

Spectral analysis of the light scattered from a chemically relaxing fluid: Binary mixture

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The spectral distribution of light scattered by a two-species chemically relaxing fluid 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. Under these conditions the damping of the propagating modes is a sum of a term due solely to chemical relaxation and terms due solely to transport, whereas the damping of the nonpropagating modes contains mixed terms. The intensity factors of the propagating modes are constants, whereas those of the nonpropagating modes exhibit a k dependence. This k dependence of the nonpropagating modes is of some significance for the analysis of the Rayleigh line.

I. INTRODUCTION

The possibility of probing relaxation phenomena with light scattering spectroscopy has been recognized for some time¹ and the development of laser light sources has made the accurate experimental determination of light scattering spectra a reality.² In particular, the determination of chemical relaxation times using light scattering spectroscopy has attracted attention. This possibility has been investigated experimentally³ and its macroscopic theoretical treatment has also received attention.⁴⁻⁸ It is instructive to review these theoretical developments.

Berne *et al.*⁴ calculated the spectral distribution of light scattered from a chemically reactive ternary mixture within the limitation that the fluctuations in the optical dielectric constant were due only to concentration fluctuations and with, moreover, neglect of the coupling of the concentration fluctuations to other thermodynamic variables in their calculation for the spectral densities of the concentration fluctuations. The pioneering work of Blum and Salsburg,⁵ on the multi-component, multireaction case, does not neglect, *a priori*, the dependence of the optical dielectric constant on any of the thermodynamic state variables and does carry out the development from a complete set of linearized hydrodynamic equations. These authors provide a normal-mode analysis using a perturbation treatment, the validity of which, in practice for liquids, is limited to scattering vectors of magnitude k for which the frequency of the sound modes is small compared to the inverse chemical relaxation time. Knirk and Salsburg⁶ removed this limitation but at the ex-

pense of neglect of all dissipative processes except chemical reactions. Schurr⁷ directed attention to a simpler system (four species, one reaction), for which he considered the case where the dependence of the optical dielectric constant on all thermodynamic variables except concentrations could be ignored. He then obtained, directly, an expression for the spectral distribution of scattered light, stopping short of a general normal-mode analysis. The reduction of his general expression, as carried out by Schurr for particular situations (defined by inequalities among the transport coefficients, the chemical reaction rate, and the shift in frequency of the scattered light), allows ready interpretation of the spectrum in the so-called "fast reaction" and "slow reaction" limits.

A scheme which, under certain conditions, allows a tractable normal-mode analysis for both nonreactive and reactive systems has been presented recently.⁸⁻¹⁰ The application¹¹ of this scheme to the analysis of the light scattering spectrum of a two-species chemically relaxing system is presented here and is, in fact, an extension, to the reactive case, of the sound-mode decoupling scheme developed by Mountain and Deutch¹² for the nonreactive binary-mixture case. Although it is a treatment of a far simpler system, the work presented here extends that of Blum, Salsburg, and Knirk by dealing with a range of k values for which the transport terms and the chemical relaxation terms are of the same order of magnitude. Furthermore, the easily interpreted expressions for the spectrum one so obtains cover the region between the slow-reaction and fast-reaction limiting cases discussed by Schurr.

II. CALCULATION OF THE SPECTRUM

A. Spectral distribution of scattered light

The spectral intensity distribution of the polarized component of light scattered from an isotropic system is proportional to $S_\epsilon(k, \omega)$, which is the spectral density of $\delta\epsilon(\vec{k}, t)$, the \vec{k} th spatial Fourier component of the fluctuation in the local optical dielectric constant. The optical dielectric constant can be considered to be a function of the thermodynamic state of the system and, consequently, one can write $S_\epsilon(k, \omega)$ in terms of the spectral densities of the fluctuations in any complete set of thermodynamic variables multiplied by the appropriate derivatives of the dielectric constant with respect to these variables. The required spectral densities can, on invoking the Wiener-Khinchin theorem, be obtained as the temporal Fourier transforms of the corresponding time correlation functions. These, in turn, can, on applying Onsager's assumption concerning the average regression of fluctuations, be obtained by solving the linearized hydrodynamic equations.

For the purpose of analysis the spectral densities so obtained are frequently expressed in terms of normal-mode contributions, even though this involves the calculation of the eigenvalues and eigenvectors of the hydrodynamic matrix. It has been shown⁹ that this task can be materially simplified by employing a set of statistically independent and normalized variables $\{\beta_i(\vec{k}, t)\}$, with a definite signature under time reversal, to represent the \vec{k} th spatial Fourier component of the fluctuations in the state variables. The linearized hydrodynamic equations in terms of the β variables are denoted by

$$\frac{\partial \underline{\beta}(\vec{k}, t)}{\partial t} = -\underline{K}(\vec{k})\underline{\beta}(\vec{k}, t), \quad (2.1)$$

where the hydrodynamic matrix \underline{K} has the symmetry

$$\underline{K}^T = \underline{E}\underline{K}\underline{E} \quad (2.2)$$

(\underline{E} is the signature matrix of the β variables). As a consequence the transformation matrices which

$$\frac{\partial s}{\partial t} - \left(\frac{\partial s}{\partial c}\right)_{p,T} \frac{\partial c}{\partial t} = \frac{\lambda}{\rho T} \nabla^2 T + D \frac{k_T}{T} \left(\frac{\partial A}{\partial c}\right)_{p,T} \left[\nabla^2 c + \frac{k_p}{p} \nabla^2 p \right] + \frac{(\partial h / \partial c)_{p,T}}{T} \frac{1}{\tau_{T,p}} \left[\delta c - \left(\frac{\partial c}{\partial T}\right)_{p,A} \delta T - \left(\frac{\partial c}{\partial p}\right)_{T,A} \delta p \right]. \quad (2.10)$$

The thermodynamic variables appearing in Eqs. (2.7)–(2.10) have the following meaning: ρ is the mass density, T is the temperature, p is the pressure, s is the specific entropy, h is the

diagonalize \underline{K} ,

$$\underline{V}^{-1} \underline{K} \underline{V} = \underline{\Lambda}, \quad (2.3)$$

have the symmetry property

$$\underline{V}^{-1} = \underline{V}^T \underline{E}. \quad (2.4)$$

The spectral densities of the even β variables, which in this case describe the fluctuations in the thermodynamic variables, can now be written down as

$$S_{\beta_i \beta_m}(k, \omega) = \frac{1}{\pi} \text{Re} \sum_f \frac{V_{if} V_{mf}}{\lambda_f + i\omega}, \quad (2.5)$$

where the summation f runs over all eigenvalues of the hydrodynamic matrix. With this normal-mode representation of the spectral densities one can express the spectral distribution of the scattered light as

$$I(k, \omega) = C \sum_{i,m} \left(\frac{\partial \epsilon}{\partial B_i}\right) \left(\frac{\partial \epsilon}{\partial B_m}\right) \frac{1}{\pi} \text{Re} \sum_f \frac{V_{if} V_{mf}}{\lambda_f + i\omega}, \quad (2.6)$$

where C contains a number of experimental parameters and physical constants and the quantities $\partial \epsilon / \partial B_i$ are the derivatives of the optical dielectric constant appropriate to the fluctuations β_i .

B. Eigenvalues and eigenvectors of the hydrodynamic matrix

The hydrodynamic equations for a two-species chemically relaxing fluid can readily be obtained using the methods of irreversible thermodynamics (see, e.g., Refs. 13 and 14), and in linearized form can be written as

$$\frac{\partial \rho}{\partial t} + \rho \text{div } \vec{v} = 0, \quad (2.7)$$

$$\rho \frac{\partial \text{div } \vec{v}}{\partial t} = -\nabla^2 p + \left(\frac{4}{3}\eta + \zeta\right) \nabla^2 \text{div } \vec{v}, \quad (2.8)$$

$$\frac{\partial c}{\partial t} = D \left[\nabla^2 c + \frac{k_T}{T} \nabla^2 T + \frac{k_p}{p} \nabla^2 p \right] - \frac{1}{\tau_{T,p}} \left[\delta c - \left(\frac{\partial c}{\partial T}\right)_{p,A} \delta T - \left(\frac{\partial c}{\partial p}\right)_{T,A} \delta p \right], \quad (2.9)$$

specific enthalpy, and c denotes the mass fraction of the species with the highest partial specific enthalpy. We will refer to this species as species 1 and to the other species as species 2.

The affinity A is here defined as $A = \mu_1 - \mu_2$. Further k_p/p is a purely thermodynamic quantity defined by

$$\frac{k_p}{p} = \frac{(\partial A / \partial p)_{T,c}}{(\partial A / \partial c)_{p,T}}$$

The transport coefficients which appear in Eqs. (2.7)–(2.10) are the shear viscosity η , the bulk viscosity ζ , the diffusion coefficient D , the thermal-diffusion coefficient $k_T D$, and the heat-conductivity coefficient λ . Finally $\tau_{T,p}$ is the chemical relaxation time at constant temperature and pressure. Since we consider an isotropic scattering system only the divergence of the velocity field \vec{v} is coupled to the thermodynamic variables and the Eqs. (2.7)–(2.10) are a complete set for our purposes.

As pointed out in Sec. II A it is advantageous to write the hydrodynamic equations in terms of a set of statistically independent and normalized variables; i.e., one requires a set of variables β defined by $\langle \beta_i(\vec{k}) \beta_j(\vec{k})^* \rangle = \delta_{ij}$. For the case under investigation, δs_{red} , δc , δp , and $\text{div } \vec{v}$, where $\delta s_{\text{red}} = \delta s - (\partial s / \partial c)_{p,T} \delta c$ are chosen as the statis-

tically independent fluctuations. Then in normalized form the required set of variables β is given by

$$\begin{aligned} \beta_1(\vec{k}, t) &= \left(\frac{\rho}{k_B V C_{p,c}} \right)^{1/2} \delta s_{\text{red}}(\vec{k}, t), \\ \beta_2(\vec{k}, t) &= \left(\frac{\rho(\partial A / \partial c)_{p,T}}{k_B V T} \right)^{1/2} \delta c(\vec{k}, t), \\ \beta_3(\vec{k}, t) &= \left(\frac{\chi_{s,c}}{k_B V T} \right)^{1/2} \delta p(\vec{k}, t), \\ \beta_4(\vec{k}, t) &= \left(\frac{\rho}{k_B V T k^2} \right)^{1/2} (\text{div } \vec{v})(\vec{k}, t). \end{aligned} \quad (2.11)$$

In Eq. (2.11) k_B is Boltzmann's constant, V is the volume in which the fluctuations are considered, $C_{p,c}$ is the specific heat at constant pressure and concentration, and $\chi_{s,c}$ is the adiabatic compressibility at constant concentration. Spatially Fourier transforming the hydrodynamic equations (2.7)–(2.10) and expressing these equations in terms of the β variables of Eq. (2.11) one obtains the hydrodynamic matrix $\underline{K}(k)$ given by Eq. (2.12):

$$\underline{K}(k) = \begin{bmatrix} D_T k^2 + r_T \tau_{T,p}^{-1} & k_T D \left(\frac{\partial A / \partial c}{T C_{p,c}} \right)^{1/2} k^2 - \tau_{T,p}^{-1} r_T^{1/2} & C_1 k^2 + C_2 \tau_{T,p}^{-1} & 0 \\ k_T D \left(\frac{\partial A / \partial c}{T C_{p,c}} \right)^{1/2} k^2 - \tau_{T,p}^{-1} r_T^{1/2} & D k^2 + \tau_{T,p}^{-1} & C_3 k^2 + C_4 \tau_{T,p}^{-1} & 0 \\ C_1 k^2 + C_2 \tau_{T,p}^{-1} & C_3 k^2 + C_4 \tau_{T,p}^{-1} & C_5 k^2 + r_M \frac{C_{p,A}}{C_{p,c}} \tau_{T,p}^{-1} & k c_\infty \\ 0 & 0 & -k c_\infty & C_6 k^2 \end{bmatrix} \quad (2.12)$$

In Eq. (2.12)

$$C_1 = \left(\frac{\rho T}{\chi_{s,c} C_{p,c}} \right)^{1/2} \left[D_T \frac{\alpha_c}{\rho} + D \frac{k_T}{T} \left(\frac{\partial v}{\partial c} \right)_{p,T} \right],$$

$$C_2 = \left(\frac{\rho}{T \chi_{s,c} C_{p,c}} \right)^{1/2} \left(\frac{\partial h}{\partial c} \right)_{p,T}$$

$$\times \left[\left(\frac{\partial c}{\partial T} \right)_{p,A} \frac{\alpha_c T}{\rho C_{p,c}} + \left(\frac{\partial c}{\partial p} \right)_{T,A} \right],$$

$$C_3 = \left(\frac{\rho(\partial A / \partial c)_{p,T}}{\chi_{s,c}} \right)^{1/2} \left[D \frac{k_p}{p} + k_T D \frac{\alpha_c}{\rho C_{p,c}} \right],$$

$$C_4 = - \left(\frac{\rho(\partial A / \partial c)_{p,T}}{\chi_{s,c}} \right)^{1/2} \left[\left(\frac{\partial c}{\partial T} \right)_{p,A} \frac{\alpha_c T}{\rho C_{p,c}} + \left(\frac{\partial c}{\partial p} \right)_{T,A} \right],$$

$$C_5 = D_T \left(\frac{C_{p,A}}{C_{p,c}} - 1 \right) + \frac{D c_\infty^2}{\rho^2} \left(\frac{\partial \rho}{\partial c} \right)_{p,T}$$

$$\times \left(\frac{\partial \rho / \partial c}{\partial A / \partial c} \right)_{p,T} + 2 \frac{k_T (\partial \rho / \partial T)_{p,c}}{C_{p,c}},$$

$$C_6 = \left(\frac{4}{3} \eta + \zeta / \rho \right),$$

$$D_T = \lambda / \rho C_{p,c}$$

(thermal diffusivity),

$$r_T = (C_{p,A} - C_{p,c}) / C_{p,c}$$

(thermal relaxation strength),

$$r_M = (\chi_{s,A} - \chi_{s,c}) / \chi_{s,c}$$

(mechanical relaxation strength),

$$c_\infty = (1 / \rho \chi_{s,c})^{1/2}$$

(high-frequency sound velocity),

$$\alpha_c = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{p,c}$$

(thermal expansion coefficient at constant composition). The subscript A indicates that a particular thermodynamic derivative is taken at constant affinity equal to zero.

It has been shown¹⁰ that, when the damping terms in the hydrodynamic matrix \underline{K} are much smaller than the frequency of the sound wave,

then satisfactory approximations to the eigenvalues and eigenvectors can be obtained by, in effect, partitioning \underline{K} .¹⁵ In the present case this procedure can be followed if k is restricted to a range of values such that

$$D_T k^2 \ll kc_\infty, \quad Dk^2 \ll kc_\infty, \quad \left(\frac{4}{3}\eta + \zeta\right)k^2/\rho \ll kc_\infty, \quad (2.13)$$

$$\tau_{T,p}^{-1} \ll kc_\infty. \quad (2.14)$$

The conditions of Eq. (2.13) require that k be smaller than some maximum value and can, of course, always be met for sufficiently small k . For liquid mixtures the magnitude of the transport coefficients is such that, even for the maximum scattering vectors encountered in light scattering experiments ($k^{\max} \simeq 2 \times 10^5 \text{ cm}^{-1}$) the conditions given in Eq. (2.13) are generally satisfied. The condition of Eq. (2.14), which of course is a reflection of the chemical relaxation process, requires, in contrast to Eq. (2.13), that k be larger than some minimum value which depends on $\tau_{T,p}$. In order that this minimum lies in the region of scattering vectors commonly realized in light scattering experiments the inverse of the chemical relaxation time should be 10^9 sec^{-1} or smaller.

In order to facilitate the discussion of the partitioning scheme referred to above we denote the upper left 2×2 block of the matrix \underline{K} by \underline{K}^I and the lower right 2×2 block by \underline{K}^{II} and write the diagonalizing matrices as

$$(\underline{V}^I)^{-1} \underline{K}^I \underline{V}^I = \Lambda^I \quad \text{and} \quad (\underline{V}^{II})^{-1} \underline{K}^{II} \underline{V}^{II} = \Lambda^{II}. \quad (2.15)$$

The eigenvalues of \underline{K}^I and \underline{K}^{II} are satisfactory¹⁵ approximations to, respectively, the real and complex eigenvalues of \underline{K} , i.e.,

$$\lambda_{1,2} \simeq \lambda_{1,2}^I = \frac{1}{2}(K_{11} + K_{22}) \pm \frac{1}{2}[K_{11} - K_{22}]^2 + 4K_{12}^2]^{1/2}, \quad \lambda_1 > \lambda_2 \quad (2.16)$$

$$\lambda_3 \simeq \lambda_1^{II} \simeq \frac{1}{2}(K_{33} + K_{44}) + iK_{34}, \quad (2.17)$$

$$\lambda_4 \simeq \lambda_2^{II} \simeq \frac{1}{2}(K_{33} + K_{44}) - iK_{34}.$$

The eigenvectors of \underline{K} to the same relative degree of accuracy can be represented by

$$\underline{V} \simeq \begin{bmatrix} V_{11}^I & V_{12}^I & V_{13}^{(I)} & V_{13}^{(I)*} \\ V_{21}^I & V_{22}^I & V_{23}^{(I)} & V_{23}^{(I)*} \\ 0 & 0 & V_{11}^{II} & V_{11}^{II*} \\ x & x & x & x \end{bmatrix}, \quad (2.18)$$

where the superscript 1 indicates that the elements are correct¹⁵ to terms of order a/kc_∞ .

From Eq. (2.15) one obtains

$$V_{11}^I = V_{22}^I = \left(\frac{\lambda_1^I - K_{22}}{\lambda_1^I - \lambda_2^I} \right)^{1/2}, \quad (2.19)$$

$$V_{12}^I = -V_{21}^I = \left(\frac{\lambda_2^I - K_{22}}{\lambda_2^I - \lambda_1^I} \right)^{1/2}. \quad (2.20)$$

(It has been assumed that $K_{12} = K_{21} < 0$, i.e., that the chemical relaxation term is dominant in $K_{12} = K_{21}$.)

$$V_{11}^{II} = \frac{1}{\sqrt{2}} + \frac{i(K_{44} - K_{33})}{kc_\infty 2\sqrt{2}}. \quad (2.21)$$

The elements $V_{13}^{(I)}$ and $V_{23}^{(I)}$ can be obtained directly from the corresponding elements of \underline{K} as [see Ref. 10, Eq. (12)]

$$V_{13}^{(I)} = -iK_{13}/kc_\infty\sqrt{2}, \quad (2.22)$$

$$V_{23}^{(I)} = -iK_{23}/kc_\infty\sqrt{2}. \quad (2.23)$$

The elements for the last row of \underline{V} are not displayed since they are not required to define the spectral distribution of scattered light.

C. Normal-mode contributions to the spectrum

The spectral intensity distribution given by Eq. (2.6) can be split into two parts:

$$I(k, \omega) = I^R(k, \omega) + I^B(k, \omega).$$

The first term, which is associated with the two nonpropagating modes, is centered at $\omega = 0$ and may be referred to as the Rayleigh peak. The second term which is associated with the two propagating modes consists of lines centered, respectively, at $\omega \simeq \pm kc_\infty$ which are commonly referred to as the Stokes and anti-Stokes Brillouin peaks.

In the present case the Rayleigh peak can be written as the sum of two Lorentzians:

$$I^R(k, \omega) = C \left[Z_1 \frac{1}{\pi} \frac{\lambda_1}{\lambda_1^2 + \omega^2} + Z_2 \frac{1}{\pi} \frac{\lambda_2}{\lambda_2^2 + \omega^2} \right], \quad (2.24)$$

where the strength factors of, respectively, modes 1 and 2 are given by

$$Z_1 = \left(\frac{\partial \epsilon}{\partial B_1} V_{11}^I + \frac{\partial \epsilon}{\partial B_2} V_{21}^I \right)^2, \quad (2.25)$$

$$Z_2 = \left(\frac{\partial \epsilon}{\partial B_1} V_{12}^I + \frac{\partial \epsilon}{\partial B_2} V_{22}^I \right)^2. \quad (2.26)$$

The Stokes and anti-Stokes Brillouin lines are each others mirror image and are given by

$$I_{\text{Stokes}}^B(k, \omega) = I_{\text{anti-Stokes}}^B(k, -\omega) = C \left[Z^B \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + (\omega + kc_\infty)^2} + Y^B \frac{1}{\pi} \frac{(\omega + kc_\infty)}{\Gamma^2 + (\omega + kc_\infty)^2} \right], \quad (2.27)$$

where $\Gamma = \text{Re}\lambda_{3,4}$. The strength factor of the Lorentzian contribution to the Brillouin peaks is given by

$$Z^B = \frac{1}{2} \left(\frac{\partial \epsilon}{\partial B_3} \right)^2 \quad (2.28)$$

and the "strength" of the non-Lorentzian part of the Brillouin lines is given by

$$Y^B = - \sum_{i=1,2} \left(\frac{\partial \epsilon}{\partial B_i} \right) \left(\frac{\partial \epsilon}{\partial B_3} \right) \frac{K_{i3}}{k c_\infty} + \left(\frac{\partial \epsilon}{\partial B_3} \right)^2 \frac{(K_{44} - K_{33})}{k c_\infty}. \quad (2.29)$$

Although defined by rather cumbersome expressions the damping and the Lorentzian and non-Lorentzian strength factors determining the shape of the Brillouin lines can be written in the form

$$\begin{aligned} \Gamma &= D_1 k^2 + D_2 \tau_{T,p}^{-1}, \\ Z^B &= D_3, \\ Y^B &= (D_4 k^2 + D_5 \tau_{T,p}^{-1}) / k c_\infty, \end{aligned}$$

where D_1 – D_5 are constants, the explicit form of which can be obtained from Eqs. (2.17), (2.28), and (2.29). On the other hand, the damping and strength factors for the normal-mode contributions to the Rayleigh peak can not be separated into transport and chemical relaxation terms in the entire k range considered. The reason for this nonadditivity is the coupling, described in \underline{K}^1 , of entropy and concentration fluctuations due to the chemical reaction. The effect of this coupling will be most pronounced for k values for which $K_{11} \approx K_{22}$. The k value for which $K_{11} = K_{22}$ will be referred to as the resonance scattering vector

$$k^{\text{res}} = \left[\frac{(1 - r_T) \tau_{T,p}^{-1}}{D_T - D} \right]^{1/2}. \quad (2.30)$$

The evident separation into transport terms and chemical relaxation terms obviates the need for any further analysis of the contributions to the Brillouin lines. On the other hand, the effect of the nonadditivity of the transport and chemical relaxation terms on the analysis of the shape of the central peak does warrant further discussion.

III. RAYLEIGH PEAK

The k dependence of the real eigenvalues and eigenvectors is conveniently discussed in terms of three regions: $k \gg k^{\text{res}}$, $k \approx k^{\text{res}}$, and $k \ll k^{\text{res}}$, where in all cases k , of course, must still satisfy Eqs. (2.13) and (2.14). This k dependence will be illustrated by reference to the results of calculations of the eigenvalues and eigenvectors

for the case where $\tau_{T,p} = 10^{-7}$ sec and an arbitrary but representative set of values is used for the material parameters and transport coefficients (for details see the legend of Fig. 1). For the chemical relaxation time used in the calculation the thermal diffusion term in $K_{12} = K_{21}$ can safely be neglected. Actually in all the following considerations it will be assumed that the chemical relaxation term in $K_{12} = K_{21}$ is much larger than the thermal diffusion term.

For k values such that $k \gg k^{\text{res}}$ the real eigenvalues are simply

$$\begin{aligned} \lambda_1 &\approx D_T k^2 + r_T \tau_{T,p}^{-1}, \\ \lambda_2 &\approx D k^2 + \tau_{T,p}^{-1}. \end{aligned} \quad (3.1)$$

No such separation into transport and chemical terms can be effected in the region $k \approx k^{\text{res}}$ and the real eigenvalues must be taken as given by Eq. (2.16). When $k \ll k^{\text{res}}$ the eigenvalues are given by

$$\begin{aligned} \lambda_1 &\approx D k^2 + (1 + r_T) \tau_{T,p}^{-1}, \\ \lambda_2 &\approx D_T k^2. \end{aligned} \quad (3.2)$$

The eigenvalues λ_1 and λ_2 displayed in Fig. 1 illustrate these features.

The coefficients required to specify the eigenvalues corresponding to the normal modes are given by the elements of \underline{V}^1 and the normal modes $\gamma_1(\vec{k}, t)$ and $\gamma_2(\vec{k}, t)$ can be written as

$$\begin{aligned} \gamma_1(\vec{k}, t) &= A \beta_1(\vec{k}, t) - B \beta_2(\vec{k}, t), \\ \gamma_2(\vec{k}, t) &= B \beta_1(\vec{k}, t) + A \beta_2(\vec{k}, t), \end{aligned} \quad (3.3)$$

where $A = V_{11}^1 = V_{22}^1$ and $B = V_{12}^1 = -V_{21}^1$. For $k \gg k^{\text{res}}$ it can be seen from Eqs. (2.19) and (2.20) that $A \rightarrow 1$ and $B \rightarrow 0$. Thus mode 1 becomes the reduced entropy fluctuation (δs_{red}) and mode 2 the concentration fluctuation (δc). In the region of $k \approx k^{\text{res}}$ no such classification is possible for the reduced entropy and concentration fluctuations are distributed between the two modes—indeed at k^{res} $A = B$ and the mixing is complete. For the case $k \ll k^{\text{res}}$ it is easily shown from Eqs. (2.19) and (2.20) that

$$A \rightarrow \frac{r_T}{1 + r_T} \quad \text{and} \quad B \rightarrow \frac{1}{1 + r_T}.$$

The reduced entropy fluctuation is now primarily described by mode 2 and the concentration fluctuation by mode 1. The values of A and B presented in Fig. 2 illustrate these features.

In order to assess the effect of the k dependence of the nonpropagating normal modes on the Rayleigh line one must take into account the sensitivity of the dielectric constant to fluctuations β_1 and β_2 . Introducing W , defined by

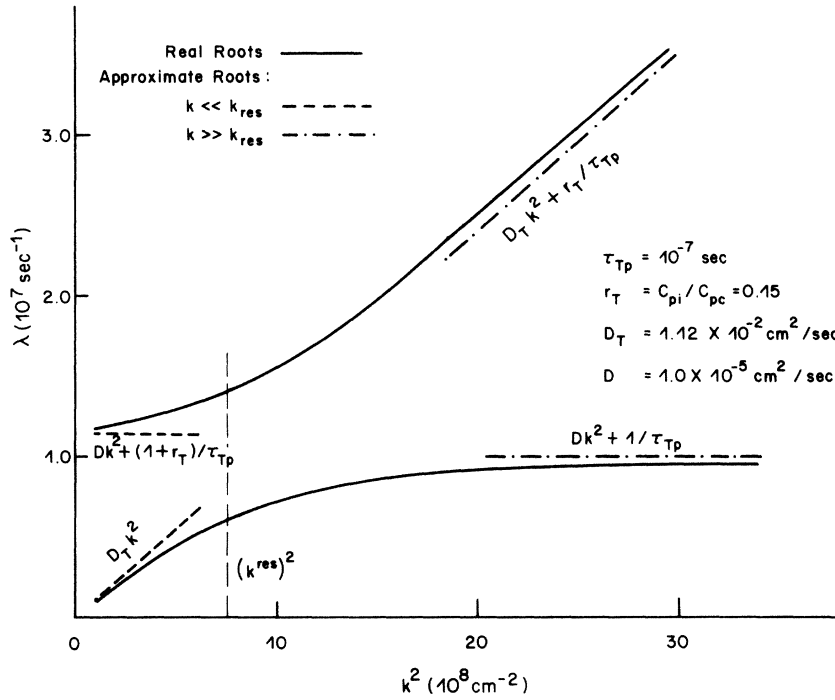


FIG. 1. Dependence of the real roots on the scattering vector.

$$W = \frac{(\partial \epsilon / \partial B_2)}{(\partial \epsilon / \partial B_1)} = \left(\frac{TC_{p,c}}{(\partial A / \partial c)_{p,T}} \right)^{1/2} \frac{(\partial \epsilon / \partial c)_{p,T}}{T(\partial \epsilon / \partial T)_{p,c}},$$

$$Z_2 = \left(\frac{\partial \epsilon}{\partial B_1} \right)^2 [B + WA]^2 = \left(\frac{\partial \epsilon}{\partial B_1} \right)^2 Z'_2. \quad (3.5)$$

allows the strength factor given by Eqs. (2.25) and (2.26) to be written as

$$Z_1 = \left(\frac{\partial \epsilon}{\partial B_1} \right)^2 [A - WB]^2 = \left(\frac{\partial \epsilon}{\partial B_1} \right)^2 Z'_1, \quad (3.4)$$

The effect of W on the k dependence of the strength factors is discussed in terms of three values of W : $|W| \ll 1$, $|W| = 1$, and $|W| \gg 1$. For $W \gg 1$ and for $W \ll 1$ the strength factors Z_1 and Z_2 cross one another as k goes from $k \ll k^{res}$ to $k \gg k^{res}$. This exchange is simply a reflection of

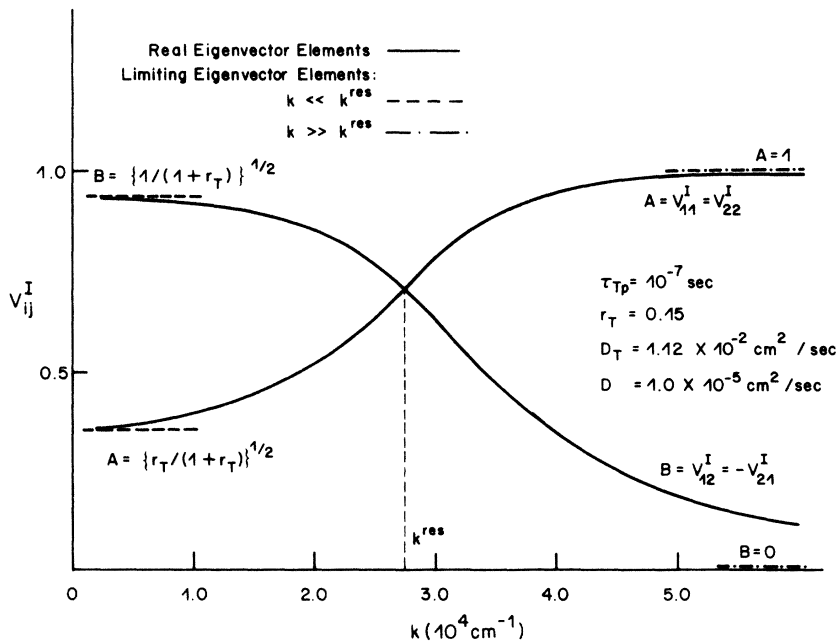


FIG. 2. Dependence of the eigenvector elements on the scattering vector.

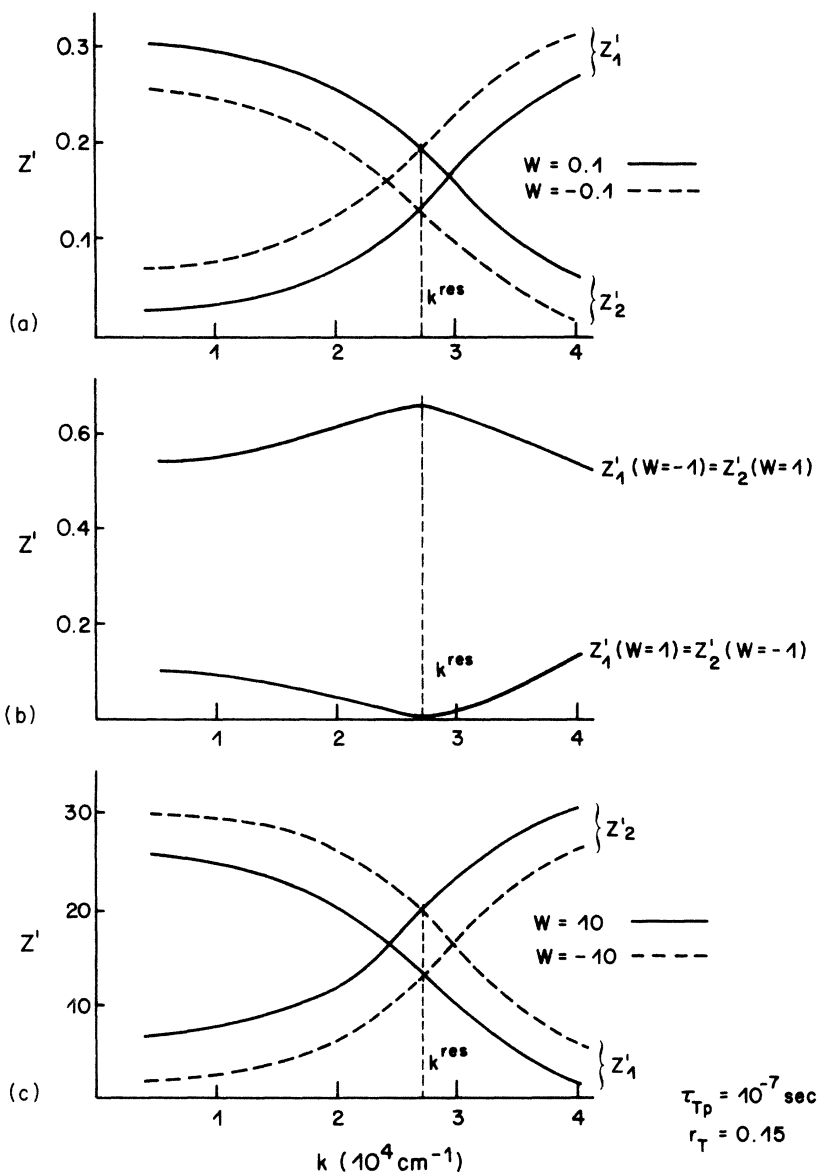


FIG. 3. Strength factors of the nonpropagating normal modes.

the crossover in normal-mode character discussed earlier in this section and illustrated in Fig. 3(a)–3(c). Indeed, as the dielectric derivatives become more and more disparate ($W \rightarrow \infty$ or $W \rightarrow 0$) the crossover point occurs closer to k^{res} , lying, in the limit, at $k = k^{\text{res}}$. For the case $|W| = 1$, one of the strength factors goes to zero at $k = k^{\text{res}}$ (since $A = B$), and for $k \gg k^{\text{res}}$ or $k \ll k^{\text{res}}$ the strength factors approach one another. In general, the strength factors Z_1 and Z_2 do vary considerably with k but their sum is a constant. Specifically,

$$Z_1 + Z_2 = \left(\frac{\partial \epsilon}{\partial B_1} \right)^2 (W^2 + 1).$$

The features of Z_1 and Z_2 discussed above are

illustrated by calculations presented in Fig. 3 for the cases $W = \pm 10$, ± 1 , and ± 0.1 .

The preceding part of this section has provided a general discussion of the damping and strength factors of the nonpropagating normal modes as a function of k and the ratio W of the dielectric constants involved. Using this as a basis, the shape of the Rayleigh line may be examined with the assistance of Eq. (2.24). We consider, as an example, the case $|W| \ll 1$, a situation for which the chemical reaction affects the Rayleigh line in a manner hitherto not explicitly discussed. To facilitate the discussion we present in Fig. 4(a)–4(d) the individual nonpropagating normal-mode contributions and their sum (i.e., the Rayleigh line) for a range of k values around k^{res} for

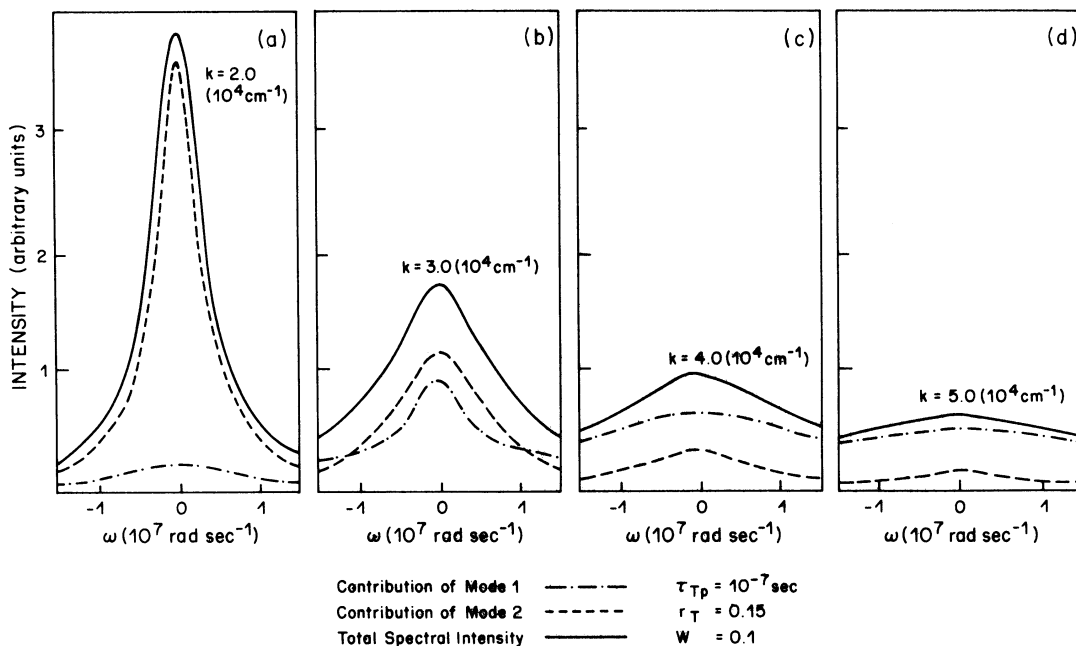


FIG. 4. Normal-mode decomposition of the spectral intensity.

the case $W = 0.1$. In this situation (i.e., where $W = 0.1$) the spectrum is dominated by entropy fluctuations. One thus expects the strength factor of normal-mode 2 to dominate for $k \ll k^{\text{res}}$ and that of normal-mode 1 to dominate for $k \gg k^{\text{res}}$ [cf. Figs. 2 and 3(a)]. The strength factor of normal-mode 2 is multiplied by its narrow Lorentzian-shape function to generate the narrow and intense contribution dominating the Rayleigh line in Fig. 4(a). The strength factor for normal-mode 1 is multiplied by its broad ($\lambda_1 > \lambda_2$) Lorentzian-shape function to give the broad and intense contribution which is dominant in Fig. 4(d). Hence for both $k \ll k^{\text{res}}$ and $k \gg k^{\text{res}}$ one can safely interpret the Rayleigh peak as being due to a single Lorentzian. Unfortunately the width of that Lorentzian is due mainly to heat diffusion damping and it may be difficult to discern a chemical relaxation contribution.

For k values close to k^{res} the two normal modes have, as depicted in Figs. 4(b) and 4(c), approximately equal intensities [recall Figs. 2 and 3(a)]. Since the damping factors in this region of k are also comparable (see Fig. 1) the necessary analysis of the Rayleigh line in terms of two Lorentzians appears feasible. Although the individual

damping factors λ_1 and λ_2 have no simple k dependence in the resonance region, the minimum of $\lambda_1 - \lambda_2$ occurring, for k_T small, at k^{res} is approximately $2 r_T^{1/2} \tau_{T,p}^{-1}$. This feature suggests that even though the contributions due to entropy fluctuations dominate the Rayleigh line the chemical relaxation may still be probed.

IV. CONCLUSIONS

It is possible to extend the scheme for decoupling the pressure fluctuations from those in entropy and concentration to the calculation of the light scattering spectrum of a chemically relaxing fluid. The coupling introduced by the chemical reaction leads to a distribution of entropy and concentration fluctuations in all nonpropagating normal modes.

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