present paper, we shall base an approximate analytic theory on the expressions for the transport coefficients in binary mixtures[4] in terms of the partial dynamic structure factors $S_{ij}(q, \omega)$. It is relevant here to mention the work of Clark[5] on binary gas mixtures, and in particular on the helium-xenon mixture with xenon dilute, where dynamical structure factors are obtained via inelastic light scattering from the density fluctuations. Relevant earlier work in the same general area is that of Sugawara *et al.*[6]

The outline of the paper is then as follows. In section 2, the formulae for atomic transport, and in particular mutual diffusion and longitudinal viscosity, are summarized in terms of number-concentration dynamical structure factors. These formulae are then employed in section 3, though now approximately, to link a combination of the mutual diffusion coefficient D_{12} and the longitudinal viscosity $\frac{4}{3}\eta + \zeta$, with η the shear and ζ the bulk viscosities, to the self-diffusion coefficients D_1 and D_2 in the mixture, together with quantities accessible from thermodynamic measurements.

2. TRANSPORT COEFFICIENTS RELATED TO DYNAMICAL STRUCTURE FACTORS

For components 1 and 2 in a binary liquid mixture, one evidently has three pair correlation functions $g_{11}(r)$, $g_{22}(r)$ and $g_{12}(r)$, with corresponding static structure factors $S_{ij}(q)$; $i, j = 1, 2$. Their dynamical generalizations $S_{ij}(q, \omega)$ are central to the description of atomic transport in such mixtures, as shown in ref. 4. There, the number-concentration functions S_{NN}, S_{CC} and S_{NC} proved the correct tools to use in writing explicit formulae for diffusion and viscosity in the mixture.

To be specific, we briefly summarize the definitions of these number-concentration functions. Let the total number density at position $\mathbf{r}$ at time t, say $n(\mathbf{r}, t)$, be written in terms of the densities of the two components as

$$n(\mathbf{r}, t) = n_1(\mathbf{r}, t) + n_2(\mathbf{r}, t). \tag{2.1}$$

Taking the Fourier transform of $n(\mathbf{r}, t)$ as $\tilde{n}(\mathbf{q}, t)$, then

$$S_{NN}(q, \omega) = \frac{1}{2\pi N}\int dt \exp(-i\omega t)\langle \tilde{n}^\dagger(\mathbf{q}, 0)\tilde{n}(\mathbf{q}, t)\rangle. \tag{2.2}$$

Similarly, defining the local deviation from the mean concentration c as

$$\delta c(\mathbf{r}, t) = \frac{V}{N}[c_2 \delta n_1(\mathbf{r}, t) - c_1 \delta n_2(\mathbf{r}, t)] \tag{2.3}$$

with Fourier transform $\tilde{c}(q, t)$ one has

$$S_{CC}(q, \omega) = \frac{N}{2\pi}\int dt \exp(-i\omega t)\langle \tilde{c}(\mathbf{q}, 0)c(\mathbf{q}, t)\rangle. \tag{2.4}$$

S_{NC} is less important in what follows than S_{CC} and S_{NN} but is defined by an obvious extension of eqns. (2.3) and (2.4).

In terms of the original partial dynamical structure factors $S_{ij}(q, \omega)$, one has explicitly:

$$S_{NN}(q, \omega) = c_1 S_{11}(q, \omega) + c_2 S_{22}(q, \omega) + 2(c_1 c_2)^{1/2} S_{12}(q, \omega) \tag{2.5}$$

and

$$S_{CC}(q, \omega) = c_1 c_2 [c_2 S_{11}(q, \omega) + c_1 S_{22}(q, \omega) - 2(c_1 c_2)^{1/2} S_{12}(q, \omega)]. \tag{2.6}$$

With these definitions, let us summarize the results for the transport coefficients.

2.1 *Limiting forms of S_{NN} and S_{CC} determining mutual diffusion and viscosity coefficients*

The above formulae, representing density and concentration fluctuations, can be used in conjunction with the fluctuation-dissipation theorem to write formulae for the mutual diffusion coefficient D_{12} and the combination $\frac{4}{3}\eta + \zeta$ of the shear (η) and bulk

(ζ) viscosities of the liquid mixture.[2] The results are:

$$D_{12} = \pi\beta\left(\frac{\partial^2 G}{\partial c_2^2}\right)\lim_{\omega\to 0}\omega^2\lim_{q\to 0}\frac{1}{q^2}S_{CC}(q,\omega) \tag{2.7}$$

with $\beta = (k_B T)^{-1}$ and G the Gibbs free energy of the liquid mixture.[2] The corresponding result for $\frac{4}{3}\eta + \zeta$ is given in terms of $S_{NN}(q, \omega)$ by

$$\tfrac{4}{3}\eta + \zeta = \pi\beta\lim_{\omega\to 0}\omega^4\lim_{q\to 0}\frac{1}{q^4}S_{NN}(q,\omega). \tag{2.8}$$

These results (2.7) and (2.8) are formally exact for isotropic mixtures but, so far, of course, one does not have explicit expressions for $S_{NN}(q, \omega)$ and $S_{CC}(q, \omega)$ in analytic form for any mixture. Therefore, in the following section, we shall make appropriate approximations to S_{11} and S_{22} so that a suitable linear combination of D_{12} and $\frac{4}{3}\eta + \zeta$ appearing in eqns. (2.7) and (2.8) can be written in terms of self-diffusion coefficients D_1 and D_2 defined in the mixture, plus knowledge from thermodynamic measurements.

3. APPROXIMATE RELATION OF D$_{12}$ AND $\frac{4}{3}\eta + \zeta$ TO SELF-DIFFUSION COEFFICIENTS

To motivate the approximations proposed below, consider next the forms S_{NN} and S_{CC} in eqns. (2.5) and (2.6) in relation to the transport formulae (2.7) and (2.8). In for example the dilute Xe-He gas mixture studied by Clark,[5] it seems clear that it would be very advantageous to eliminate the 'cross-correlation' function $S_{12}(q, \omega)$ appearing in eqns. (2.5) and (2.6). This we propose to do, but now only approximately, by combining the transport formulae (2.7) and (2.8). Where the approximations enter is in the limiting processes involved in these expressions for D_{12} and $\frac{4}{3}\eta + \zeta$. The limit involved in D_{12} has ω^2/q^2 whereas that in $\frac{4}{3}\eta + \zeta$ has the factor ω^4/q^4. In this latter expression, which is reflecting collective fluctuations of the mixture, a rather natural approximation is to replace the factor ω^2/q^2 by the square of the velocity of sound v_s^2.

Motivated by the above discussion let us write

$$\frac{D_{12}}{\pi\beta\left(\frac{\partial^2 G}{\partial c_2^2}\right)c_1c_2} + \frac{(\frac{4}{3}\eta + \zeta)}{\pi\beta v_s^2} = \lim_{\omega\to 0}\omega^2\lim_{q\to 0}\frac{1}{q^2}\frac{S_{CC}(q,\omega)}{c_1c_2} + \frac{1}{v_s^2}\lim_{\omega\to 0}\omega^4\lim_{q\to 0}\frac{1}{q^4}S_{NN}(q,\omega) \tag{3.1}$$

While this eqn. (3.1) is still exact for isotropic mixtures to this point, we note that if we return to eqns. (2.5) and (2.6) for S_{NN} and S_{CC} respectively, then replacing ω^2/q^2 in the S_{NN} term of eqn. (3.1) by the approximation v_s^2 allows the cancellation of the cross-term S_{12}. However, the remaining terms involving S_{11} and S_{12} in the S_{NN} contribution to eqn. (3.1) must simultaneously be approximated in such a way that the limit resulting from the replacement of ω^2/q^2 by v_s^2 exists. This can be achieved by generalizing the approximation introduced by Vineyard[7] for a pure liquid, to write in the mixture:

$$S_{ii}(q, \omega) \simeq S_{ii}(q) S_{ii}^{(s)}(q, \omega). \tag{3.2}$$

Once this eqn. (3.2) is inserted in the limits involving S_{11} and S_{22} in eqn. (3.1), after replacing ω^2/q^2 by v_s^2 in the S_{NN} term, then the limits in the self-functions $S_{ii}^{(s)}$ merely lead to D_i/π and hence

$$\frac{D_{12}}{\pi\beta\left(\dfrac{\partial^2 G}{\partial c_2^2}\right)c_1 c_2} + \frac{(\frac{4}{3}\eta + \zeta)}{\pi\beta v_s^2} = S_{11}(0)\frac{D_1}{\pi} + S_{22}(0)\frac{D_2}{\pi}. \tag{3.3}$$

Eqn. (3.3) is the basic relation sought between diffusion and viscosity coefficients in the mixture. It should work best when there are small mass differences between the two components of the alloy.

4. DISCUSSION AND SUMMARY

It will now be of considerable interest to test eqn. (3.3) on mixtures over a wide range of concentration. One would want, ideally, to measure $\frac{4}{3}\eta + \zeta$ by sound-wave attenuation, and the three diffusion constants D_{12} and the self-diffusion constants D_1 and D_2 also as a function of concentration. The thermodynamic information required, namely v_s^2, $\partial^2 G/\partial c_2^2$, $S_{11}(0)$ and $S_{22}(0)$ is already available for a range of mixtures, from liquid metal alloys[8] to mixtures of rare gases.

Of course, eqn. (3.2) is known not to be quantitative when applied directly to analyze neutron scattering data on one-component liquids. While this does not preclude its usefulness in approximating the right-hand-side of eqn. (3.1), it is clear that experimental test of its consequences through eqn. (3.3) is important in deciding how refinements or modifications to it should be made in atomic transport theory in mixtures.

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