

# Spectral Analysis of the Light Scattered from a Chemically Relaxing Fluid: A Ternary Mixture

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*Received 28th October, 1974*

The spectral distribution of light scattered by a ternary fluid mixture containing two chemically reactive species and one nonreactive species is considered and a normal mode analysis is carried out for a range of  $k$ -values for which the pressure fluctuations are decoupled from those in entropy and concentration. The expressions obtained for both the lorentzian and non-lorentzian contributions to the Brillouin lines are straightforward extensions of those obtained for the binary reactive mixture. The damping and strength factors of the three lorentzian contributions to the Rayleigh line are rather complicated functions of the transport coefficients and chemical relaxation time. As illustrative examples the situations where (a) the nonreactive species or (b) the two reactive species are present in very low concentration are considered in some detail.

In recent years there has been substantial activity related to the use of light scattering spectroscopy for studying multicomponent fluid systems. Among other things, the possibility of determining chemical relaxation times has attracted considerable attention, both experimentally<sup>1-4</sup> as well as theoretically.<sup>5-11</sup>

General procedures for the theoretical analysis of light scattering spectra of multicomponent fluids have been discussed by Jordan and Jordan,<sup>12</sup> Blum<sup>13</sup> and by the present authors.<sup>14</sup> We have applied our method to the analysis of light scattered from a binary chemically relaxing fluid mixture<sup>15</sup> (that paper will subsequently be referred to as I) and a ternary nonreactive mixture<sup>16</sup> (that paper will subsequently be referred to as II). In this paper we consider the light scattering spectrum of a ternary mixture consisting of two reactive species and a third nonreactive species† (hereafter referred to as solvent), using the techniques developed in ref. (14) and drawing heavily upon the results obtained in I and II.

Our principal concern shall be the analysis of the Rayleigh line, since as will be shown, the expressions obtained for both the lorentzian and non-lorentzian contributions to the Brillouin lines are straightforward extensions of those obtained for the binary reactive mixture. Our attention will thus be directed to a discussion of the real eigenvalues and corresponding eigenvectors of the hydrodynamic matrix. Rather than utilize the general expressions which result for these eigenvalues we consider, in

† The light scattering spectrum for a binary mixture with internal molecular relaxation, a system bearing a formal similarity to the situation treated in this paper, has been studied by Kapral and Desai.<sup>17</sup>

some detail, two limiting cases which allow one to obtain simple and transparent expressions for the light scattering spectrum. These special cases occur when: (a) the nonreactive species is present in very low concentration and (b) the reactive species are present in low concentration.

### SPECTRUM OF SCATTERED LIGHT

The reader is referred to previous papers<sup>14</sup> for the development of the argument, which allows the expression for the spectral distribution of the light scattered by a multicomponent fluid to be given as

$$I(k, \omega) = C \sum_{l,m} \left( \frac{\partial \epsilon}{\partial B_l} \right) \left( \frac{\partial \epsilon}{\partial B_m} \right) \frac{1}{\pi} \operatorname{Re} \sum_f \frac{V_{lf} V_{mf}}{\lambda_f + i\omega}. \quad (1)$$

Here  $k$  is the magnitude of the scattering vector,  $\omega$  is the shift in frequency of the scattered light and  $C$  contains a number of experimental parameters and physical constants. The quantities  $(\partial \epsilon / \partial B_l)$  are the derivatives of the optical dielectric constant appropriate to the fluctuations  $\beta_l$ , the  $k$ th spatial fourier components of which are statistically independent and normalized (i.e., they satisfy the relation  $\langle \beta_l(\mathbf{k}) \beta_m^*(\mathbf{k}) \rangle = \delta_{lm}$ ). The fluctuations in the optical dielectric constant are determined by the fluctuations in the thermodynamic state variables and thus the summation over  $l$  and  $m$  in eqn (1) extends over only the even variables of the set  $\{\beta_l\}$  since these represent the fluctuations in the thermodynamic variables of the system. The  $\lambda_f$  and the  $V_{lf}$  represent the eigenvalues and eigenvector elements, respectively, of the hydrodynamic matrix  $\mathbf{K}(k)$  which results upon expressing the spatially fourier transformed set of hydrodynamic equations in terms of the variables  $\beta_l(\mathbf{k}, t)$ .

### THE HYDRODYNAMIC MATRIX

The derivation of the hydrodynamic matrix proceeds along the same lines as in I and II. In order to display the link between the present paper and I and II as clearly as possible it is convenient to label the reactive species 1 and 3, i.e.,  $1 \rightleftharpoons 3$  and the solvent as 2. As in II we use the mass fractions of species 1 and 2 as the independent concentration variables. The hydrodynamic equations can be readily obtained using the methods of irreversible thermodynamics<sup>18</sup> and in linearized form can be written as

$$\frac{\partial \rho}{\partial t} = -\rho_0 \operatorname{div} \mathbf{v} \quad (2)$$

$$\rho_0 \frac{\partial \operatorname{div} \mathbf{v}}{\partial t} = -\nabla^2 p + \left(\frac{4}{3}\eta + \zeta\right) \nabla^2 \operatorname{div} \mathbf{v} \quad (3)$$

$$\rho_0 \frac{\partial c_1}{\partial t} = -\operatorname{div} \mathbf{J}_1 - J \quad (4)$$

$$\rho_0 \frac{\partial c_2}{\partial t} = -\operatorname{div} \mathbf{J}_2 \quad (5)$$

$$\rho_0 T_0 \frac{\partial s}{\partial t} = -\operatorname{div} \mathbf{J}_{q,\text{red}} - T_0 \sum_{i=1,2} \left( \frac{\partial s}{\partial c_i} \right)_{pTc_j \neq i} \operatorname{div} \mathbf{J}_i + J A. \quad (6)$$

Here  $\mathbf{J}_1$  and  $\mathbf{J}_2$  are the diffusion flows of components 1 and 2 respectively and  $\mathbf{J}_{q,\text{red}}$  is the reduced heat flow. These flows are given by the same expressions as in II (see eqn II(6) and II(7)) and in general the thermodynamic variables and transport coefficients appearing in eqn (2) — (6) have the same meaning as in II. Due to the

presence of the chemical reaction extra terms appear in the equations for  $c_1$  and  $s$ . The affinity,  $A$ , of the chemical reaction is

$$A = \mu_1 - \mu_3 = \hat{\mu}_1 \quad (7)$$

and  $J$  is the rate of the chemical reaction. Within the framework of irreversible thermodynamics one obtains for  $J$  the following linear phenomenological equation

$$J = \frac{\rho_0}{\tau_{Tp}} \left[ \delta c_1 - \left( \frac{\partial c_1}{\partial c_2} \right)_{pTA} \delta c_2 - \left( \frac{\partial c_1}{\partial T} \right)_{pc_2A} \delta T - \left( \frac{\partial c_1}{\partial p} \right)_{Tc_1A} \delta p \right] \quad (8)$$

where  $\tau_{Tp}$  is the chemical relaxation time at constant temperature, pressure and concentration of the solvent. In the following we will omit the subscripts  $T$  and  $p$  of  $\tau_{Tp}$  and unless stated otherwise  $\tau$  means  $\tau_{Tp}$ .

The procedure for the normal mode analysis, alluded to above, requires that the hydrodynamic equations be expressed in terms of normalized statistically independent fluctuations,  $\beta_i(\mathbf{k}, t)$ , with the normalized pressure fluctuation as one of that set. As in II we choose  $\delta s_{\text{red}}$ ,  $\delta c_{1,\text{red}}$ ,  $\delta c_2$ ,  $\delta p$  and  $\text{div } \mathbf{v}$  as the statistically independent set of fluctuations, where

$$\delta s_{\text{red}} = \delta s - \sum_{i=1,2} \left( \frac{\partial s}{\partial c_i} \right)_{pTc_{j \neq i}} \delta c_i \quad (9)$$

$$\delta c_{1,\text{red}} = \delta c_1 - \left( \frac{\partial c_1}{\partial c_2} \right)_{pT\hat{\mu}_1} \delta c_2. \quad (10)$$

The utility of the reduced variables may be appreciated by considering, for example, the expression for  $J$  in terms of these variables. One easily finds that

$$J = \frac{\rho_0}{\tau_{Tp}} \left[ \delta c_{1,\text{red}} - \left( \frac{\partial c_1}{\partial T} \right)_{pc_2A} \delta s_{\text{red}} - \left\{ \left( \frac{\partial c_1}{\partial T} \right)_{pc_2A} \frac{\alpha_c T}{\rho C_{pc}} + \left( \frac{\partial c_1}{\partial p} \right)_{Tc_2A} \right\} \delta p \right] \quad (11)$$

where  $\alpha_c$  is the thermal expansion coefficient at constant concentration and  $C_{pc}$  is the specific heat at constant pressure and concentration. The fact that as far as concentration variables are concerned the chemical reaction rate only depends upon  $\delta c_{1,\text{red}}$  will turn out to be a valuable feature in the analysis of the light scattering spectrum.

Except for the formal replacement of  $C_p$  by  $C_{pc}$  and  $\chi_s$  by  $\chi_{sc}$ , the normalization factors of the statistically independent variables are the same as in II (see II eqn (11)).

On spatially fourier transforming the hydrodynamic equations and expressing these equations in terms of the normalized statistically independent fluctuations  $\beta_i(\mathbf{k}, t)$  one obtains for the hydrodynamic equations

$$\frac{\partial \beta(\mathbf{k}, t)}{\partial t} = -\mathbf{K}(\mathbf{k}) \beta(\mathbf{k}, t). \quad (12)$$

From the Onsager symmetry relations it follows that  $\mathbf{K}(\mathbf{k})$  has the structure displayed in eqn (13)

$$\mathbf{K} = \left[ \begin{array}{ccc|ccc} & & & K_{14} & 0 & \\ & & & K_{24} & 0 & \\ & & & K_{34} & 0 & \\ \hline K_{14} & K_{24} & K_{34} & & & \\ 0 & 0 & 0 & & \mathbf{K}^{\text{II}} & \end{array} \right]. \quad (13)$$

The matrix  $\mathbf{K}^I$  in eqn (13) is a  $3 \times 3$  symmetric matrix that can be written as follows

$$\mathbf{K}^I = \mathbf{K}_t^I + \mathbf{K}_r^I \quad (14)$$

where  $\mathbf{K}_t^I$  and  $\mathbf{K}_r^I$  contain contributions arising from transport processes and chemical reactions respectively. Here  $\mathbf{K}_t^I$  has the same form as the  $\mathbf{K}^I$  matrix for ternary non-reactive mixture (see II eqn (14)) and the elements of  $\mathbf{K}_r^I$  correspond to the terms obtained for the binary reactive mixture (see I eqn (2.12)).

$$\mathbf{K}_r^I = \begin{bmatrix} r_T \tau^{-1} & -r_T^{\frac{1}{2}} \tau^{-1} & 0 \\ -r_T^{\frac{1}{2}} \tau^{-1} & \tau^{-1} & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (15)$$

where  $r_T$  is the thermal relaxation strength. The fact that in  $\mathbf{K}^I$  the terms related to the chemical relaxation process only occur in the upper left  $2 \times 2$  block is due to the choice of variables.

The matrix  $\mathbf{K}^{II}$ , a  $2 \times 2$  antisymmetric matrix, can also be written as a sum of transport terms ( $\mathbf{K}_t^{II}$ ) and chemical reaction contributions ( $\mathbf{K}_r^{II}$ ). After the (purely formal) substitution of  $C_p$  by  $C_{pc}$ ,  $\alpha$  by  $\alpha_c$  and  $c_0 = (\rho_0 \chi_s)^{-\frac{1}{2}}$  by  $c_\infty = (\rho_0 \chi_{sc})^{-\frac{1}{2}}$ ,  $\mathbf{K}_t^{II}$  has the same form as the  $\mathbf{K}^{II}$  matrix for the ternary nonreactive mixture (see II, eqn (15)). The chemical reaction contribution is the same as for the binary reactive mixture.

$$\mathbf{K}_r^{II} = \begin{bmatrix} r_M \frac{C_{pA}}{C_{pc}} \tau^{-1} & 0 \\ 0 & 0 \end{bmatrix} \quad (16)$$

where  $r_M$  is the mechanical relaxation strength and  $C_{pA}$  is the specific heat at constant pressure and affinity.

Finally the remaining elements of  $\mathbf{K}$ ,  $K_{i4}$  ( $i = 1, 2, 3$ ) can be written as

$$K_{i4} = K_{i4,t} + K_{i4,r} \quad (i = 1, 2, 3). \quad (17)$$

The transport terms  $K_{i4,t}$  are, again with the replacement of  $C_p$  by  $C_{pc}$ ,  $\alpha$  by  $\alpha_c$  and  $\chi_s$  by  $\chi_{sc}$ , the same as for the ternary nonreactive mixture. The chemical reaction contributions  $K_{14,r}$  and  $K_{24,r}$  are the same as the chemical reaction parts of the element  $K_{13}$  and  $K_{23}$  in the  $\mathbf{K}$  matrix for the binary reactive mixture and  $K_{34,r} = 0$ .

The reason for splitting the hydrodynamic matrix into the parts  $\mathbf{K}^I$  and  $\mathbf{K}^{II}$  is that, as has been shown by the authors,<sup>14</sup> when the dissipative terms in the hydrodynamic matrix are much smaller than the frequency of the sound wave, then satisfactory approximations to the real and complex eigenvalues and the corresponding eigenvectors can be obtained from  $\mathbf{K}^I$  and  $\mathbf{K}^{II}$  respectively. In the calculations of the light scattering spectrum we shall assume that the above conditions, i.e.,

$$\tau^{-1}, D_{ij}k^2, D_i^T k^2, \frac{(4/3\eta + \zeta)}{\rho} k^2 \ll kc_\infty,$$

are fulfilled.

#### THE BRILLOUIN PEAKS

The Brillouin lines consist of a lorentzian and a nonlorentzian part centred on  $\omega = \pm kc_\infty$  (Stokes and anti-Stokes lines).

$$\begin{aligned} I_{\text{Stokes}}^B(k, \omega) &= I_{\text{anti-Stokes}}^B(k, -\omega) \\ &= \frac{C}{\pi} \left\{ \frac{Z^B \Gamma}{\Gamma^2 + (\omega + kc_\infty)^2} + \frac{Y^B(\omega + kc_\infty)}{\Gamma^2 + (\omega + kc_\infty)^2} \right\}. \end{aligned} \quad (18)$$

Using the same procedures as were used in I and II one easily obtains expressions for the damping and strength factors. The damping factor can be written as the sum of a transport part ( $\Gamma_t$ ) and a chemical reaction part ( $\Gamma_r$ )

$$\Gamma = \Gamma_t + \Gamma_r. \quad (19)$$

Here  $\Gamma_t$  is given by the same expression as  $\Gamma$  for a ternary nonreactive mixture (see II eqn (27)) and  $\Gamma_r$  is the same as for a binary reactive mixture

$$\Gamma_r = \frac{1}{2} r_M \frac{C_{pA}}{C_{pc}} \tau^{-1}. \quad (20)$$

The strength factor of the lorentzian contribution,  $Z^B$ , is the same as in the case of the ternary nonreactive mixture

$$\begin{aligned} Z^B &= \frac{1}{2} \left( \frac{\partial \varepsilon}{\partial B_4} \right)^2 \\ &= \frac{1}{2} (k_B T V / \chi_{sc}) \left( \frac{\partial \varepsilon}{\partial p} \right)_{sc1c2}^2. \end{aligned} \quad (21)^*$$

The amplitude of the non-lorentzian part of the Brillouin lines,  $Y^B$ , is given by the same expression in terms of the elements of the  $\mathbf{K}$  matrix as for the ternary nonreactive mixture (see II, eqn (36)). Since these elements are a sum of a transport part and a chemical reaction part,  $Y^B$  can be written as a sum of the above mentioned parts. Thus

$$Y^B = Y_t^B + Y_r^B \quad (22)$$

where

$$Y_{t,r}^B = \sum_{j=1}^3 \left( \frac{\partial \varepsilon}{\partial B_j} \right) \left( \frac{\partial \varepsilon}{\partial B_4} \right) \frac{K_{j4t,r}}{2kc_\infty} - \left( \frac{\partial \varepsilon}{\partial B_4} \right)^2 \frac{(K_{44})_{t,r} - (K_{55})_{t,r}}{2kc_\infty}. \quad (23)$$

From the definition of the  $\beta$  variables it follows that

$$\begin{aligned} \frac{\partial \varepsilon}{\partial B_1} &= [k_B T^2 V / \rho C_{pc}]^{\frac{1}{2}} \left( \frac{\partial \varepsilon}{\partial T} \right)_{pc1c2} \\ \frac{\partial \varepsilon}{\partial B_2} &= [k_B T V / \rho \hat{\mu}_{11}]^{\frac{1}{2}} \left( \frac{\partial \varepsilon}{\partial c_1} \right)_{pTc_2} \\ \frac{\partial \varepsilon}{\partial B_3} &= \left[ k_B T V / \rho \left( \frac{\partial \hat{\mu}_2}{\partial c_2} \right)_{pT\hat{\mu}_1} \right]^{\frac{1}{2}} \left( \frac{\partial \varepsilon}{\partial c_2} \right)_{pT\hat{\mu}_1}. \end{aligned} \quad (24)$$

#### THE RAYLEIGH LINE

The Rayleigh line can be written, as in the case of the nonreactive ternary mixture, as a sum of three lorentzians.

$$I^R(k, \omega) = \frac{C}{\pi} \sum_{f=1}^3 Z_f \frac{\lambda_f}{\lambda_f^2 + \omega^2}. \quad (25)$$

Under the restrictions stated in section 3, i.e., that the dissipative terms in the hydrodynamic matrix are much smaller than the frequency of the sound wave, the real

\* In this paper, Boltzmann's constant is given the symbol  $k_B$  instead of the usual symbol  $k$ .

eigenvalues of the hydrodynamic matrix and the corresponding eigenvectors are, to good approximations, given by the eigenvalues and eigenvectors of  $\mathbf{K}^I$ , i.e.,

$$\lambda_f \simeq \lambda_f^I \quad (26)$$

$$Z_f \simeq \sum_{l,m=1}^3 \left( \frac{\partial \varepsilon}{\partial B_l} \right) \left( \frac{\partial \varepsilon}{\partial B_m} \right) V_{lf}^I V_{mf}^I \quad (27)$$

here  $\lambda_f^I$  and  $V_{lf}^I$  represent eigenvalue and eigenvector elements respectively of  $\mathbf{K}^I$ . Analytic expressions for these eigenvalues and eigenvector elements can be written out, however they are difficult to interpret.

Further, in the present case, because of the presence of chemical relaxation contributions, the term  $K_{12}(=K_{21})$  can not be taken as small and consequently the perturbation treatment carried out in II is no longer applicable. In view of this we consider, in some detail, two special cases for which one can obtain expressions for the Rayleigh peak which are amenable to interpretation.

#### A. DILUTE NONREACTIVE SPECIES

In II it has been argued that when  $c_2$  tends to zero  $D_2^T$  and  $D_{21}$  tend to zero proportionally to  $c_2$  and  $\hat{\mu}_{22}$  goes to infinity like  $c_2^{-1}$  whereas  $\hat{\mu}_{11}$  and  $\hat{\mu}_{12}$  remain finite. From the above dependencies it follows that in the limit where the nonreactive species becomes very dilute  $\mathbf{K}^I$  reduces to the following form.

$$\mathbf{K}^I = \begin{bmatrix} D_T k^2 + r_T \tau^{-1} & D_1^T \left[ \frac{\hat{\mu}_{11}}{C_{pc} T} \right]^{\frac{1}{2}} k^2 - r_T^{\frac{1}{2}} \tau^{-1} & 0 \\ K_{12} & D_{11} k^2 + \tau^{-1} & 0 \\ 0 & 0 & D_{22} k^2 \end{bmatrix}. \quad (28)$$

In this limit the lower right  $1 \times 1$  partition characterizes a "nonreactive mode" with damping factor  $D_{22} k^2$ . Further, the upper left  $2 \times 2$  block of this  $\mathbf{K}^I$  matrix has the same form as the  $\mathbf{K}^I$  matrix for the binary reactive mixture and thus the eigenvalues and corresponding eigenvectors of that block of the  $\mathbf{K}^I$  matrix will be those encountered in the binary reactive mixture. It should be pointed out that the corresponding normal modes are a linear combination of the variables  $\delta s_{\text{red}}$  and  $\delta c_{1,\text{red}}$  and not, as in a binary reactive mixture, a combination of  $\delta s_{\text{red}}$  and  $\delta c_1$ .

The spectral analysis is most easily accomplished if conditions can be found where the strength factors are such that one or other of these contributing modes dominates the Rayleigh line. The strength factors given in eqn (27) are sensitive to the derivatives  $(\partial \varepsilon / \partial B_i)$ , ( $i = 1, 2, 3$ ) which, in turn, are functions of the dielectric derivatives  $\partial \varepsilon / \partial c_i$  and  $\partial \varepsilon / \partial T$  and, through the derivatives  $(\partial \hat{\mu}_i / \partial c_j)$ , of the concentration. For example

$$Z_3 \simeq \left( \frac{\partial \varepsilon}{\partial B_3} \right)^2 = \left[ \frac{k_B T V}{\rho (\partial \hat{\mu}_2 / \partial c_2)_{pT\hat{\mu}_1}} \right] \left( \frac{\partial \varepsilon}{\partial c_2} \right)_{pT\hat{\mu}_1}^2$$

and since  $\hat{\mu}_{22} \rightarrow \infty$  as  $c_2 \rightarrow 0$  it is clear that  $Z_3$  may be small even though  $(\partial \varepsilon / \partial c_2)_{pT\hat{\mu}_1}$  is relatively large. Taking into account the preceding points and introducing the ratios:

$$W = \left[ \frac{TC_{pc}}{\hat{\mu}_{11}} \right]^{\frac{1}{2}} \frac{(\partial \varepsilon / \partial c_1)_{pTc_2}}{T(\partial \varepsilon / \partial T)_{pc1c_2}}$$

and

$$H = \frac{(\partial \varepsilon / \partial c_2)_{pT\hat{\mu}_1}}{(\partial \varepsilon / \partial c_1)_{pTc_2}}$$

with  $\rho \simeq 1 \text{ g cm}^{-3}$ ,  $T \simeq 300 \text{ K}$ ,  $\tau^{-1} \simeq 10^7 \text{ s}^{-1}$ , we can make the following observations.

The contribution of the entropy mode relative to that of the reactive species mode\* can be minimized by selecting systems for which  $W \simeq 10$  for then  $Z_1/Z_2 \simeq 10^\dagger$ . Further, the contribution of the nonreactive species mode can be minimized by requiring that  $H$  is of order unity and  $c_2 \simeq 5 \times 10^{-2}$  for then  $Z_1/Z_3 \simeq 10$ . If these conditions can be met the broad lorentzian line is essentially that due to the "chemical reaction mode". On the other hand, even though the nonreactive species is dilute, let us again say  $c_2 \simeq 5 \times 10^{-2}$ , its contribution may still dominate that arising from the reactive species. For example, leaving  $W$  unchanged and increasing  $H$ , say to  $H \simeq 10$ , we find  $Z_3/Z_1 \simeq 10$ , with the result that the dominant feature is a strong narrow peak due to the "nonreactive mode".

It is not feasible to assess all the possible combinations here although the foregoing should illustrate that such assessments might profitably be undertaken to establish the likelihood of obtaining the desired results experimentally.

#### B. THE REACTIVE SPECIES ARE DILUTE

We now consider the case when the reactive species are present in low concentration. In that case it appears to be most convenient to choose the mass fractions of the reactive species as the independent concentration variables. Hence we label the reactive species as 1 and 2, i.e.,  $1 \rightleftharpoons 2$  and the nonreactive species as 3. Starting from the appropriate phenomenological equations and using the fact that the reactive species are present in low concentration one easily obtains the following form for  $\mathbf{K}^1$ .

$$\mathbf{K}^1 = \begin{bmatrix} D_T k^2 & 0 & 0 \\ 0 & D_{11} k^2 + \left( \frac{\hat{\mu}_{11}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) \tau^{-1} & - \left( \frac{[\hat{\mu}_{11} \hat{\mu}_{22}]^{\frac{1}{2}}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) \tau^{-1} \\ 0 & - \left( \frac{[\hat{\mu}_{11} \hat{\mu}_{22}]^{\frac{1}{2}}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) \tau^{-1} & D_{22} k^2 + \left( \frac{\hat{\mu}_{22}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) \tau^{-1} \end{bmatrix}. \quad (29)$$

One can write analytic expressions for the roots and eigenvectors for the above  $\mathbf{K}^1$  matrix and from there on calculate the shape of the Rayleigh line. Rather than deal with these general expressions we consider the limit where  $\tau^{-1} \gg D_{11} k^2$ ,  $D_{22} k^2$  (but  $\tau^{-1} \ll k c_\infty$ , since otherwise the decoupling from the sound modes would no longer be valid). One of the roots of the above  $\mathbf{K}^1$  matrix is

$$\lambda_1 = D_T k^2. \quad (30a)$$

Under the above-mentioned assumption the remaining two roots are given, to good approximation, by

$$\lambda_2 = \frac{1}{\tau} + \left( \frac{D_{11} \hat{\mu}_{11} + D_{22} \hat{\mu}_{22}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) k^2 \quad (30b)$$

$$\lambda_3 = \left( \frac{D_{11} \hat{\mu}_{22} + D_{22} \hat{\mu}_{11}}{\hat{\mu}_{11} + \hat{\mu}_{22}} \right) k^2. \quad (30c)$$

\* As pointed out in I, one must use the notion of single chemical reaction mode with caution in the region of  $k \simeq k_{\text{res}}$ .

† If  $k < k_{\text{res}}$  the strength factor of the "chemical reaction mode" is  $Z_1$  but if  $k > k_{\text{res}}$  the strength factor of interest is  $Z_2$ .



To zero'th order (i.e., neglecting  $D_{11}k^2$  and  $D_{22}k^2$ ) the corresponding normal modes are

$$\begin{aligned}\gamma_1 &= \delta s_{\text{red}} \\ \gamma_2 &= [\hat{\mu}_{11} + \hat{\mu}_{22}]^{-\frac{1}{2}} [\hat{\mu}_{11} \delta c_1 - \hat{\mu}_{22} \delta c_2] \\ \gamma_3 &= \left[ \frac{\hat{\mu}_{11} + \hat{\mu}_{22}}{\hat{\mu}_{11} \hat{\mu}_{22}} \right]^{-\frac{1}{2}} [\delta c_1 + \delta c_2].\end{aligned}\quad (31)$$

The strength factors now follow immediately.

$$\begin{aligned}Z_1 &= \frac{k_B T^2 V}{\rho C_{pc}} \left( \frac{\partial \varepsilon}{\partial T} \right)_{pc_1 c_2}^2 \\ Z_2 &= \frac{k_B T V}{\rho (\hat{\mu}_{11} + \hat{\mu}_{22})} \left[ \left( \frac{\partial \varepsilon}{\partial c_1} \right)_{pTc_2} - \left( \frac{\partial \varepsilon}{\partial c_2} \right)_{pTc_1} \right]^2 \\ Z_3 &= \frac{k_B T V}{\rho (\hat{\mu}_{11} + \hat{\mu}_{22})} \left[ \left( \frac{\hat{\mu}_{22}}{\hat{\mu}_{11}} \right)^{\frac{1}{2}} \left( \frac{\partial \varepsilon}{\partial c_1} \right)_{pTc_2} + \left( \frac{\hat{\mu}_{11}}{\hat{\mu}_{22}} \right)^{\frac{1}{2}} \left( \frac{\partial \varepsilon}{\partial c_2} \right)_{pTc_1} \right]^2.\end{aligned}\quad (32)$$

A question that has been raised in the recent literature<sup>4</sup> is the relative magnitude of  $Z_2$  compared to  $Z_3$ . From eqn (32) it appears that the most important factor is the relative sign of  $(\partial \varepsilon / \partial c_1)_{pTc_2}$  and  $(\partial \varepsilon / \partial c_2)_{pTc_1}$ . If they both have the same sign, then most likely  $Z_3 > Z_2$ , but if they have different signs  $Z_3 < Z_2$ . Since in order to measure the chemical relaxation time it is obviously advantageous to have  $Z_2 > Z_3$ , one should select a solvent such that  $(\partial \varepsilon / \partial c_1)_{pTc_2}$  and  $(\partial \varepsilon / \partial c_2)_{pTc_1}$  have different signs. For example, by selecting a system for which

$$(\partial \varepsilon / \partial c_1)_{pTc_2} \simeq -(\partial \varepsilon / \partial c_2)_{pTc_1} \quad \text{and} \quad \hat{\mu}_{11} \simeq \hat{\mu}_{22}$$

it is clear that  $Z_2 \gg Z_3$ . In addition by choosing again  $W \simeq 10$  it follows that  $Z_2/Z_1 \simeq 100$ ; hence the Rayleigh peak is dominated by the lorentzian component due to the chemical reaction mode.

### CONCLUDING REMARKS

The spectral decomposition of the light scattered from a ternary fluid mixture undergoing chemical relaxation has been given in detail for two limiting cases. Although the expressions obtained would be less amenable to interpretation the required expression could be readily given for situations spanned by these limiting cases. The ease with which such analyses can be formulated, derives, in large measure, from the representation of the hydrodynamic equations in terms of statistically independent normalized variables (of which pressure is one) and an appropriate choice for the independent concentration variables. The possibility of extending these methods to the case of multicomponent fluids with several chemical relaxation processes should also be apparent.

This work has been supported by grants from The National Research Council of Canada and from The North Atlantic Treaty Organization.

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