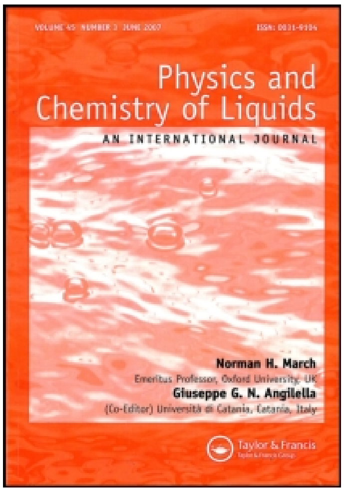

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Dynamical structure factors for a fluid binary mixture in the hydrodynamic limit

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Dynamical Structure Factors for a Fluid Binary Mixture in the Hydrodynamic Limit[†]

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Using the correlation functions obtained by Cohen *et al*, the expressions for the number-concentration dynamical structure factors for a binary alloy are given in the hydrodynamic limit. Kubo relations are derived and presented via some new structure factors, which, although not directly connected to the scattering in the mixture, are linearly related to the number-concentration structure factors. The second moments for the various structure factors are also given. Finally, sound attenuation in binary mixtures is briefly discussed.

I. INTRODUCTION

In a recent paper on the electrical resistivities of alloys Bhatia and Thornton[1] introduced the number-concentration (N-C) dynamical structure factors. $S_{NN}(\vec{q},\omega)$, $S_{NC}(\vec{q},\omega)$ and $S_{CC}(\vec{q},\omega)$, to describe the structural aspects of scattering processes in binary alloys. The expressions for the long-wavelength (wave-vector, $\vec{q}\rightarrow 0$) and high-temperature limit of the three N-C static structure factors were derived for fluid alloys, and recently the calculation has been extended to include the corresponding results for solid mixtures[2]. As a natural continuation

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of this program we present here the hydrodynamic limit ($q \rightarrow 0$; angular frequency, $\omega \rightarrow 0$) of the N-C dynamical structure factors for a fluid.

The usual procedure in such a calculation is, following a proposal by Landau and Placzek[3], to use the linearized hydrodynamic equations of irreversible thermodynamics to describe the relaxation in time of relevant fluctuating thermodynamic variables in the fluid. This procedure has been utilized, mainly for one component systems, by a number of authors in a variety of physical situations[4-8]. Conveniently, Cohen *et al.*[9] have recently considered the case of binary fluid mixtures and among their results are expressions for correlations between mass-density and mass-concentration[10]. In order to obtain expressions for the N-C dynamical structure factors from these correlations we find it convenient to construct some new (M-X) dynamical structure factors in Section II, which are essentially the Fourier transform of the mass-density and mass-concentration correlation functions. Although these structure factors are not *directly* connected to scattering in the alloy, they are linearly related to the N-C structure factors. It is noted that the thermodynamic quantities entering the equations of Cohen *et al.* are implicitly evaluated at constant mass and we find, as might be expected, that the results for $S_{NN}(q,\omega)$ etc., are much simpler if these quantities are evaluated at constant number. The relevant change of variables and transformation details are given in the Appendix. Hence, in Section III we give the resulting expressions for the N-C dynamical structure factors in the hydrodynamic limit.

The next section contains some exact results (Kubo-relations) for the transport coefficients in a binary alloy. The M-X structure factors are more intimately related to transport in the mixture than are the N-C structure factors, so the expressions for the transport coefficients are given in terms of the appropriate limiting values of these former functions. Also included in this section are the second moments of the various structure factors.

Finally, in Section V a brief discussion is given on sound attenuation in fluid binary mixtures, and in particular, of the attenuation caused by mutual diffusion. The sound attenuation is related to the width of the Brillouin peaks and the general expression obtained (always assuming the sound wave-length is large compared to the mean free path of the molecules) is specialized to rederive the known results for an ideal gas mixture.

Before proceeding further, we should mention that our discussion (as also that of Ref. 9) is, strictly speaking, limited to mixtures of 'simple' liquids, i.e. (a) liquids in which effects of relaxation of energy between the internal (vibrational or rotational) degrees of freedom and translational degrees of freedom can be neglected, and (b) which are not highly associated liquids, like glycerine, where structural relaxation occurs on a time scale comparable to the frequency of thermal sound waves responsible for scattering. A non-simple or 'relaxing' liquid has to be described by additional thermodynamic 'order' parameters and the expression[6,7,11] for the dynamical structure factor even for such a one component liquid is much more involved than the corresponding expression (Eq. 36, below) for a simple liquid. It is hoped to consider mixtures of relaxing liquids in a subsequent publication.

II. M–X DYNAMICAL STRUCTURE FACTORS

In order to make contact between the hydrodynamic correlation functions presented by Cohen *et al.* and the N-C dynamical structure factors it is both convenient and illustrative to introduce some new dynamical structure factors. These functions, though not as closely connected to the scattering in a binary mixture as the N-C structure factors, are intimately related to the transport coefficients.

Consider then a binary alloy within a volume V having N_α ($\alpha = 1,2$) atoms of the type α which contribute a mass M_α to the total mass, M ($= M_1 + M_2$), of all N ($= N_1 + N_2$) atoms in the mixture. Let $\rho_\alpha = M_\alpha/V$ be the mean mass-density of the α-species, and define the mean mass-concentration, x, by

$$x = M_1/M = \rho_1/\rho \tag{1}$$

where $\rho = M/V$ is the mean mass-density. Also, for later purposes, we have for the mean number-concentration $c = N_1/N$.

If $\rho_\alpha(\vec{r},t)$ denotes the local mass-density at time t for species α, then the local fluctuation in this quantity is given by

$$\delta\rho_\alpha(\vec{r},t) = \rho_\alpha(\vec{r},t) - \rho_\alpha = m_\alpha \delta n_\alpha(\vec{r},t) \tag{2}$$

Here, $\delta n_\alpha(\vec{r},t)$ is the fluctuation in the local number-density operator of species α which is introduced in Ref. 1, and used there to construct the N-C dynamical structure factors. Further, m_α is the molar mass, per atom, of species α

$$m_\alpha = M_\alpha/N_\alpha \, [= (\partial M/\partial N_\alpha)_{N_\beta}]. \tag{3}$$

We now form the local fluctuations in the total mass density and mass-concentration, namely

$$\delta\rho(\vec{r},t) = \delta\rho_1(\vec{r},t) + \delta\rho_2(\vec{r},t) \tag{4}$$

and

$$\delta x(\vec{r},t) = \rho^{-1}[(1-x)\,\delta\rho_1(\vec{r},t) - x\delta\rho_2(\vec{r},t)]. \tag{5}$$

Making the Fourier expansions

$$\delta\rho(\vec{r},t) = (\tfrac{1}{V}) \sum_{\vec{q}} M(\vec{q},t)\, e^{-i\vec{q}\cdot\vec{r}} \tag{6}$$

and

$$\delta x(\vec{r},t) = \sum_{\vec{q}} X(\vec{q},t)\, e^{-i\vec{q}\cdot\vec{r}}, \tag{7}$$

we have

$$M(\vec{q},t) = M^{\dagger}(-\vec{q},t) = \int e^{i\vec{q}\cdot\vec{r}}\, \delta\rho(\vec{r},t)\, d^3r \tag{8}$$

and

$$X(\vec{q},t) = X^{\dagger}(-\vec{q},t) = (\tfrac{1}{V}) \int e^{i\vec{q}\cdot\vec{r}}\, \delta x(\vec{r},t)\, d^3r. \tag{9}$$

In terms of the Fourier coefficients (8) and (9) we define the M-X dynamical structure factors as

$$S_{MM}(\vec{q},\omega) = \frac{1}{2\pi M} \int e^{-i\omega t}\, dt \langle M^{\dagger}(\vec{q},0)\, M(\vec{q},t)\rangle, \tag{10}$$

$$S_{MX}(\vec{q},\omega) = \frac{1}{4\pi} \int e^{-i\omega t}\, dt \langle M^{\dagger}(\vec{q},0)\, X(\vec{q},t) + X^{\dagger}(\vec{q},0)\, M(\vec{q},t)\rangle, \tag{11}$$

$$S_{XX}(\vec{q},\omega) = \frac{M}{2\pi} \int e^{-i\omega t}\, dt \langle X^{\dagger}(\vec{q},0)\, X(\vec{q},t)\rangle: \tag{12}$$

where <....> denotes an ensemble average. Clearly, via equation (2), these functions may be related to the Fourier transforms of the $\delta n_\alpha(\vec{r},t)$, and hence to the N-C structure factors of Ref. 1. We find,

$$\begin{aligned} S_{MM} &= m[S_{NN} + 2\delta_m S_{NC} + \delta_m^2 S_{CC}], \\ S_{MX} &= \frac{m}{y}[S_{NC} + \delta_m S_{CC}], \\ S_{XX} &= \frac{m}{y^2}[S_{CC}], \end{aligned} \tag{13}$$

and hence also

$$\begin{aligned} m\, S_{NN} &= S_{MM} - 2\delta_m y S_{MX} + \delta_m^2 y^2 S_{XX}, \\ m\, S_{NC} &= y S_{MX} - \delta_m y^2 S_{XX}. \end{aligned} \tag{14}$$

In (13) and (14)

$$m = cm_1 + (1-c)m_2 \; [= (\partial M/\partial N)_c] \tag{15}$$

is the mean molar mass, per atom,

$$\delta_m = \frac{m_1 - m_2}{m} = \left[\frac{1}{M}\left(\frac{\partial M}{\partial c}\right)_N\right] \tag{16}$$

is the fractional change in mass with number-concentration, and, finally,

$$y = \frac{m^2}{m_1 m_2} = \frac{c(1-c)}{x(1-x)}. \tag{17}$$

The mass-density, mass-concentration hydrodynamic correlations of Cohen *et al.* are essentially, apart from trivial factors, the time-dependent correlations on the r.h.s. of Eqs. (10)-(12). Utilising Eqs. (13) and (14), therefore, it is a straightforward matter to obtain expressions for $S_{NC}(q,\omega)$ etc., in the hydrodynamic limit.

III. N–C DYNAMICAL STRUCTURE FACTORS IN THE HYDRODYNAMIC LIMIT

The thermodynamic quantities entering the equations of Cohen *et al.* are all implicitly evaluated at constant mass and, in order to simplify the expressions we obtain for $S_{NN}(q,\omega)$ etc., we have transformed these to variables which are evaluated at constant total number. Relevant transformation details are given in the Appendix. We obtain,

$$\begin{aligned} S_{NN}(q,\omega) = \frac{Nk_BT}{2\pi V}\,\frac{\kappa_T}{\gamma}\Bigg[&\frac{2A_1Xq^2}{\omega^2+X^2q^4} + \frac{2A_2Yq^2}{\omega^2+Y^2q^4} \\ &+ \left[\frac{\Gamma q^2}{(\omega+C_0q)^2+\Gamma^2q^4} + \frac{\Gamma q^2}{(\omega-C_0q)^2+\Gamma^2q^4}\right] \\ &+ A_3\frac{q}{C_0}\left[\frac{\omega+C_0q}{(\omega+C_0q)^2+\Gamma^2q^4} - \frac{\omega-C_0q}{(\omega-C_0q)^2+\Gamma^2q^4}\right]\Bigg] \end{aligned} \tag{18}$$

where k_B is Boltzmann's constant, κ_T $\left(= -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_{T,c,N}\right)$ is the isothermal compressibility, γ $(= C_p/C_v)$ is the ratio of the heat capacities at constant pressure and volume and C_0 $(= [\partial P/\partial\rho]^{1/2}_{S,c} = [\gamma/\rho\kappa_T]^{1/2})$ is the adiabatic speed of sound.

Further, in Equation (18) we have

$$2\Gamma = b + \chi(\gamma - 1) + \frac{\gamma DVZ}{\kappa_T}\,\Sigma^2, \tag{19}$$

$$2X = (\chi + \mathscr{D}) + [(\chi + \mathscr{D})^2 - 4\chi D]^{1/2}, \tag{20}$$

$$2Y = (\chi + \mathscr{D}) - [(\chi + \mathscr{D})^2 - 4\chi D]^{1/2}, \tag{21}$$

$$A_1 = \frac{(1-\gamma)}{(X-Y)}\left[D - X - \frac{2Dk_T\delta}{T\alpha_T} + \frac{(Y-D)\delta^2 C_P}{ZT\alpha_T^2}\right], \tag{22}$$

$$A_2 = \frac{(1-\gamma)}{(Y-X)}\left[D - Y - \frac{2Dk_T\delta}{T\alpha_T} + \frac{(X-D)\delta^2 C_P}{ZT\alpha_T^2}\right], \tag{23}$$

and

$$A_3 = (3\Gamma - b) + \frac{2V\gamma D}{\kappa_T}\,\delta_m\,\Sigma. \tag{24}$$

Here, $\chi(=\frac{V\lambda}{C_p})$ is the thermal diffusivity, where λ is the coefficient of thermal conductivity, k_T is the thermal diffusion ratio[12], D is the coefficient of mutual diffusion, $\alpha_T\,(=\frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_{P,c,N})$ is the coefficient of thermal expansion and $b = (\zeta + \frac{4}{3}\eta)/\rho$, where ζ and η are the bulk and shear viscosities, respectively. Also, if $v_\alpha = [\partial V/\partial N_\alpha]_{P,T,N_\beta}$ $(\beta \neq \alpha)$ denotes the partial molar volume, per atom, of species α, we have for the mean molar volume, per atom, v,

$$v = \left[\frac{\partial V}{\partial N}\right]_{P,T,c} = cv_1 + (1-c)v_2, \tag{25}$$

and for the N-C dilatation[1],

$$\delta = \frac{1}{V}\left[\frac{\partial V}{\partial c}\right]_{P,T,N} = \frac{v_1 - v_2}{v} \tag{26}$$

Further,

$$\Sigma = \frac{1}{Z}(\delta - \delta_m) + \frac{k_T\alpha_T}{C_P}, \tag{27}$$

and

$$\mathscr{D} = D[1 + \frac{k_T^2 Z}{TC_p}], \tag{28}$$

where

$$Z = \left[\frac{\partial \mu_c}{\partial c}\right]_{P,T,N} = \left[\frac{\partial^2 G}{\partial c^2}\right]_{P,T,N}. \tag{29}$$

G denotes Gibb's energy and $\mu_c = N(\mu_1 - \mu_2)$, where μ_α (= $\left[\frac{\partial G}{\partial N_\alpha}\right]_{P,T,N\beta}$) denotes the chemical potential per atom of type α.

We also obtain,

$$S_{NC}(q,\omega) = \frac{Nk_BT}{2\pi}\left[\frac{2A_4Xq^2}{\omega^2+X^2q^4} + \frac{2A_5Yq^2}{\omega^2+Y^2q^4}\right.$$
$$\left. + A_6\frac{q}{C_0}\left[\frac{\omega+C_0q}{(\omega+C_0q)^2+\Gamma^2q^4} - \frac{\omega-C_0q}{(\omega-C_0q)^2+\Gamma^2q^4}\right]\right], \tag{30}$$

where

$$A_4 = (Y-X)^{-1}\,[(D-Y)\frac{\delta}{Z} + \frac{Dk_T\alpha_T}{C_p}], \tag{31}$$

$$A_5 = (X-Y)^{-1}\,[(D-X)\frac{\delta}{Z} + \frac{Dk_T\alpha_T}{C_p}], \tag{32}$$

and

$$A_6 = -D\,\Sigma. \tag{33}$$

Finally,

$$S_{CC}(q,\omega) = \frac{Nk_BT}{2\pi Z}\left[\frac{2A_7Xq^2}{\omega^2+X^2q^4} + \frac{2A_8Yq^2}{\omega^2+Y^2q^4}\right], \tag{34}$$

where

$$\left.\begin{aligned} A_7 &= (Y-D)/(Y-X), \\ A_8 &= (X-D)/(X-Y). \end{aligned}\right] \tag{35}$$

and

The expression for the dynamical structure factor for a one-component liquid may be obtained from the above equations by taking the limit $c = 0$, whence $S_{NC} = S_{CC} = 0$ and $S_{NN} \equiv S(q,\omega)$, with

$$S(q,\omega) = \frac{Nk_BT}{2\pi V}\frac{\kappa_T}{\gamma}\left[\frac{2(\gamma-1)\chi q^2}{\omega^2+\chi^2q^4} + \frac{\Gamma q^2}{(\omega+C_0q)^2+\Gamma^2q^4} + \frac{\Gamma q^2}{(\omega-C_0q)^2+\Gamma^2q^4} + \frac{A_3q}{C_0}\left[\frac{\omega+C_0q}{(\omega+C_0q)^2+\Gamma^2q^4} - \frac{\omega_0-C_0q}{(\omega-C_0q)^2+\Gamma^2q^4}\right]\right] \tag{36}$$

where now $\Gamma = \frac{1}{2}[b + \chi(\gamma-1)]$ and $A_3 = 3\Gamma\,.-b$.

The above expressions of $S_{NN}(q,\omega)$ etc., are exact (in the hydrodynamic limit) to the first order in $\Gamma q/C_0$ [13] or aq/C_0, where *a* stands for the transport coefficients b, χ or MDC_0^2/Z. Care, however, has to be taken to include the non-Lorentzian contributions in $S_{NN}(q,\omega)$ or $S(q,\omega)$ (terms in A_3) and $S_{NC}(q,\omega)$ (term in A_6). The importance of including such terms has been pointed out previously[14] and we find that they make vital contributions in the derivation of the Kubo-relations given in the next section.

The central or Rayleigh component in $S_{NN}(q,\omega)$ is seen to consist generally of the sum of two Lorentzians (terms in A_1 and A_2), the width of one Lorentzian being largely controlled by thermal conduction and the other by mutual diffusion. This is most easily seen by putting $k_T = 0$ in (20)-(23) (its contribution is typically expected to be small in comparison with that of χ or D), whereupon the width of one peak becomes χq^2 and the other Dq^2. The integrated intensity under the former peak is now $(N/V)k_BT(\gamma-1)\kappa_s$, as in the Rayleigh component for a pure material, and under the latter, $Nk_BT\delta^2/Z$. Hence, in this case ($k_T = 0$), the contribution to the Rayleigh component by mutual diffusion is scaled by the relative partial molar volumes of the species in the mixture.

The two Doppler-shifted peaks (Brillouin components) centered at frequencies $\omega = \pm C_0q$ arise, as in the one-component case, from sound propagation in opposite directions (for a given $\vec{q}$) and their width, Γq^2, is controlled by acoustic attenuation.

It is interesting to note that the ratio of the integrated intensity (I_0) of the Rayleigh components in $S_{NN}(q,\omega)$ to that of the doublet Brillouin side peaks ($2I_1$) is quite generally given by (k_T not necessarily zero),

$$\frac{I_0}{2I_1} = \frac{A_1 + A_2}{1} = (\gamma-1)\left[1 + \frac{C_p\delta^2}{ZT\alpha_T^2}\right], \tag{37}$$

not just $(\gamma-1)$ as in the case of one component non-relaxing liquids.

The 'non-Lorentzian' terms in $S_{NN}(q,\omega)$ (and in $S_{NC}(q,\omega)$) make no contribution to the integrated intensity and, usually, only a small contribution to the intensity distribution. However, if $\Gamma q/C_0$ is not much less than unity, they can markedly affect the position and shape of the Brillouin peaks in $S_{NN}(q,\omega)$.

The two Lorentzians in $S_{NC}(q,\omega)$ primarily arise, respectively, from diffusive processes and the coupling between this type of mode and the thermal conductive mode. If the coupling is zero ($k_T = 0$) the latter component is no longer present and the width of the remaining Lorentzian is simply Dq^2. The two components in $S_{CC}(q,\omega)$ behave in a similar manner.

The static structure factors $S_{NN}(q)$, $S_{NC}(q)$ and $S_{CC}(q)$ may be obtained simply by integrating $S_{NN}(q,\omega)$, $S_{NC}(q,\omega)$ and $S_{CC}(q,\omega)$, respectively, over all values of ω. One finds using (18), (30) and (34)

$$(\kappa_{T,\mu_c,N} = -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_{T,\mu_c,N})$$

$$S_{NN}(q) = \frac{Nk_BT}{V}\kappa_{T,\mu_c,N} = \frac{Nk_BT}{V}(\kappa_T + \frac{V\delta^2}{Z}), \tag{38}$$

$$S_{NC}(q) = -Nk_BT\frac{\delta}{Z}, \tag{39}$$

$$S_{CC}(q) = \frac{Nk_BT}{Z}. \tag{40}$$

These expressions agree with the results (in the same limit, q → 0) presented in Ref. 1, and are applicable equally to simple and relaxing liquids.

IV. KUBO RELATIONS AND SECOND MOMENTS

In this section we present some exact results for binary mixtures.

The hydrodynamic expressions for the dynamical structure factors given in the previous section may be expanded in series and appropriate limits taken to generate Kubo-relations for the transport coefficients in a binary mixture. We find,

$$\lim_{\omega\to 0}\omega^4 \lim_{q\to 0}\frac{1}{q^4}S_{MM}(q,\omega) = \frac{k_BT}{\pi}\frac{(\zeta + \frac{4}{3}\eta)}{\rho}, \tag{41}$$

$$\lim_{\omega\to 0}\omega^4 \lim_{q\to 0}\frac{1}{q^4}S_{MX}(q,\omega) = \frac{k_BT}{\pi}\frac{\gamma VD\Sigma}{y\kappa_T}, \tag{42}$$

$$\lim_{\omega\to 0}\omega^2 \lim_{q\to 0}\frac{1}{q^2}S_{XX}(q,\omega) = \frac{Mk_BT}{\pi}\frac{D}{Z_x}, \tag{43}$$

where $Z_x = (\partial^2 G/\partial x^2)_{P,T,M}$. These results are presented in terms of the M-X structure factors as the transport coefficients, at least in Eqs. (41) and (42), are clearly (using Eq. (13) more closely related to these functions than the N-C structure factors. This is to be expected as the relevant transport coefficients are essentially connected to correlations between momenta and forces, which are merely time-derivatives of *mass-densities*.

It is noted that Equation (41) has the form of the well known result for the one component case, with $(\frac{1}{m})\, S_{MM}(q,\omega)$ playing the role of $S(q,\omega)$, the Van-Hove dynamical structure factor. Also, using (13) and (A3), (43) may be written

$$\lim_{\omega\to 0} \omega^2 \lim_{q\to 0} \frac{1}{q^2} S_{CC}(q,\omega) = \frac{Nk_BT}{Z}\,\frac{D}{\pi} \quad , \tag{44}$$

which should be compared with the corresponding result for a one component system,

$$\lim_{\omega\to 0} \omega^2 \lim_{q\to 0} \frac{1}{q^2}\, S_s(q,\omega) = \frac{D'}{\pi} \tag{45}$$

Here $S_s(q,\omega)$ is the self part of $S(q,\omega)$ and D^1 is the coefficient of self-diffusion.

The second moments of the various structure factors may be quite generally calculated for classical liquids following the procedure of De Gennes[15]. Writing, $(\epsilon,\epsilon' = N,C;M,X)$

$$\int_{-\infty}^{\infty} \frac{\omega^2}{q^2}\, S_{\epsilon,\epsilon'}(q,\omega)\, d\omega = \eta^{(2)}_{\epsilon\epsilon'} \tag{46}$$

we find,

$$\eta^{(2)}_{NN} = \left[\frac{c_1}{m_1} + \frac{c_2}{m_2}\right] k_BT \tag{47}$$

$$\eta^{(2)}_{NC} = c_1 c_2 \left[\frac{1}{m_1} - \frac{1}{m_2}\right] k_BT \tag{48}$$

$$\eta^{(2)}_{CC} = c_1 c_2\, \frac{Y}{m}\, k_BT \tag{49}$$

and, consequently,

$$\eta^{(2)}_{MM} = k_BT \tag{50}$$

$$\eta^{(2)}_{MX} = 0 \tag{51}$$

$$\eta^{(2)}_{XX} = \frac{c_1 c_2}{y} k_B T = x_1 \, x_2 \, k_B T \tag{52}$$

Once more the expressions involving the M-X structure factors are simpler. Again, the reason is that the second moments involve consideration of momentum correlations, which are related to the time derivatives of correlations between *mass-densities*.

The fourth moments may also be obtained in a similar manner, but are rather lengthy and will not be presented here.

V. SOUND ATTENUATION IN MIXTURES

The width, Γq^2, of the Brillouin components in $S_{NN}(q,\omega)$ is related to the acoustic attenuation in the medium. Explicitly, the amplitude attenuation per wavelength, α, is given by (using (19))

$$\frac{\alpha}{\omega} = \frac{2\pi\Gamma}{C_0^2} = \frac{\pi(\zeta + \frac{4}{3}\eta)}{\rho C_0^2} + \frac{\pi(\gamma - 1)\lambda M}{\rho C_0^2 C_p} + \left[\frac{\alpha}{\omega}\right]_D \tag{53}$$

where

$$[\alpha/\omega]_D = (\pi MD/Z)\,[(\delta - \delta_m) + Zk_T\alpha_T/C_p]^2 \tag{54}$$

The first two terms on the right hand side of (53) are the well known results for attenuation caused by viscosity and thermal conductivity, respectively[16]. The last term in (53), i.e. Eq. (54), gives the contribution due to diffusion[17], and it is this term we shall consider in more detail.

Clearly, by taking the appropriate approximate expressions for G in a binary mixture[18] we may evaluate $[\alpha/\omega]_D$ for regular, ideal, athermal, etc., solutions. However, rather than adopting this procedure here we choose, for illustration, to make contact with previous work by considering the case of an ideal gas mixture. Here, we have $PV = Nk_BT$, so that $\delta = 0$, $\alpha_T = 1/T$, $\kappa_T = 1/P$, and, further, for an ideal solution,

$$Z = Nk_BT/c(1-c) \tag{55}$$

Hence, we obtain

$$\left[\frac{\alpha}{\omega}\right]_D = \pi Dc(1-c)\,\frac{\rho}{P}\left[\frac{(m_2-m_1)}{m} + \frac{(\gamma-1)}{\gamma}\,\beta\right]^2 \tag{56}$$

where $\beta = k_T/c(1-c)$, the thermal diffusion factor[19], has been introduced. This formula has been derived previously[20-22] from kinetic theory calculations, and has been verified experimentally for noble gas mixtures of various compositions[23].

VI. CONCLUSION AND SUMMARY

In this paper the expression for the three number-concentration dynamical structure factors $S_{NN}(\vec{q},\omega)$, $S_{NC}(\vec{q},\omega)$ and $S_{CC}(\vec{q},\omega)$ in the fluid hydrodynamic limit ($q \to 0$, $\omega \to 0$) have been presented.

Three new dynamical structure factors $S_{MM}(\vec{q},\omega)$, $S_{MX}(\vec{q},\omega)$ and $S_{XX}(\vec{q},\omega)$, which are closely related to mass-density, mass-concentration correlations in a binary mixture, are introduced. These functions, though not directly connected to the scattering like $S_{NN}(q,\omega)$ etc., are, in the appropriate limits, intimately related, as shown, to the transport coefficients in the mixture.

A general expression for the sound attenuation in a fluid mixture is given, and is applied to the case of an ideal gas mixture in order to rederive a result previously obtained by kinetic theory calculations.

For completeness the second moments of the various dynamical structure factors for classical fluids are presented. These results, along with the expressions for the transport coefficients in the same Section, will be used in a subsequent paper to discuss viscosity and mutual diffusion in binary isotopic mixtures.[24]

Appendix

The transformation between the thermodynamic variables (M,x) used in Ref. 9 to (N,c) used in Ref. 1 is made via

$$\Delta c = y\Delta x \tag{A1}$$

and

$$\frac{\Delta N}{N} = \frac{\Delta M}{M} - y\delta_m \Delta x \tag{A2}$$

We then find after some algebra

$$Z_x = \left[\frac{\partial \mu_x}{\partial x}\right]_{P,T,M} = \left[\frac{\partial^2 G}{\partial x^2}\right]_{P,T,M} = y^2 Z \quad , \tag{A3}$$

$$\frac{1}{V}\left[\frac{\partial V}{\partial x}\right]_{P,T,M} \equiv \delta_x = y(\delta - \delta_m) \quad , \tag{A4}$$

and

$$-\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_{T,\mu_x,M} = \kappa_T + \frac{V\delta_x^2}{Z_x} = \kappa_T + \frac{V(\delta-\delta_m)^2}{Z} \tag{A5}$$

where $\mu_x = M(\frac{\mu_1}{m_1} - \frac{\mu_2}{m_2})$. The second equality in (A3) follows from the differential expression for the Gibb's energy:

$$\Delta G = -S\Delta T + V\Delta P + \mu_x \Delta x + \mu_M \Delta M \, , \tag{A6}$$

where we have written $\mu_M = x\frac{\mu_1}{m_1} + (1-x)\frac{\mu_2}{m_2}$.

The important quantities which transform trivially are

$$\begin{aligned} &\kappa_{T,x,M} = \kappa_{T,c,N} \equiv \kappa_T && \text{(similarly } \kappa_s\text{)} \\ &C_{p,x,M} = C_{p,c,N} \equiv C_p && \text{(similarly } C_v\text{)} \\ &\alpha_{T,x,M} = \alpha_{T,c,N} \equiv \alpha_T && \end{aligned} \tag{A7}$$

To illustrate the symmetry between the two sets of variables, the long-wavelength limit of the M-X static structure factors may be calculated, either by integrating the hydrodynamic $S_{MM}(q,\omega)$, etc., over all ω, or using thermodynamic fluctuation theory. Either way one finds,

$$S_{MM}(0) = \frac{Mk_BT}{V}\,\kappa_{T,\mu_x,M} = \frac{Mk_BT}{V}\,[\kappa_T + \frac{V\delta_x^2}{Z_x}] \tag{A8}$$

$$S_{MX}(0) = -\frac{Mk_BT\delta_x}{Z_x} \tag{A9}$$

$$S_{XX}(0) = \frac{Mk_BT}{Z_x} \tag{A10}$$

These should be compared with (38)-(40), and may be checked using (13) and (A3)-(A5).

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12. The thermal diffusion ratio, k_T, used here is the same as that introduced in Ref. 19, p. 144. The ratio used in Ref. 9 is that defined in L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, 1959), p. 224, and is 1/y times ours.
13. $(2\pi\Gamma q/C_0)$ represents the sound attenuation per wavelength, and in "simple" liquids, invariably $\Gamma q/C_0 << 1$. The modifications that occur in the expression for $S(q,\omega)$ for a one component liquid when this condition is not satisfied are discussed in Ref. 6-8.
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17. Clearly, from the form of Equation (54), care must be taken in choosing the correct sign for k_T in an actual calculation. Typically, k_T takes the sign of δ_m when $|\delta_m|>>|\delta|$, and that of δ when $|\delta|>>|\delta_m|$. The former is generally true (in most gases at least), so the terms δ_m and $Zk_T\alpha_T/C_p$ in (54) tend to cancel. For a more detailed discussion about the sign of k_T, see Ref. 19, p. 255. In this connexion it may be noted that in the expression (14.3.20) for $[\alpha/\omega]_D$ in Ref. 16 k_T should read $(-k_T)$. If $k_T=0$, (54) reduces, on using the relations (A3) and (A4) to eqn. (14.3.13) of Ref. 16.
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