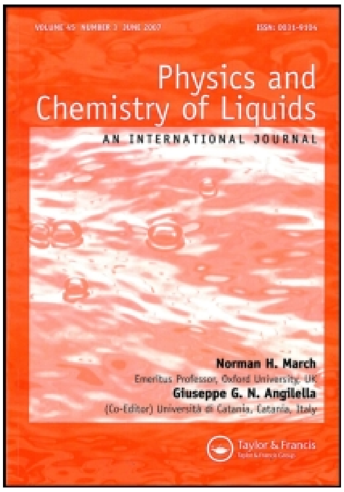

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Hydrodynamic Correlation Functions for Binary Mixtures†

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Abstract—Correlation functions of various local thermodynamic variables of binary mixtures are obtained from the linearized hydrodynamic equations following the method of Mountain and Deutch. " Non-Lorentzian " parts of the time Fourier transformed correlation functions which have not been included by these authors are obtained here and their effect on the light scattering spectrum considered. An extension of the treatment by Fox and Uhlenbeck of Landau and Lifshitz hydrodynamical fluctuation theory to binary mixtures has been accomplished and correlation functions of the " fluctuating forces " are obtained for this case.

1. Introduction

In this article we present a comprehensive analysis of the time correlation functions of the local thermodynamic variables for a binary mixture computed according to the linearized hydrodynamic equations.(1) The outline of the calculation is presented in Sec. 2 and the results for correlation functions in terms of various convenient sets of local thermodynamic variables are presented in Sec. 3. The complete set of hydrodynamic correlation functions for the binary fluid has previously not been available although some results have been reported.(2–4)

One important application of these hydrodynamic correlation functions is to light scattering. For a binary fluid, outside the critical region, the frequency spectrum of the scattered light is directly related to the space and time Fourier transforms of these correlation functions. This problem has been considered in detail by Mountain and Deutch.(3) These authors, however, did not include in their calculation of the correlation functions small terms that give rise to " non-Lorentzian " terms in the spectrum. The terms that were

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neglected are of order (ak^2/C_0k) where a is a transport coefficient, k the wave vector, and C_0 the adiabatic speed of sound. Omission of these terms also results in certain thermodynamic variables being uncoupled from others.(5) The terminology " Lorentzian " and " non-Lorentzian " contribution refers to terms in the correlation functions of the form $\exp[-\alpha t]\cos(\beta t)$ and $\exp[-\alpha t]\sin\beta t$, respectively, because of their evident manifestation in the spectrum.

In the calculation presented here these small terms are retained and a complete analysis is accomplished to terms linear in the transport coefficients. The cross correlations, previously found to be zero, are present, and in Sec. 4 we show that these contributions lead to " non-Lorentzian " contributions to the spectrum. The important conclusion for light scattering, as might have been expected by analogy to the one component case, is that the " non-Lorentzian " contributions appear primarily at the side Brillouin peaks and do not affect the complicated structure of the central Rayleigh component. This conclusion supports the recent experimental interpretation(6–9) of the central peak in binary solution light scattering where " non-Lorentzian " contributions have been entirely neglected.

In the final section we extend the treatment, recently presented by Fox and Uhlenbeck,(10) of Landau and Lifshitz(11) hydrodynamical fluctuation theory to binary fluids. It is encouraging to see that the general formulation of hydrodynamical fluctuation theory can be extended to cases other than the simple one component system.

2. The Hydrodynamic Equations

The linearized hydrodynamic equations for the binary mixture are the continuity equation

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = -\rho_0\psi(\mathbf{r},t) \tag{2.1}$$

where $\psi(\mathbf{r},t) = \operatorname{div}[\mathbf{u}(\mathbf{r},t)]$; the Navier–Stokes equation from which we only retain the longitudinal part,

$$\rho_0\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\nabla^2 p + \rho_0 b\nabla^2\psi; \tag{2.2}$$

the diffusion equation

$$\rho_0 \frac{\partial c(\mathbf{r}, t)}{\partial t} = -\operatorname{div}(\mathbf{j}) \tag{2.3}$$

where $\mathbf{j}$ is the linearized diffusion flux

$$\mathbf{j} = -\rho_0 D\left[\nabla c + \frac{k_T}{T_0}\nabla T + \frac{k_p}{p_0}\nabla p\right]; \tag{2.4}$$

and the entropy equation

$$\rho_0 T_0 \frac{\partial s(\mathbf{r}, t)}{\partial t} = \kappa \nabla^2 T - \left[k_T\left(\frac{\partial \mu}{\partial c}\right)_{p,T} - T_0\left(\frac{\partial \mu}{\partial T}\right)_{p,c}\right]\operatorname{div}\mathbf{j}. \tag{2.5}$$

In these equations $\rho(\mathbf{r}, t)$ is the mass density; $s(\mathbf{r}, t)$, the local entropy per unit mass; $c(\mathbf{r}, t)$, the local mass fraction of one component; $T(\mathbf{r}, t)$, the local temperature; and $p(\mathbf{r}, t)$, the local pressure. The transport coefficients appearing in these equations are (1) $b = (\frac{4}{3}\eta_s + \eta_v)/\rho_0$ where η_s and η_v are the shear and bulk viscosity respectively; (2) k_T, the thermal diffusion ratio; and (3) D, the diffusion coefficient. Equilibrium values are denoted by the subscript zero and thermodynamic derivatives that appear are understood to be evaluated at equilibrium. The thermodynamic quantity k_p is defined to be

$$k_p = \left[p_0\left(\frac{\partial \mu}{\delta p}\right)_{T,c} \Big/ \left(\frac{\partial \mu}{\partial c}\right)_{p,T}\right]. \tag{2.6}$$

In addition we have the thermodynamic relationship

$$\mathrm{d}g = \rho^{-1}\,\mathrm{d}p - s\,\mathrm{d}T + \mu\,\mathrm{d}c \tag{2.7}$$

where g is the Gibbs free energy per unit mass and the chemical potential μ appearing in the above equations is the difference in the chemical potential per unit mass of the two components

$$\mu = \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2}. \tag{2.8}$$

The set of Eqs. (2.1)–(2.5) is a closed set of equations for the binary mixture. If the entropy is expanded in terms of p, c, and T and use is made of Eq. (2.3), the entropy transport equation may be written as

$$\rho_0 C_{p,c}\frac{\partial T}{\partial t} - \rho_0 k_T\left(\frac{\partial \mu}{\partial c}\right)_{p,T}\frac{\partial c}{\partial t} + \rho_0 T_0\left(\frac{\partial s}{\partial p}\right)_{T,c}\frac{\partial p}{\partial t} = \kappa \nabla^2 T \tag{2.9}$$

where $C_{p,c}$ is the heat capacity per unit mass at constant pressure and concentration.

The time dependence of the correlation functions of the local thermodynamic variables is computed according to these linearized hydrodynamic equations. The procedure to be followed for the binary fluid is described in detail in Ref. (3). Three thermodynamic variables are required to characterize the state of a binary system. The linearized hydrodynamic equations are written in terms of the three variables selected and the variable ψ. These four variables will be denoted $N_i(\mathbf{r}, t)$, $i = 1, 2, 3, 4$. The resulting set of equations may be written as

$$\frac{\partial \mathbf{N}(\mathbf{r}, t)}{\partial t} = -\int \mathrm{L}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{N}(\mathbf{r}', t)\, \mathrm{d}\mathbf{r}' \tag{2.10}$$

where the matrix $\mathrm{L}(\mathbf{r}, \mathbf{r}')$ is non-singular. In terms of Fourier–Laplace transforms we have

$$\mathrm{M}(\mathbf{k}, z) \cdot \hat{\mathbf{N}}(\mathbf{k}, z) = \mathbf{N}(\mathbf{k}) \tag{2.11}$$

where

$$\mathrm{M}(\mathbf{k}, z) = z\mathrm{I} + \mathrm{L}(\mathbf{k})$$

with I, the identity matrix. In Eq. (2.11) $\hat{\mathbf{N}}(\mathbf{k}, z)$ is a column vector whose elements are the Fourier–Laplace transforms of the variables $N_i(\mathbf{r}, t)$,

$$\hat{N}_i(\mathbf{k}, z) = \int_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r} - zt)\, N_i(\mathbf{r}, t). \tag{2.12}$$

The elements of the vector $\mathbf{N}(\mathbf{k})$ are the space Fourier transforms of $N_i(\mathbf{r}, 0)$,

$$N_i(\mathbf{k}) = \int \mathrm{d}\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r})\, N_i(\mathbf{r}, 0). \tag{2.13}$$

The solutions of Eq. (2.11) may be expressed as

$$\hat{N}_i(\mathbf{k}, z) = [\det \mathrm{M}(\mathbf{k}, z)]^{-1} \sum_j P_{ij}(\mathbf{k}, z)\, N_j(\mathbf{k}) \tag{2.14}$$

where the P_{ij} are algebraic functions. The correlation function matrix follows from Eq. (2.14),

$$\langle \hat{N}_i(\mathbf{k}, z)\, N_l(-\mathbf{k}) \rangle = [\det \mathrm{M}(\mathbf{k}, z)]^{-1} \sum_j P_{ij}(\mathbf{k}, z) \langle N_j(\mathbf{k})\, N_l(-\mathbf{k}) \rangle. \tag{2.15}$$

The correlation functions are expressed in terms of the time by taking the inverse Laplace transform of Eq. (2.15),

$$\langle N_i(\mathbf{k},t)N_l(-\mathbf{k})\rangle\,(t>0)$$

$$=(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\exp(i\omega t)\langle \hat{N}_i(\mathbf{k},i\omega)N_l(-\mathbf{k})\rangle. \quad (2.16)$$

Away from critical points k^{-1} is much greater than the range of molecular correlations and an acceptable procedure for computing the equilibrium averages $\langle N_j(\mathbf{k})N_l(-\mathbf{k})\rangle$ is⁽¹⁾

$$\lim_{k\to 0}\frac{1}{V}\langle N_j(\mathbf{k})N_l(-\mathbf{k})\rangle=\frac{1}{\Omega}\overline{\delta N_j\,\delta N_l}. \quad (2.17)$$

In this equation it is understood that the thermodynamic limit is taken before $k\to 0$. The bar superscript denotes a grand canonical average referred to a macroscopic volume element of the fluid which is small compared to k^{-1} and hence small compared to the overall volume of the system V.

The quadratic fluctuation averages $\overline{\delta N_j\,\delta N_l}$ can be computed by thermodynamic fluctuation theory. In thermodynamic fluctuation theory the probability of a fluctuation $W[\delta\mathbf{N}]$ is proportional to $\exp[\Delta S_T(\delta\mathbf{N})/k_B]$ where ΔS_T is the change in entropy of system plus surroundings caused by the fluctuation $\delta\mathbf{N}$. To compute ΔS_T for a system we must define the system by keeping one extensive variable fixed. If the volume is held fixed the resulting fluctuation formulas, obtained in the Gaussian approximation, are identical to results obtained for averages of fluctuations in the grand canonical ensemble. If the total mass (or number) is held fixed the fluctuation formulas obtained from thermodynamic fluctuation theory in the Gaussian approximation are identical to results obtained for averages of fluctuations in the isothermal–isobaric ensemble. Provided that the thermodynamic quantities, N_i, are expressed as intensive quantities, e.g., temperature, pressure, energy per unit mass, the results for the averages of quadratic fluctuations $(\delta N_j\,\delta N_l)$ will be the same in all cases.⁽¹²⁾ Here we express all our thermodynamic variables as intensive quantities and compute for convenience the fluctuation averages by thermodynamic fluctuation theory in the scheme where the arbitrary fixed extensive variable is the mass M. In this case[(13)]

$$\frac{\Delta S_T}{k_B} = -\frac{M}{2k_BT_0}[\delta s\,\delta T - \delta v\,\delta p + \delta\mu\,\delta c]. \tag{2.18}$$

In the Gaussian approximation $\overline{\delta s\,\delta c} \neq 0$ and $\overline{\delta T\,\delta p} \neq 0$ and either of the obvious choices of the three thermodynamic variables, (s, p, c) or (T, p, c) result in cross terms appearing in Eq. (2.15). Accordingly, as done in Ref. (3), we choose the set of variables (ϕ, p, c) where

$$\phi = T - \frac{T_0\alpha_T}{C_{p,c}\rho_0}p; \qquad \left[\delta\phi = \delta T - \frac{T_0\alpha_T}{C_{p,c}\rho_0}\delta p\right] \tag{2.19}$$

and α_T is the thermal expansion coefficient $\alpha_T = -\rho_0{}^{-1}(\partial\rho/\partial T)_{p,c}$. In terms of these variables, in the Gaussian approximation,

$$\frac{\Delta S_T}{k_B} = -\frac{M}{2k_BT_0}\left[\frac{C_{p,c}}{T_0}(\delta\phi)^2 + \frac{\beta_{s,c}}{\rho_0}(\delta p)^2 + \left(\frac{\partial\mu}{\partial c}\right)_{p,T}(\delta c)^2\right], \tag{2.20}$$

where $\beta_{s,c}$ is the adiabatic compressibility,

$$\beta_{s,c} = \rho_0{}^{-1}\left(\frac{\partial\rho}{\partial p}\right)_{s,c} = \beta_{T,c}/\gamma,$$

$\beta_{T,c} = \rho_0{}^{-1}(\partial\rho/\partial p)_{T,c}$ is the isothermal compressibility and $\gamma = C_{p,c}/C_{v,c}$. This choice of variables assures that the matrix of equilibrium correlation functions $\langle \mathbf{N}(\mathbf{k})\mathbf{N}(-\mathbf{k})\rangle$ is diagonal in the small $\mathbf{k}$ limit with a resulting simplification in Eq. (2.15).

The new variable ϕ, as constructed, is a linear combination of T and p. If one expands T as a function of the variables p, c and s, it is an easy matter to show that

$$\delta\phi = \frac{T_0}{C_{p,c}}\left[\delta s + \left(\frac{\partial\mu}{\partial T}\right)_{p,c}\delta c\right]. \tag{2.21}$$

This is an important representation of the new variable ϕ since it shows that ϕ is a linear combination of s and c but independent of p. Since s and c fluctuations do not propagate as a sound wave while the variable p does, we may expect that the coupling between ϕ and p will be of a different character than that between ϕ and s or c. In the original treatment[(3)] ϕ was found to be uncoupled to p for all times. Here we show that these variables are coupled to terms that have a " non-Lorentzian " character.

If the elements of $\mathbf{N}$ are taken to be c, p, ϕ and ψ, the 4 × 4 matrix $\mathbf{M}$ has the form

$$\mathbf{M} = \begin{bmatrix} z + Dk^2 & D\mathscr{P}k^2 & \dfrac{Dk_T}{T_0}k^2 & 0 \\ C_0{}^2\rho_0{}^2 D\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}k^2 & z + C_0{}^2\rho_0{}^2 D\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}^2k^2 + C_0{}^2\dfrac{T_0\alpha_T{}^2}{C_{p,c}}\chi k^2 & \rho_0 C_0{}^2\left[\dfrac{\rho_0 Dk_T}{T_0}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}k^2 + \alpha_T\chi k^2\right] & \rho_0 C_0{}^2 \\ \dfrac{Dk_T}{C_{p,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}k^2 & \dfrac{Dk_T}{C_{p,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}k^2 + \dfrac{T_0\alpha_T}{\rho_0 C_{p,c}}\chi k^2 & z + \dfrac{Dk_T{}^2}{T_0 C_{p,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}k^2 + \chi k^2 & 0 \\ 0 & -\dfrac{k^2}{\rho_0} & 0 & z + bk^2 \end{bmatrix}$$

where we have introduced $\chi = \kappa/\rho_0 C_{p,c}$, the adiabatic speed of sound $C_0^2 = (\partial p/\partial \rho)_{s,c}$, and $\mathscr{P} = k_p/p_0 + k_T \alpha_T/\rho_0 C_{p,c}$.

It is now possible to determine the correlation functions of interest for the binary fluid. The results are given in the next section.

3. Correlation Functions of the Binary Fluid

To terms linear in the transport coefficients the dispersion relation for the binary fluid is

$$\det \mathrm{M} = (z+z_1)(z+z_2)(z-iC_0k+\Gamma k^2)(z+iC_0k+\Gamma k^2) = 0 \quad (3.1)$$

where

$$\Gamma = \frac{1}{2}\left[b+\chi(\gamma-1)+D\rho_0^2 C_0^2 \left(\frac{\partial \mu}{\partial c}\right)_{p,T} \mathscr{P}^2\right] \quad (3.2)$$

$$z_1 = \frac{k^2}{2}(\chi+\mathscr{D}) + \frac{k^2}{2}[(\chi+\mathscr{D})^2 - 4\chi D]^{1/2} \quad (3.3)$$

$$z_2 = \frac{k^2}{2}(\chi+\mathscr{D}) - \frac{k^2}{2}[(\chi+\mathscr{D})^2 - 4\chi D]^{1/2} \quad (3.4)$$

with

$$\mathscr{D} = D\left[1+\frac{k_T^2}{T_0 C_{p,c}}\left(\frac{\partial \mu}{\partial c}\right)_{p,T}\right].$$

The resulting correlation functions are

$$\frac{\langle p(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle|p(\mathbf{k})|^2\rangle} = e^{-\Gamma k^2 t}\cos C_0 kt + \frac{(b-\Gamma)k}{C_0} e^{-\Gamma k^2 t}\sin C_0 kt \quad (3.5)$$

$$\frac{\langle \phi(\mathbf{k},t)\phi(-\mathbf{k},0)\rangle}{\langle|\phi(\mathbf{k})|^2\rangle} = \frac{z_1 - Dk^2}{z_1 - z_2} e^{-z_1 t} + \frac{z_2 - Dk^2}{z_2 - z_1} e^{-z_2 t} \quad (3.6)$$

$$\frac{\langle c(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(\mathbf{k})|^2\rangle} = \frac{z_2 - Dk^2}{z_2 - z_1} e^{-z_1 t} + \frac{z_1 - Dk^2}{z_1 - z_2} e^{-z_2 t} \quad (3.7)$$

$$\frac{\langle \phi(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(\mathbf{k})|^2\rangle} = \frac{T_0}{C_{p,c}}\left(\frac{\partial \mu}{\partial c}\right)_{p,T} \frac{\langle c(\mathbf{k},t)\phi(-\mathbf{k},0)\rangle}{\langle|\phi(\mathbf{k})|^2\rangle}$$

$$= \frac{(\partial\mu/\partial c)_{p,T}}{C_{p,c}} \frac{Dk^2 k_T}{z_1 - z_2}(e^{-z_1 t} - e^{-z_2 t}). \quad (3.8)$$

When compared with the results of Ref. (3) the p–p correlation function is modified by the presence of " non-Lorentzian " terms, whereas the correlation functions involving only ϕ and c remain unmodified. Finally, the correlation functions ϕ–p and c–p which were determined to be identically zero in Ref. (3) consist of purely "non-Lorentzian" terms,

$$\frac{\langle c(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle|p(\mathbf{k})|^2\rangle} = \frac{\beta_{s,c}}{\rho_0(\partial\mu/\partial c)_{p,T}} \frac{\langle p(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(k)|^2\rangle}$$

$$= -\frac{D\mathscr{P}k}{C_0} e^{-\Gamma k^2 t} \sin C_0 kt \tag{3.9}$$

$$\frac{\langle p(\mathbf{k},t)\phi(-\mathbf{k},0)\rangle}{\langle|\phi(\mathbf{k})|^2\rangle} = \frac{\rho_0 C_{p,c}}{T_0\beta_{s,c}} \frac{\langle \phi(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle|p(\mathbf{k})|^2\rangle}$$

$$= -\beta_{s,c}^{-1}\left[\alpha_T\chi + \frac{Dk_T\rho_0}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}\right]\frac{k}{C_0} e^{-\Gamma k^2 t}\sin C_0 kt. \tag{3.10}$$

The cross correlations in Eqs. (3.9) and (3.10) do not affect the complex central Rayleigh peak of the light scattering spectrum of a binary mixture which arises from the diffusive mode, the heat mode and the coupling between them.

The correlation functions for the variables (s, p, c) may also be determined. Besides the concentration–concentration correlation given by Eq. (3.7) these correlation functions are

$$\begin{aligned}\frac{\langle s(\mathbf{k},t)s(-\mathbf{k},0)\rangle}{\langle|s(\mathbf{k})|^2\rangle} &= \frac{e^{-z_1 t}}{z_1 - z_2}\left\{z_1 - Dk^2 - \left(\frac{\partial\mu}{\partial T}\right)_{p,c}\left(\frac{\partial T}{\partial s}\right)_{p,\mu}\right.\\ &\qquad \left.\cdot\left[\left(\frac{\partial\mu}{\partial c}\right)_{p,T}^{-1}\left(\frac{\partial\mu}{\partial T}\right)_{p,c}(z_1+z_2-2Dk^2) + \frac{2Dk_T}{T_0}k^2\right]\right\}\\ &\quad + \frac{e^{-z_2 t}}{z_2 - z_1}\left\{z_2 - Dk^2 - \left(\frac{\partial\mu}{\partial T}\right)_{p,c}\left(\frac{\partial T}{\partial s}\right)_{p,\mu}\right.\\ &\qquad \left.\cdot\left[\left(\frac{\partial\mu}{\partial c}\right)_{p,T}^{-1}\left(\frac{\partial\mu}{\partial T}\right)_{p,c}(z_1+z_2-2Dk^2) + \frac{2Dk_T}{T_0}k^2\right]\right\}\end{aligned} \tag{3.11}$$

$$\begin{aligned}\frac{\langle s(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(\mathbf{k})|^2\rangle} &= \left(\frac{\partial\mu}{\partial c}\right)_{p,T}\left(\frac{\partial s}{\partial T}\right)_{p,\mu}\frac{\langle c(\mathbf{k},t)s(-\mathbf{k},0)\rangle}{\langle|s(\mathbf{k})|^2\rangle}\\ &= \frac{e^{-z_1 t}}{z_1 - z_2}\left[\left(\frac{\partial\mu}{\partial T}\right)_{p,c}(z_2 - Dk^2) + \frac{Dk_T}{T_0}k^2\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right]\\ &\quad + \frac{e^{-z_2 t}}{z_2 - z_1}\left[\left(\frac{\partial\mu}{\partial T}\right)_{p,c}(z_1 - Dk^2) + \frac{Dk_T}{T_0}k^2\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right].\end{aligned} \tag{3.12}$$

Equations (3.11) and (3.12) may be obtained from Eqs. (2.20) and the set of Eqs. (3.6), (3.7) and (3.8). Alternatively, they may be obtained via a procedure similar to the one presented in Sec. 2 where the linearized hydrodynamic equations are written directly in terms of the variables s, p, c and ψ. We also find a coupling between s and p which is of first order and consists only of " non-Lorentzian " terms,

$$\frac{\langle s(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle|p(\mathbf{k})|^2\rangle} = \frac{\rho_0^{-1}\beta_{s,c}}{(\partial T/\partial s)_{p,\mu}} \frac{\langle p(\mathbf{k},t)s(-\mathbf{k},0)\rangle}{\langle|s(\mathbf{k})|^2\rangle}$$

$$= \left\{-\frac{\alpha_T}{\rho_0}\chi + D\mathscr{P}\left[\left(\frac{\partial\mu}{\partial T}\right)_{p,c} - \frac{k_T}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right]\right\}$$

$$\cdot\frac{k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt. \tag{3.13}$$

Finally the correlation functions of the set of variables ρ, T and c may be obtained by expressing ρ and T in terms of variables whose correlation functions have already been evaluated or by proceeding as in Sec. 2 with the hydrodynamic equations expressed in terms of ρ, T, c and ψ. Lengthy but straightforward calculations yield

$$\frac{\langle \rho(\mathbf{k},t)\rho(-\mathbf{k},0)\rangle}{\langle|\rho(\mathbf{k})|^2\rangle} = \frac{\beta_{s,c}}{\beta_{T,\mu}}\left\{\frac{e^{-z_1 t}}{z_1 - z_2}\left[(1-\rho_0 C_0{}^2\beta_{T,\mu})(z_2 - Dk^2) - (1-\gamma)\right.\right.$$

$$\left.\cdot\left(z_1 + z_2 - 2Dk^2 - \frac{2Dk_T}{T_0}\left(\frac{\partial T}{\partial c}\right)_{p,\rho} k^2\right)\right]$$

$$+\frac{e^{-z_2 t}}{z_2 - z_1}\left[(1-\rho_0 C_0{}^2\beta_{T,\mu})(z_1 - Dk^2) - (1-\gamma)\right.$$

$$\left.\cdot\left(z_1 + z_2 - 2Dk^2 - \frac{2Dk_T}{T_0}\left(\frac{\partial T}{\partial c}\right)_{p,\rho} k^2\right)\right]$$

$$\left.+ e^{-\Gamma k^2 t}\cos C_0 kt + (3\Gamma - b)\frac{k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt\right\}, \tag{3.14}$$

$$\begin{aligned}\frac{\langle T(\mathbf{k},t)T(-\mathbf{k},0)\rangle}{\langle|T(\mathbf{k})|^2\rangle} &= \frac{1}{\gamma}\frac{e^{-z_1t}}{z_1-z_2}(z_1-Dk^2) \\ &\quad +\frac{1}{\gamma}\frac{e^{-z_2t}}{z_2-z_1}(z_2-Dk^2)+(1-1/\gamma)\,e^{-\Gamma k^2t}\cos C_0kt \\ &\quad -(1-1/\gamma)\left[\Gamma+2\chi-b+\frac{2Dk_T\rho_0}{T_0\alpha_T}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}\right] \\ &\quad \cdot\frac{k}{C_0}e^{-\Gamma k^2t}\sin C_0kt, \end{aligned} \tag{3.15}$$

$$\begin{aligned}\frac{\langle\rho(\mathbf{k},t)T(-\mathbf{k},0)\rangle}{\langle|T(\mathbf{k})|^2\rangle} &= \frac{\rho_0{}^3\beta_{T,\mu}C_{v,c}}{T_0}\frac{\langle T(\mathbf{k},t)\rho(-\mathbf{k},0)\rangle}{\langle|\rho(\mathbf{k})|^2\rangle} \\ &= \frac{1}{\gamma}\frac{e^{-z_1t}}{z_1-z_2}\left[\frac{Dk_T}{T_0}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}k^2-\rho_0\alpha_T(z_1-Dk^2)\right] \\ &\quad +\frac{1}{\gamma}\frac{e^{-z_2t}}{z_2-z_1}\left[\frac{Dk_T}{T_0}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}k^2-\rho_0\alpha_T(z_2-Dk^2)\right] \\ &\quad +\rho_0\beta_{s,c}\left(\frac{\partial p}{\partial T}\right)_{p,c}e^{-\Gamma k^2t}\cos C_0kt \\ &\quad +\frac{\rho_0}{\gamma}\left[\alpha_T(\Gamma-\chi)-\frac{Dk_T\rho_0}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}\right] \\ &\quad \cdot\frac{k}{C_0}e^{-\Gamma k^2t}\sin C_0kt, \end{aligned} \tag{3.16}$$

$$\begin{aligned}\frac{\langle\rho(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(\mathbf{k})|^2\rangle} &= \rho_0{}^3\beta_{T,\mu}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\frac{\langle c(\mathbf{k},t)\rho(-\mathbf{k},0)\rangle}{\langle|\rho(\mathbf{k})|^2\rangle} \\ &= \frac{e^{-z_1t}}{z_2-z_1}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}\left[z_2+D\rho_0{}^2\left(\frac{\partial\mu}{\partial\rho}\right)_{p,T}\mathscr{P}k^2\right] \\ &\quad +\frac{e^{-z_2t}}{z_1-z_2}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}\left[z_1+D\rho_0{}^2\left(\frac{\partial\mu}{\partial\rho}\right)_{p,T}\mathscr{P}k^2\right] \\ &\quad -\rho_0{}^2\left(\frac{\partial\mu}{\partial c}\right)_{p,T}D\mathscr{P}\frac{k}{C_0}e^{-\Gamma k^2t}\sin C_0kt, \end{aligned} \tag{3.17}$$

and

$$
\begin{aligned}
\frac{\langle c(\mathbf{k},t)T(-\mathbf{k},0)\rangle}{\langle|T(\mathbf{k})|^2\rangle} &= \frac{C_{v,c}}{T_0}\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\frac{\langle T(\mathbf{k},t)c(-\mathbf{k},0)\rangle}{\langle|c(\mathbf{k})|^2\rangle} \\
&= \frac{Dk_Tk^2}{T_0\gamma(z_1-z_2)}\,(e^{-z_1t}-e^{-z_2t}) - \alpha_T\beta_{T,c}^{-1}D\mathscr{P} \\
&\quad\cdot\frac{k}{C_0}\,e^{-\Gamma k^2t}\sin C_0kt, \qquad (3.18)
\end{aligned}
$$

where $\beta_{T,\mu} = \rho_0^{-1}(\partial\rho/\partial p)_{T,\mu}$. For comparison, the hydrodynamic correlation functions for the one component system are included in Appendix A.

4. The Light Scattering Spectrum

The intensity of the scattered light $I(R_0, k, \omega)$ is proportional to the generalized structure factor

$$
I(R_0,k,\omega) = I_0\left[\frac{k_0^4V\sin^2\Phi}{32\pi^3R_0^2\rho_0}\right]S(k,\omega)
$$

with

$$
S(k,\omega) = 2M\,\mathrm{Re}\,\langle\hat{\epsilon}(\mathbf{k},\omega)\,\epsilon(-\mathbf{k})\rangle \qquad (4.1)
$$

where ϵ is the dielectric constant. Expressing ϵ as a function of p, ϕ and c we get for $S(\mathbf{k},\omega)$

$$
\begin{aligned}
S(\mathbf{k},\omega) &= \left(\frac{\partial\epsilon}{\partial p}\right)_{s,c}^2\frac{k_BT_0\rho_0}{\beta_{s,c}}\left[\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega+C_0k)^2}+\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega-C_0k)^2}\right] \\
&\quad+\left(\frac{\partial\epsilon}{\partial c}\right)_{p,T}^2k_BT_0\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\left(\frac{2}{z_2-z_1}\right)\left[\frac{z_1(z_2-Dk^2)}{z_1^2+\omega^2}-\frac{z_2(z_1-Dk^2)}{z_2^2+\omega^2}\right] \\
&\quad+\left(\frac{\partial\epsilon}{\partial T}\right)_{p,c}^2\frac{k_BT_0^2}{C_{p,c}}\left(\frac{2}{z_2-z_1}\right)\left[\frac{z_1(Dk^2-z_1)}{z_1^2+\omega^2}-\frac{z_2(Dk^2-z_2)}{z_2^2+\omega^2}\right] \\
&\quad+\left(\frac{\partial\epsilon}{\partial T}\right)_{p,c}\left(\frac{\partial\epsilon}{\partial c}\right)_{p,T}\frac{2k_BT_0}{C_{p,c}}\left(\frac{2Dk^2k_T}{z_1-z_2}\right)\left[\frac{z_1}{z_1^2+\omega^2}-\frac{z_2}{z_2^2+\omega^2}\right] \\
&\quad+\frac{k_BT_0\rho_0}{\beta_{s,c}}\frac{k}{C_0}\left[\left(\frac{\partial\epsilon}{\partial p}\right)_{s,c}^2(b-\Gamma)-2\left(\frac{\partial\epsilon}{\partial p}\right)_{s,c}\left(\frac{\partial\epsilon}{\partial c}\right)_{p,T}D\mathscr{P}\right. \\
&\quad\left.-2\left(\frac{\partial\epsilon}{\partial p}\right)_{s,c}\left(\frac{\partial\epsilon}{\partial T}\right)_{p,c}\left(\frac{T_0\alpha_T}{\rho_0C_{p,c}}\chi+\frac{Dk_T\mathscr{P}}{C_{p,c}}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right)\right] \\
&\quad\cdot\left[\frac{\omega+C_0k}{(\omega+C_0k)^2+(\Gamma k^2)^2}-\frac{\omega-C_0k}{(\omega-C_0k)^2+(\Gamma k^2)^2}\right] \qquad (4.2)
\end{aligned}
$$

The last term which was not included by Mountain and Deutch(3) consists of " non-Lorentzian " contributions to the Brillouin peaks centered at $\pm C_0 k$. These terms will tend to distort the Brillouin peaks and shift their integrated intensity toward the central Rayleigh peak.(15) When the dielectric constant in Eq. (4.1) is expressed in terms of the variables p, s and c, the p–p correlation function will give rise to the Brillouin peaks, the c–c, s–s and s–c correlations will produce the central peak, and the p–s and p–c will give rise to " non-Lorentzian " additions to the Brillouin peaks. The important point to note about this new expression for the spectrum of the binary fluid is that the " non-Lorentzian " terms primarily contribute to the side Brillouin doublets as in the one component case. Provided the doublets are well separated from the central component there will be little distortion of the central Rayleigh line. This conclusion is of some importance since it establishes that, for a well separated spectrum, " non-Lorentzian " terms need not be included for the analysis of the central part of the spectrum. Experimental verification of the rather complicated structure of the central component for binary mixtures has not yet been reported and remains a matter of considerable interest.

In the limit of small concentration the thermal diffusion ratio k_T tends to zero and one obtains for the central peak from Eq. (4.2)

$$\lim_{k_T \to 0} S(\mathbf{k}, \omega)^{cen} = \left(\frac{\partial \epsilon}{\partial c}\right)^2_{p,T} \frac{k_B T_0}{(\partial \mu / \partial c)_{p,T}} \frac{2Dk^2}{\omega^2 + (Dk^2)^2}$$

$$+ \left(\frac{\partial \epsilon}{\partial T}\right)^2_{p,c} \frac{k_B T_0^2}{C_{p,c}} \frac{2\chi k^2}{\omega^2 + (\chi k^2)^2} \tag{4.3}$$

which is identical to the expression obtained by Mountain and Deutch(3) for this case. However it is not true, as is sometimes stated,(8,9) that in the limit of low concentration the entropy and concentration fluctuations decouple to give rise to the two separate Lorentzian components in Eq. (4.3). Indeed from Eqs. (3.7), (3.11), and (3.12) one may show that the s–s correlation function depends upon both the thermal diffusivity χ and the diffusion constant D

while the s–c and c–c correlation functions depend on D only.

$$\lim_{k_T\to 0} M\,\mathrm{Re}\,\langle s(\mathbf{k},\omega)s(-\mathbf{k},0)\rangle = k_B C_{p,c}\frac{\chi k^2}{\omega^2+(\chi k^2)^2} + k_B T_0\frac{(\partial\mu/\partial T)^2_{p,c}}{(\partial\mu/\partial c)_{p,T}}\frac{Dk^2}{\omega^2+(Dk^2)^2} \tag{4.4}$$

$$\lim_{k_T\to 0} M\,\mathrm{Re}\,\langle s(\mathbf{k},\omega)c(-\mathbf{k},0)\rangle = -k_B T_0\frac{(\partial\mu/\partial T)_{p,c}}{(\partial\mu/\partial c)_{p,T}}\frac{Dk^2}{\omega^2+(Dk^2)^2} \tag{4.5}$$

$$\lim_{k_T\to 0} M\,\mathrm{Re}\,\langle c(\mathbf{k},\omega)c(-\mathbf{k},0)\rangle = \frac{k_B T_0}{(\partial\mu/\partial c)_{p,T}}\frac{Dk^2}{\omega^2+(Dk^2)^2}. \tag{4.6}$$

These expressions clearly indicate in the dilute limit the contribution of diffusion to the entropy correlations and the non-vanishing coupling between the entropy and concentration fluctuations. If the dielectric fluctuations in Eq. (4.1) are expressed in terms of s and c at constant p, then in the limit of $k_T \to 0$ use of Eqs. (4.4)–(4.6) yields Eq. (4.3). On the other hand, the variables c and ϕ (or T as far as the central line is concerned) decouple when $k_T \to 0$. The variables c and s do not. Of course either set leads to the same expression for the spectrum.

Finally we note that for many binary mixtures an adequate form for the dielectric constant at optical frequencies is given by the Clausius–Mossoti formula

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3}\left[\left(\frac{\alpha_1}{m_1}\right)\rho_1 + \left(\frac{\alpha_2}{m_2}\right)\rho_2\right] \tag{4.7}$$

where α_i is the molecular polarizability of component i and ρ_i is the mass density of component i. In terms of c, the mass fraction of component 1, one finds

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi}{3}\rho\left[\left(\frac{\alpha_1}{m_1}-\frac{\alpha_2}{m_2}\right)c + \frac{\alpha_2}{m_2}\right] \tag{4.8}$$

so that $\epsilon = \epsilon(\rho, c)$. One can find systems for which the effective polarizabilities are equal for the two components

$$\frac{\alpha_1}{m_1} = \frac{\alpha_2}{m_2}. \tag{4.9}$$

In this case the dielectric constant is a function of density only and the light scattering spectrum will arise from the density–density correlation function given in Eq. (3.14). This accidental equality of the effective polarizability may advantageously be used to study density–density correlation functions for binary systems, for example in the critical region. The precision is limited of course by how accurately the equality Eq. (4.9) is realized.

5. Hydrodynamical Fluctuations

The Landau and Lifshitz theory of hydrodynamical fluctuations has recently been put on a firm basis by Fox and Uhlenbeck who derive fluctuating hydrodynamic equations for a one component system.⁽¹⁰⁾ The general procedure developed by Fox and Uhlenbeck may be employed to treat more complex hydrodynamic situations In this section we present the results obtained for binary systems. Our objective is the calculation of correlation functions of the random functions associated with the fluctuating hydrodynamic variables.

If instead of the original set of variables $N_i = c, p, \phi$ and ψ we use the slightly modified variables $a_i(\mathbf{r}, t)$, $i = 1$ to 6,

$$a_1(\mathbf{r}, t) = \left[\rho_0\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right]^{1/2} c(\mathbf{r}, t), \qquad a_2(\mathbf{r}, t) = \beta_{s,c}^{1/2}\, p(\mathbf{r}, t)$$
$$a_3(\mathbf{r}, t) = (\rho_0 C_{p,c}/T_0)^{1/2}\phi(\mathbf{r}, t), \quad \text{and} \quad a_\alpha(\mathbf{r}, t) = \rho_0{}^{1/2} u_\alpha(\mathbf{r}, t) \tag{5.1}$$

with $\alpha = 4$, 5, 6 in Eq. (2.10), the matrix $\mathrm{L}(\mathbf{r}, \mathbf{r}')$ of that equation becomes symmetric with respect to interchange of indices

$$L_{ij}(\mathbf{r}, \mathbf{r}') = L_{ji}(\mathbf{r}, \mathbf{r}')$$

and may be decomposed into a symmetric and anti-symmetric part with respect to the argument

$$L_{ij}(\mathbf{r}, \mathbf{r}') = A_{ij}(\mathbf{r}, \mathbf{r}') + S_{ij}(\mathbf{r}, \mathbf{r}')$$

and

$$L_{ij}(\mathbf{r}', \mathbf{r}) = -A_{ij}(\mathbf{r}, \mathbf{r}') + S_{ij}(\mathbf{r}, \mathbf{r}').$$

The hydrodynamic set of linearized equations for binary mixtures may then be written as

$$\frac{\partial \mathbf{a}(\mathbf{r}, t)}{\partial t} + \int \mathrm{A}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{a}(\mathbf{r}', t)\, d\mathbf{r}' = -\int \mathrm{S}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{a}(\mathbf{r}', t)\, d\mathbf{r}' \tag{5.2}$$

which is a form identical to that obtained by Fox and Uhlenbeck⁽¹⁰⁾ for the one component case. The 6×6 anti-symmetric and symmetric matrices $\mathrm{A}(\mathbf{r}, \mathbf{r}')$ and $\mathrm{S}(\mathbf{r}, \mathbf{r}')$ are defined by

$$\mathsf{A}(\mathbf{r},\mathbf{r}') = \left[\begin{array}{cc} 0 & 0 \\ \\ 0 & 0 \\ \\ 0 & 0 \\ \\ 0 & (\rho_0\beta_{s,c})^{-1/2}\dfrac{\partial}{\partial r_\alpha}\,\partial(\mathbf{r}-\mathbf{r}') \end{array}\right.$$

and,

$$\mathsf{S}(\mathbf{r},\mathbf{r}') = \left[\begin{array}{cc} D\,\delta_{\mu\nu} & \left[\dfrac{\rho_0}{\beta_{s,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\right]^{1/2} D\mathscr{P}\,\delta_{\mu\nu} \\ \\ \left[\dfrac{\rho_0}{\beta_{s,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\right]^{1/2} D\mathscr{P}\,\delta_{\mu\nu} & \dfrac{T_0}{\beta_{s,c}}\left[\dfrac{\rho_0 D}{T_0}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}^2 + \dfrac{\alpha_T{}^2\chi}{\rho_0 C_{p,c}}\right]\delta_{\mu\nu} \\ \\ \left[\dfrac{(\partial\mu/\partial c)_{p,T}}{T_0 C_{p,c}}\right]^{1/2} Dk_T\,\delta_{\mu\nu} & \begin{array}{l}\left(\dfrac{T_0}{\rho_0\beta_{s,c}C_{p,c}}\right)^{1/2} \\ \qquad \cdot\left[\dfrac{\rho_0 Dk_T}{T_0}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P} + \alpha_T\chi\right]\delta_{\mu\nu}\end{array} \\ \\ 0 & 0 \end{array}\right. .$$

$$\left.\begin{matrix} 0 & 0 \\ 0 & (\rho_0\beta_{s,c})^{-1/2}\dfrac{\partial}{\partial r_\alpha}\,\delta(\mathbf{r}-\mathbf{r}') \\ 0 & 0 \\ 0 & 0 \end{matrix}\right] \tag{5.3}$$

$$\left.\begin{matrix} \left[\dfrac{(\partial\mu/\partial c)_{p,T}}{T_0C_{p,c}}\right]^{1/2} Dk_T\,\delta_{\mu\nu} & 0 \\ \left(\dfrac{T_0}{\rho_0\beta_{s,c}C_{p,c}}\right)^{1/2} \cdot\left[\dfrac{\rho_0Dk_T}{T_0}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}+\alpha_T\chi\right]\delta_{\mu\nu} & 0 \\ \left[\dfrac{Dk_T{}^2}{T_0C_{p,c}}\left(\dfrac{\partial\mu}{\partial c}\right)_{p,T}+\chi\right]\delta_{\mu\nu} & 0 \\ 0 & \dfrac{1}{\rho_0}\,[\eta_s(\delta_{\alpha\nu}\delta_{\mu\beta}+\delta_{\alpha\beta}\delta_{\mu\nu}) + (\eta_v-\frac{2}{3}\eta_s)\delta_{\alpha\mu}\delta_{\beta\nu}] \end{matrix}\right] \frac{\partial^2}{\partial r_\mu\partial r_\nu}\,\delta(\mathbf{r}-\mathbf{r}') \tag{5.4}$$

where we have used the convention of summation over repeated indices.

From the expression of the total entropy

$$S = \int_V \rho s \, \mathrm{d}v$$

and the use of Eqs. (2.1) and (2.5) we may compute the time rate of change of the entropy to be

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}t} = \dot{S} = \frac{1}{T_0}\int \Bigg\{ & \left[2\eta_s D_{\alpha\beta} D_{\alpha\beta} + \left(\eta_v - \frac{2}{3}\eta_s\right) D_{\gamma\gamma}^2\right] + \rho_0 D \left(\frac{\partial \mu}{\partial c}\right)_{p,T} (\nabla c)^2 \\ & + \frac{1}{T_0}\left[\frac{\rho_0 D k_T{}^2}{T_0}\left(\frac{\partial \mu}{\partial c}\right)_{p,T} + \rho_0 C_{p,c}\chi\right](\nabla \phi)^2 \\ & + T_0\left[\frac{\rho_0 D \mathscr{P}^2}{T_0} + \frac{\alpha_T{}^2 \chi}{\rho_0 C_{p,c}}\right](\nabla p)^2 \\ & + 2\frac{\rho_0 D k_T}{T_0}\left(\frac{\partial \mu}{\partial c}\right)_{p,T} (\nabla c)\cdot(\nabla \phi) + 2\rho_0 D \left(\frac{\partial \mu}{\partial c}\right)_{p,T} \mathscr{P} (\nabla c)\cdot(\nabla p) \\ & + 2\left[\frac{\rho_0 D k_T}{T_0}\left(\frac{\partial \mu}{\partial c}\right)_{p,T} \mathscr{P} + \alpha_T \chi\right](\nabla \phi)\cdot(\nabla p)\Bigg\} \, \mathrm{d}\mathbf{r} \end{aligned} \tag{5.5}$$

where $2D_{\alpha\beta} = \partial u_\alpha / \partial r_\beta + \partial u_\beta / \partial r_\alpha$. In obtaining the above equation the assumption of no flow of either momentum or heat flux across the bounding surface has been made. It can be shown that in terms of the variables $\mathbf{a}(\mathbf{r}, t)$ and the matrix $\mathsf{S}(\mathbf{r}, \mathbf{r}')$ the time rate of change of the total entropy, Eq. (5.5), may be written as

$$\dot{S} = \frac{1}{T_0}\int\int \mathbf{a}(\mathbf{r}, t)\cdot \mathsf{S}(\mathbf{r}, \mathbf{r}')\cdot \mathbf{a}(\mathbf{r}', t)\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}'. \tag{5.6}$$

On the other hand, it follows from the standard expression for the entropy

$$S = S_0 - \tfrac{1}{2}k_B \int\int \mathbf{a}(\mathbf{r}, t)\cdot \mathrm{E}(\mathbf{r}, \mathbf{r}')\cdot \mathbf{a}(\mathbf{r}', t)\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}' \tag{5.7}$$

and Eq. (5.2) that

$$\dot{S} = \tfrac{1}{2}k_B \iiint \{\mathbf{a}(\mathbf{r},t)\cdot[-\mathrm{A}(\mathbf{r},\mathbf{r}'')\cdot\mathrm{E}(\mathbf{r}'',\mathbf{r}')+\mathrm{E}(\mathbf{r},\mathbf{r}'')\cdot\mathrm{A}(\mathbf{r}'',\mathbf{r}')]\cdot\mathbf{a}(\mathbf{r}',t)$$

$$+\mathbf{a}(\mathbf{r},t)\cdot[\mathrm{S}(\mathbf{r},\mathbf{r}'')\cdot\mathrm{E}(\mathbf{r}'',\mathbf{r}')+\mathrm{E}(\mathbf{r},\mathbf{r}'')\cdot\mathrm{S}(\mathbf{r}'',\mathbf{r}')]$$

$$\cdot\,\mathbf{a}(\mathbf{r}',t)\}\,d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'' \tag{5.8}$$

which by comparison with Eq. (5.6) yields

$$\mathrm{E}(\mathbf{r},\mathbf{r}') = \frac{1}{k_B T_0}\,\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}'). \tag{5.9}$$

In hydrodynamic fluctuation theory a fluctuating force is added to the right-hand side of Eq. (5.2) which transforms the set of hydrodynamic equations into a set of stochastic equations of the Langevin form,

$$\frac{\partial \mathbf{a}(\mathbf{r},t)}{\partial t} = -\int [\mathrm{A}(\mathbf{r},\mathbf{r}')+\mathrm{S}(\mathbf{r},\mathbf{r}')]\cdot\mathbf{a}(\mathbf{r}',t)\,d\mathbf{r}'+\mathbf{F}(\mathbf{r},t). \tag{5.10}$$

The properties of the random " forces " for the binary system may be established in an identical fashion as that employed by Fox and Uhlenbeck for the one component case. One finds that the random forces have mean zero and correlation functions

$$\langle\mathbf{F}(\mathbf{r},t)\mathbf{F}(\mathbf{r}',t')\rangle = \delta(t-t')\int\{[\mathrm{A}(\mathbf{r},\mathbf{r}'')+\mathrm{S}(\mathbf{r},\mathbf{r}'')]\cdot\mathrm{E}^{-1}(\mathbf{r}'',\mathbf{r}')$$

$$+\mathrm{E}^{-1}(\mathbf{r},\mathbf{r}'')\cdot[\tilde{\mathrm{A}}(\mathbf{r}'',\mathbf{r}')+\tilde{\mathrm{S}}(\mathbf{r}'',\mathbf{r}')]\}\,d\mathbf{r}'' \tag{5.11}$$

where $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{S}}$ denote the transpose of A and S respectively. From Eq. (5.9) and the symmetry properties of A and S one finds

$$\langle\mathbf{F}(\mathbf{r},t)\mathbf{F}(\mathbf{r}',t')\rangle = 2k_0T_0\mathrm{S}(\mathbf{r},\mathbf{r}')\,\delta(t-t') \tag{5.12}$$

which is the same form as obtained for the one component case.(10)

If we define

$$F_1(\mathbf{r},t) = \left[\rho_0\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right]^{1/2}\nabla\cdot\tilde{\mathbf{f}}, \quad \text{and} \quad F_2(\mathbf{r},t) = \beta_{s,c}^{-1/2}\nabla\cdot\tilde{\mathbf{h}}$$

$$F_3(\mathbf{r},t) = (\rho_0T_0C_{p,c})^{-1/2}\nabla\cdot\tilde{\mathbf{g}}, \quad \text{and} \quad F_\alpha(\mathbf{r},t) = \rho_0^{-1/2}(\nabla\cdot\tilde{\mathrm{S}})_\alpha \tag{5.13}$$

we can rewrite the linearized hydrodynamic equations corresponding to Eq. (5.10) as

$$\frac{\partial c}{\partial t} = D\left[\nabla^2 c + \frac{k_T}{T_0}\nabla^2\phi + \mathscr{P}\nabla^2 p\right] + \nabla\cdot\tilde{\mathbf{f}} \tag{5.14}$$

$$\begin{aligned}\beta_{s,c}\frac{\partial p}{\partial t} + \nabla\cdot\mathbf{u} = {}& \rho_0 D\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P}\nabla^2 c + \left[\frac{\rho_0 D k_T}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P} + \alpha_T\chi\right]\nabla^2\phi \\ & + T_0\left[\frac{\rho_0 D\mathscr{P}^2}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T} + \frac{\alpha_T{}^2\chi}{\rho_0 C_{p,c}}\right]\nabla^2 p + \nabla\cdot\tilde{\mathbf{h}}\end{aligned} \tag{5.15}$$

$$\begin{aligned}\rho_0 C_{p,c}\frac{\partial\phi}{\partial t} = {}& \rho_0 D k_T\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\nabla^2 c + \left[\frac{\rho_0 D k_T{}^2}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T} + \rho_0 C_{p,c}\chi\right]\nabla^2\phi \\ & + \left[\rho_0 D k_T\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P} + T_0\alpha_T\chi\right]\nabla^2 p + \nabla\cdot\tilde{\mathbf{g}}\end{aligned} \tag{5.16}$$

$$\rho_0\frac{\partial\mathbf{u}}{\partial t} + \nabla p = \left(\eta_v + \frac{\eta_s}{3}\right)\nabla(\nabla\cdot\mathbf{u}) + \eta_s\nabla^2\mathbf{u} + \nabla\cdot\tilde{\mathbf{S}} \tag{5.17}$$

The correlation of the fluctuating terms of these equations may be readily obtained from Eqs. (5.4), (5.12) and (5.13)

$$\begin{aligned}
\langle\tilde{\mathbf{f}}(\mathbf{r},t)\tilde{\mathbf{f}}(\mathbf{r}',t')\rangle &= 2k_B T_0\frac{D}{\rho_0(\partial\mu/\partial c)_{p,T}}\,\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\,\delta(t-t') \\
\langle\tilde{\mathbf{h}}(\mathbf{r},t)\tilde{\mathbf{h}}(\mathbf{r}',t')\rangle &= 2k_B T_0{}^2\left[\frac{\rho_0 D\mathscr{P}^2}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T} + \frac{\alpha_T{}^2\chi}{\rho_0 C_{p,c}}\right]\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \\
\langle\tilde{\mathbf{g}}(\mathbf{r},t)\tilde{\mathbf{g}}(\mathbf{r}',t')\rangle &= 2k_B T_0{}^2\left[\frac{\rho_0 D k_T{}^2}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T} + \rho_0 C_{p,c}\chi\right]\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \\
\langle\tilde{\mathbf{f}}(\mathbf{r},t)\tilde{\mathbf{h}}(\mathbf{r}',t')\rangle &= 2k_B T_0 D\mathscr{P}\,\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \qquad (5.18) \\
\langle\tilde{\mathbf{f}}(\mathbf{r},t)\tilde{\mathbf{g}}(r',t')\rangle &= 2k_B T_0 D k_T\,\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \\
\langle\tilde{\mathbf{h}}(\mathbf{r},t)\tilde{\mathbf{g}}(r',t')\rangle &= 2k_B T_0{}^2\left[\frac{\rho_0 D k_T}{T_0}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\mathscr{P} + \alpha_T\chi\right]\mathrm{I}\,\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')
\end{aligned}$$

and,

$$\begin{aligned}\langle\tilde{S}_{\alpha\beta}(\mathbf{r},t)\tilde{S}_{\mu\nu}(\mathbf{r}',t')\rangle = {}& 2k_B T_0[\eta_s(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) + (\eta_v - \tfrac{2}{3}\eta_s)\delta_{\alpha\beta}\delta_{\mu\nu}] \\ & \cdot\delta(\mathbf{r}-\mathbf{r}')\delta(t-t').\end{aligned} \tag{5.19}$$

The three fluctuating " forces " $\tilde{\mathbf{f}}(\mathbf{r}, t)$, $\tilde{\mathbf{h}}(\mathbf{r}, t)$ and $\tilde{\mathbf{g}}(\mathbf{r}, t)$ are not independent. It may be seen from the above correlation functions, Eqs. (5.18), that

$$\tilde{\mathbf{h}}(\mathbf{r}, t) = \frac{\alpha_T}{\rho_0 C_{p,c}}\tilde{\mathbf{g}}(\mathbf{r}, t) - \frac{1}{\rho_0}\left(\frac{\partial \rho}{\partial c}\right)_{p,T}\tilde{\mathbf{f}}(\mathbf{r}, t). \tag{5.20}$$

Furthermore, the continuity equation, Eq. (2.1)

$$\frac{\partial \rho}{\partial t} + \rho_0 \nabla \cdot \mathbf{u} = 0$$

may easily be shown to have no fluctuation part as is the case in one component systems,(10) simply by expressing the density ρ in terms of our variables c, p and ϕ and using Eqs. (5.13–5.15) and (5.20). Finally, we note that the fluctuating stress tensor $\tilde{S}_{\alpha\beta}$ is not correlated with $\tilde{\mathbf{f}}$, $\tilde{\mathbf{h}}$, or $\tilde{\mathbf{g}}$.

Appendix A

Previous results for the correlation functions of hydrodynamic variables of one component systems have either not presented the " non-Lorentzian " contributions to the light spectrum(14,15,16) or given a non-systematic procedure of obtaining them.(17) Here the complete explicit forms of these correlations to first order in the small parameters $\chi k/C_0 = \lambda k/\rho_0 C_p C_0$ and

$$\frac{\Gamma k}{C_0} = \frac{1/2[b + a(1 - 1/\gamma)]k}{C_0}$$

have been obtained from the linearized hydrodynamic equations by the consistent approximation outlined in Sec. 2. For the variables ρ and T the results are

$$\frac{\langle \rho(\mathbf{k}, t)\rho(-\mathbf{k}, 0)\rangle}{\langle |\rho(\mathbf{k})|^2\rangle} = \left(1 - \frac{1}{\gamma}\right)\exp\left(-\frac{\lambda k^2}{\rho_0 C_p}t\right) + \frac{1}{\gamma}e^{-\Gamma k^2 t}\cos C_0 kt + \frac{1}{\gamma}\frac{(3\Gamma - b)k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt \tag{A.1}$$

$$\frac{\langle T(\mathbf{k}, t)T(-\mathbf{k}, 0)\rangle}{\langle |T(\mathbf{k})|^2\rangle} = \frac{1}{\gamma}\exp\left(-\frac{\lambda k^2}{\rho_0 C_p}t\right) + \left(1 - \frac{1}{\gamma}\right)e^{-\Gamma k^2 t}\cos C_0 kt + \left(1 - \frac{1}{\gamma}\right)\left[\Gamma - a\left(1 + \frac{1}{\gamma}\right)\right]\frac{k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt \tag{A.2}$$

$$\frac{\langle \rho(\mathbf{k},t)T(-\mathbf{k},0)\rangle}{\langle |T(\mathbf{k})|^2\rangle} = \frac{\rho_0{}^3\beta_T C_v}{T_0}\frac{\langle T(\mathbf{k},t)\rho(-\mathbf{k},0)\rangle}{\langle |\rho(\mathbf{k})|^2\rangle}$$

$$= -\frac{\rho_0\alpha_T}{\gamma}\left[\exp\left(-\frac{\lambda k^2}{\rho_0 C_p}t\right) - e^{-\Gamma k^2 t}\cos C_0 kt \right.$$

$$\left. -\left(\Gamma - \frac{a}{\gamma}\right)\frac{k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt\right]. \qquad \text{(A.3)}$$

When the linearized hydrodynamic equations are written in terms of s and p one obtains

$$\frac{\langle s(\mathbf{k},t)s(-\mathbf{k},0)\rangle}{\langle |s(\mathbf{k})|^2\rangle} = \exp\left(-\frac{\lambda k^2}{\rho_0 C_p}t\right) \qquad \text{(A.4)}$$

$$\frac{\langle p(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle |p(\mathbf{k})|^2\rangle} = e^{-\Gamma k^2 t}\cos C_0 kt + \frac{(b-\Gamma)k}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt \qquad \text{(A.5)}$$

$$\frac{\langle s(\mathbf{k},t)p(-\mathbf{k},0)\rangle}{\langle |p(\mathbf{k})|^2\rangle} = \frac{\alpha_T{}^2}{\rho_0{}^2(\gamma-1)}\frac{\langle p(\mathbf{k},t)s(-\mathbf{k},0)\rangle}{\langle |s(\mathbf{k})|^2\rangle}$$

$$= -\frac{\alpha_T}{\rho_0\gamma}\frac{ak}{C_0}e^{-\Gamma k^2 t}\sin C_0 kt. \qquad \text{(A.6)}$$

The above results may also be obtained from (A.1–A.3) by expressing ρ and T in terms of s and p. From Eqs. (A.4–A.6) it is seen that the central Rayleigh peak will be an unmodified Lorentzian line due to the entropy–entropy correlation function, whereas the Brillouin doublets will be Lorentzian lines modified by " non-Lorentzian " contributions from the pressure–pressure and pressure–entropy correlations.

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