

Spectral Analysis of Light Scattered from Fluids

H. N. W. Lekkerkerker*[†]

Faculté des Sciences, Université Libre de Bruxelles, 1050 Brussels, Belgium

W. G. Laidlaw

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The normal-mode decomposition of the spectral densities which play a role in the analysis of light-scattering spectra of fluids is treated. The inherent symmetry of the hydrodynamic matrix and the relative magnitude of its elements are utilized to develop a simple and systematic method for obtaining the eigenvalues and the required eigenvector elements. The scheme, which involves a partitioning of the hydrodynamic matrix, is shown to yield the eigenvalues correct up to terms of order k^2 and the eigenvectors correct up to terms of order k . The method is illustrated by application to a two-component fluid.

I. INTRODUCTION

In recent years there has been considerable activity, both experimentally as well as theoretically, in the study of the spectral distribution of scattered light.¹ In the usual macroscopic calculation of the light-scattering spectrum one starts from the coupled hydrodynamic equations and uses Onsager's assumption concerning the regression of fluctuations to obtain the spectral densities in terms of which the spectral intensity distribution of the scattered light can be expressed.^{2,3} To facilitate the analysis of the light-scattering spectrum, a normal-mode decomposition is frequently undertaken. To carry out this decomposition one first has to determine the eigenvalues of the hydrodynamic matrix and, subsequently, perform either a partial fraction decomposition or, as will be done here, obtain the final expressions in terms of the eigenvectors of the hydrodynamic matrix. The application of the results of such theoretical analyses to experimental data (see e.g., Ref. 4) for two-component systems suggests that light-scattering spectroscopy should be of increasing importance in the study of fluids with an arbitrary number of components. However, a larger number of components leads to a hydrodynamic matrix of dimension such that the calculation of even the approximate eigenvalues and eigenvectors becomes rather difficult.

Blum and Salsburg⁵ have given a perturbation treatment to determine the eigenvalues of the hydrodynamic matrix by expanding the entire matrix in powers of the scattering vector \vec{k} . However, the expansion of the entire matrix can be avoided and the problem materially simplified by an appropriate choice of variables which allows one to utilize the structure of the matrix. Specifically, one resorts to the use of statistically independent variables as discussed by Jordan and Jordan⁶ and

more recently employed by the present authors⁷ in studying the distribution of the eigenvalues of the hydrodynamic matrix. Further, the selection of the pressure fluctuation, suitably normalized, as one of the aforementioned set of variables, allows one to utilize conveniently the approximate decoupling of the sound modes and modes associated with heat and mass diffusion.⁶ The purpose of the present work is to develop and systematize the use of this combination of statistically independent and normalized variables and the selection of the pressure fluctuation as one of them. It will be shown, for a system described by n thermodynamic variables, that for ordinary fluids the resulting hydrodynamic matrix has a structure which allows one to obtain the real eigenvalues, correct up to terms of order k^2 , as the roots of a real symmetric matrix of dimension $n - 1$ and the two complex roots with the same relative accuracy from a two-dimensional antisymmetric matrix. It will also be shown that the components of the eigenvectors required for the normal-mode decomposition can be readily obtained, correct up to terms of order k , given only the above eigenvalues and the elements of the appropriate hydrodynamic matrix.

II. SPECTRAL COMPOSITION OF SCATTERED LIGHT

The spectral intensity distribution of the polarized component of scattered light is proportional to $S_e(k, \omega)$, where $S_e(k, \omega)$ is the spectral density of $\delta\epsilon(\vec{k}, t)$, the \vec{k} th spatial Fourier component of the fluctuation in the local dielectric constant. Here \vec{k} is the change in wave vector and ω the change in frequency upon scattering. The dielectric constant can be considered to be a function of the thermodynamic state of the system, so that $\delta\epsilon$ can be expressed in terms of the fluctuations α_i ($i = 1, \dots, n$) in the thermodynamic state variables A_i ($i = 1, \dots, n$). Consequently, one can write

$$S_{\epsilon}(k, \omega) = \sum_{i,j=1}^n \left(\frac{\partial \epsilon}{\partial A_i} \right) \left(\frac{\partial \epsilon}{\partial A_j} \right) S_{\alpha_i \alpha_j}(k, \omega), \quad (1)$$

where $S_{\alpha_i \alpha_j}(k, \omega)$ is the i, j th element of the spectral density matrix of the k th spatial Fourier components of the fluctuations $\alpha_1 \dots \alpha_n$. The spectral densities occurring on the right-hand side of Eq. (1) can, on invoking the Wiener-Khinchin theorem, be obtained as the temporal Fourier transforms of the corresponding time correlation functions, which in turn can be calculated conveniently using Onsager's assumption concerning the regression of fluctuations. For the spectral densities of even variables one obtains

$$S_{\alpha_i \alpha_j}(k, \omega) = \frac{1}{\pi} \operatorname{Re} \{ [\underline{M}(k) + i\omega \underline{I}]^{-1} \underline{X}(k) \}_{ij}, \quad (2)$$

where $\underline{M}(k)$ is the hydrodynamic matrix and $\underline{X}(k)$ is the matrix of mean-square fluctuations [see, for example, the definitions given by Eqs. (2) and (4) of Ref. 7]. It will be assumed that the scattering system is isotropic and, therefore, the thermodynamic variables are only coupled to $\operatorname{div} \vec{v}$, where \vec{v} is the velocity of the fluid. The variable $\operatorname{div} \vec{v}$ will be denoted by α_{n+1} . Thus, for an isotropic system, described by n thermodynamic variables, the hydrodynamic matrix \underline{M} is $n+1$ dimensional. Although Eq. (2) is an exact expression for the spectral density matrix, within the limitations of the theory, the elements of the matrix $[\underline{M}(k) + i\omega \underline{I}]^{-1}$ are rather complicated functions of k and ω making a direct analysis of the spectral densities difficult. This is the reason one frequently undertakes a normal-mode analysis even though this involves the calculation of the eigenvalues and the eigenvectors.

To carry out this task we employ a set of statistically independent and normalized random variables $\underline{\beta}(\vec{k}, t)$ which are linear combinations of the fluctuations $\underline{\alpha}(\vec{k}, t)$ as

$$\underline{\beta}(\vec{k}, t) = \underline{Q}(k) \underline{\alpha}(\vec{k}, t), \quad (3)$$

where the transformation $\underline{Q}(k)$ does not mix the thermodynamic fluctuations $\alpha_1 \dots \alpha_n$ with $\operatorname{div} \vec{v}$. The elements of the spectral density matrix required in Eq. (1) can now be written

$$S_{\alpha_i \alpha_j}(k, \omega) = \sum_{l,m} Q_{il}^{-1} Q_{jm}^{-1} S_{\beta_l \beta_m}(k, \omega), \quad (4)$$

where $S_{\beta_l \beta_m}(k, \omega)$ is the l, m th element of the spectral density matrix for the β variables. The hydrodynamic matrix for these variables will be denoted by \underline{K} and its eigenvector matrix by \underline{V} , i. e.,

$$\underline{V}^{-1} \underline{K} \underline{V} = \underline{\Lambda}, \quad (5)$$

where $\underline{\Lambda}$ is a diagonal matrix with elements $\lambda_1, \dots, \lambda_{n+1}$ which are the eigenvalues of \underline{K} . The normal-mode decomposition of $S_{\beta_l \beta_m}(k, \omega)$, where β_l and β_m are even variables, can then be written

as

$$S_{\beta_l \beta_m}(k, \omega) = \frac{1}{\pi} \operatorname{Re} \left(\sum_{f=1}^{n+1} \frac{V_{lf} V_{mf}}{\lambda_f + i\omega} \right). \quad (6)$$

Here we have used the symmetry property $\underline{V}^{-1} = \underline{V}^T \underline{E}$ [see Ref. 7, Eq. (20)], where \underline{E} is the signature matrix, which in the present case has the form $\underline{E} = \operatorname{Diag}\{1, \dots, 1, -1\}$.

In summary then, in order to obtain the normal-mode decomposition of the spectral distribution of scattered light one has to know the eigenvalues and eigenvectors of the hydrodynamic matrix \underline{K} (which because of its structure will, in the event, materially simplify obtaining such roots and vectors) and the transformation matrix \underline{Q} (whose structure is normally quite simple).

III. SELECTION OF VARIABLES AND THE HYDRODYNAMIC MATRIX

In this section we consider, in some detail, the form the \underline{K} matrix assumes when one chooses the normalized spatial Fourier component of the pressure fluctuation as one of the variables $\underline{\beta}$. We denote this normalized pressure fluctuation by β_n , the remaining statistically independent and normalized thermodynamic fluctuations by $\beta_1 \dots \beta_{n-1}$, and the suitably normalized variable $\operatorname{div} \vec{v}$ by β_{n+1} . The time variation of $\operatorname{div} \vec{v}$ is, according to the longitudinal Navier-Stokes equation, only directly coupled to variations in $\operatorname{div} \vec{v}$ and the pressure. Thus, the $(n+1)$ th row of \underline{K} has only two nonzero elements. Since the hydrodynamic matrix for statistically independent and normalized variables has the symmetry⁷

$$\underline{K}^T = \underline{E} \underline{K} \underline{E},$$

the $(n+1)$ th column of \underline{K} also has only two nonzero elements. Specifically \underline{K} has the structure

$$\underline{K} = \begin{bmatrix} a_{11} & \dots & a_{1, n-1} & a_{1n} & 0 \\ \vdots & & & & \\ \vdots & & & & \\ \vdots & & & & \\ a_{n-1, 1} & \dots & a_{n-1, n-1} & a_{n-1, n} & 0 \\ a_{n1} & \dots & & a_{nn} & b \\ 0 & \dots & & -b & a_{n+1, n+1} \end{bmatrix} \quad (7)$$

with $a_{ij} = a_{ji}$. The elements a_{ij} are of the type $D_T k^2$, $D k^2$, etc., where D_T is the thermal diffusivity and D is the diffusion coefficient; furthermore $b = kc_0$, where c_0 is the low-frequency sound velocity of the medium. Given the scattering vectors occurring in light-scattering experiments ($k \approx 10^5 \text{ cm}^{-1}$) and the value of the transport coefficients in fluid systems, it is clear that generally the a_{ij} 's are much smaller than b . In the next section it will become clear that it is this order of magnitude relation of the a_{ij} elements (hereafter referred to as a) to the element b ,

which in conjunction with the structure of \underline{K} displayed by Eq. (7), allows a partitioning of the \underline{K} matrix into two matrices, one of which determines the nonpropagating modes and the other the propagating modes.

IV. PARTITIONING OF THE HYDRODYNAMIC MATRIX AND THE EIGENVALUES

The smallness of the dimensionless quantities a_{ij}/b has been employed both directly² as well as indirectly, in the form of a k expansion,⁵ to determine the approximate roots of the hydrodynamic matrix. Such procedures can be systemized by utilizing the special structure of the hydrodynamic matrix given in Sec. III.

The eigenvalues of \underline{K} are given by the roots of its characteristic polynomial

$$p(\lambda) = \text{Det}(\underline{K} - \lambda \underline{I}) \quad (8)$$

which we can write as

$$p(\lambda) = p_I(\lambda)p_{II}(\lambda) + R(\lambda) \quad (9)$$

Here $p_I(\lambda)$ and $p_{II}(\lambda)$ are the characteristic polynomials of the matrices \underline{K}_I and \underline{K}_{II} , respectively, where

$$\underline{K}_I = \begin{bmatrix} a_{11} & \cdots & a_{1, n-1} \\ \vdots & & \vdots \\ a_{n-1, 1} & \cdots & a_{n-1, n-1} \end{bmatrix} \quad (10)$$

and

$$\underline{K}_{II} = \begin{bmatrix} a_{n, n} & b \\ -b & a_{n+1, n+1} \end{bmatrix}; \quad (11)$$

furthermore, $R(\lambda)$ is just the remainder. In Appendix A it will be shown that satisfactory approximations to the real and complex roots of the polynomial $p(\lambda)$ can be obtained directly from the lower-degree polynomials $p_I(\lambda)$ and $p_{II}(\lambda)$, respectively. In particular, it is shown that the $n-1$ real roots and the real part of the complex roots, so obtained, are correct up to terms of order k^2 and that the imaginary part of the complex roots is correct up to terms of order k . The advantage of this partitioning is clearly that the degree of the polynomials from which one obtains the eigenvalues is reduced; for example in the case of a five-dimensional hydrodynamic matrix one solves a cubic equation for the real roots and a quadratic equation for the complex roots rather than treating a fifth-degree polynomial.

V. EIGENVECTORS OF THE HYDRODYNAMIC MATRIX

The normal-mode analysis may be completed if

one knows the eigenvectors of the hydrodynamic matrix. The partitioning which appeared to be valuable in determining the eigenvalues is also of considerable assistance in obtaining the eigenvectors.

For example, the elements V_{ij} ($i, j = 1, \dots, n-1$) of the eigenvectors corresponding to the real eigenvalues are given, as argued in Appendix B, correct to terms of order k , by the corresponding elements of the eigenvectors of \underline{K}_I , and will be denoted by V_{ij}^I . Furthermore, in the same Appendix, it is argued that the remaining elements V_{nj} and $V_{n+1, j}$ ($j = 1, \dots, n-1$) of the eigenvectors corresponding to the real eigenvalues are of order $(a/b)^2$ and (a/b) , respectively. Although the contributions of order (a/b) of $V_{n+1, j}$ ($j = 1, \dots, n-1$) are non-negligible, they are not of importance in light scattering, since the spectral densities which play a role in the light-scattering spectrum [see Eq. (1)] do not involve these quantities [see Eq. (6)] and realize that the spectral densities $S_{\alpha_i \alpha_j}(k, \omega)$ ($i, j = 1, \dots, n$) can be expressed in terms of $S_{\beta_l \beta_m}(k, \omega)$ ($l, m = 1, \dots, n$).

As far as the eigenvectors corresponding to the complex eigenvalues are concerned, the elements V_{ij} ($i, j = n, n+1$) are given correct to terms of order k by the corresponding elements of the eigenvectors of \underline{K}_{II} , which will be denoted by V_{ij}^{II} (again see Appendix B for details). The remaining elements V_{jn} and $V_{j, n+1}$ ($j = 1, \dots, n-1$) of these eigenvectors must be considered in some detail since they do play a role in the light-scattering spectrum. Fortunately, it can readily be shown that these elements, correct to terms of order k , have the following simple form:

$$V_{jn}^{(1)} = -ia_{jn}/b\sqrt{2}, \quad j = 1, \dots, n-1 \quad (12)$$

$$V_{j, n+1}^{(1)} = V_{jn}^{(1)*} = +ia_{jn}/b\sqrt{2} \quad .$$

The superscript 1 indicates that the eigenvector elements given by Eq. (12) are correct to terms of order k , i.e., order (a/b) .

In summary then one can write the elements of \underline{V} , correct to terms of order (a/b) as

$$V = \begin{bmatrix} V_{11}^I & \cdots & V_{1, n-1}^I & V_{1n}^{(1)} & V_{1n}^{(1)*} \\ \vdots & & \vdots & \vdots & \vdots \\ V_{n-1, 1}^I & \cdots & V_{n-1, n-1}^I & V_{n-1, n}^{(1)} & V_{n-1, n}^{(1)*} \\ 0 & \cdots & 0 & V_{nn}^{II} & V_{n, n+1}^{II} \\ x & \cdots & x & x & x \end{bmatrix}, \quad (13)$$

where the elements of the $(n+1)$ th row of \underline{V} , which

do not play a role in the light-scattering spectrum, have been omitted in Eq. (13). It should be emphasized that the complex nature of the entries in the last two columns of \underline{V} will, on insertion in Eq. (6), give rise to both Lorentzian and non-Lorentzian contributions to the spectrum.

VI. ILLUSTRATION OF THE METHOD: THE SPECTRAL DENSITIES FOR A TWO-COMPONENT FLUID

The intent of Secs. IV and V has been to indicate a systematic and simple method, utilizing the inherent structure of the \underline{K} matrix and the relative magnitude of the elements therein, for obtaining a satisfactory approximation to the eigenvalues and eigenvectors. The method, which is based on a partitioning of the hydrodynamic matrix, will be the more advantageous in situations where the dimension of the hydrodynamic matrix is high, e.g., for multicomponent fluids. Here we shall, for the sake of simplicity, illustrate the method by application to a two-component nonreactive fluid. This example has recently been treated rather thoroughly by Cohen *et al.*⁸

As usual we start by writing down the linearized hydrodynamic equations⁹:

$$\frac{\partial \rho}{\partial t} = -\rho \psi, \quad (14)$$

where $\psi = \text{div} \vec{v}$:

$$\begin{bmatrix} \beta_1(\vec{k}, t) \\ \beta_2(\vec{k}, t) \\ \beta_3(\vec{k}, t) \\ \beta_4(\vec{k}, t) \end{bmatrix} = \begin{bmatrix} \left(\frac{\rho}{k_B V c_p} \right)^{1/2} & - \left(\frac{\partial s}{\partial c} \right)_{p,T} \left(\frac{\rho}{k_B V c_p} \right)^{1/2} & 0 & 0 \\ 0 & \left(\frac{\rho \left(\frac{\partial \mu}{\partial c} \right)_{p,T}}{k_B V T} \right)^{1/2} & 0 & 0 \\ 0 & 0 & \left(\frac{\chi_s}{k_B V T} \right)^{1/2} & 0 \\ 0 & 0 & 0 & \left(\frac{\rho}{k_B V T k^2} \right)^{1/2} \end{bmatrix} \begin{bmatrix} \delta s(\vec{k}, t) \\ \delta c(\vec{k}, t) \\ \delta p(\vec{k}, t) \\ \psi(\vec{k}, t) \end{bmatrix}, \quad (19)$$

where k_B is Boltzmann's constant and V is the volume in which the fluctuations are considered. Spatially Fourier transforming the hydrodynamic equations (14)–(17) and expressing these equations in terms of the β variables defined by Eq. (19) one obtains

$$\rho \frac{\partial \psi}{\partial t} = -\nabla^2 p + \left(\frac{4}{3} \eta + \zeta \right) \nabla^2 \psi, \quad (15)$$

$$\rho \frac{\partial c}{\partial t} = -\text{div} \vec{i}, \quad (16)$$

where

$$\vec{i} = -\rho D \left(\vec{\nabla} c + \frac{k_T}{T} \vec{\nabla} T + \frac{k_p}{p} \vec{\nabla} p \right),$$

$$\rho T \frac{\partial s}{\partial t} = \kappa \nabla^2 T - \left[k_T \left(\frac{\partial \mu}{\partial c} \right)_{p,T} - T \left(\frac{\partial \mu}{\partial T} \right)_{p,c} \right] \text{div} \vec{i}. \quad (17)$$

For the definition of the various quantities appearing in Eqs. (14)–(17), see Ref. 9. In order to follow the procedure outlined in Sec. III, we must choose as two of the statistically independent fluctuations ψ and δp . The remaining two statistically independent fluctuations are taken to be δs_{red} and δc , where¹⁰

$$\delta s_{\text{red}} = \delta s - \left(\frac{\partial s}{\partial c} \right)_{p,T} \delta c. \quad (18)$$

From these four variables one easily obtains, using thermodynamic fluctuation theory, the appropriate normalization factors to give the set of statistically independent and normalized variables β . The transformation $\underline{Q}(k)$ between the β variables and the α variables δs , δc , δp , and ψ can then be written explicitly as

$$\frac{\partial \underline{\beta}(k, t)}{\partial t} = -\underline{K}(k) \underline{\beta}(k, t), \quad (20)$$

where the hydrodynamic matrix $\underline{K}(k)$ is given by Eq. (21):

$$\begin{aligned}
 K(k) = & \left[\begin{array}{cccc}
 Dk_T^2 + D \frac{k_T^2}{Tc_p} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} k^2 & Dk_T \left(\frac{\partial \mu}{\partial c} \right)_{p,T} k^2 & \left[D_T \left(\frac{\partial v}{\partial T} \right)_{p,c} + D \frac{k_T}{T} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \right] \left(\frac{\rho T}{\chi_s c_p} \right)^{1/2} k^2 & 0 \\
 Dk_T \left(\frac{\partial \mu}{\partial c} \right)_{p,T} k^2 & Dk^2 & D\Phi \left(\frac{\rho \left(\frac{\partial \mu}{\partial c} \right)_{p,T}}{\chi_s} \right)^{1/2} k^2 & 0 \\
 \left[D_T \left(\frac{\partial v}{\partial T} \right)_{p,c} + D \frac{k_T}{T} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \right] \left(\frac{\rho T}{\chi_s c_p} \right)^{1/2} k^2 & D\Phi \left(\frac{\rho \left(\frac{\partial \mu}{\partial c} \right)_{p,T}}{\chi_s} \right)^{1/2} k^2 & \left[D_T(\gamma - 1) + D\rho^2 c_0^2 \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \right] \Phi^2 k^2 & kc_0 \\
 0 & 0 & \left[D_T(\gamma - 1) + D\rho^2 c_0^2 \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \right] \Phi^2 k^2 & \frac{(\frac{4}{3}\eta + \xi)k^2}{\rho}
 \end{array} \right] \quad (21)
 \end{aligned}$$

where D_T is the thermal diffusivity, $D_T = \kappa/\rho c_p$, and following Cohen *et al.*,⁸ we have introduced the quantity

$$\Phi = \frac{k_p}{p} + \frac{k_T}{c_p} \left(\frac{\partial v}{\partial T} \right)_{p,c} .$$

As indicated in Sec. IV the real roots of \underline{K} , correct to terms of order k^2 , can be obtained as the roots of \underline{K}_I , i. e., in the present case from

$$\text{Det} \begin{bmatrix} K_{11} - \lambda & K_{12} \\ K_{21} & K_{22} - \lambda \end{bmatrix} = 0 . \quad (22)$$

This yields

$$\lambda_{1,2} = \frac{1}{2}(D_T + \mathfrak{D})k^2 \pm \frac{1}{2}[(D_T + \mathfrak{D})^2 - 4D_T D]^{1/2} k^2 . \quad (23)$$

In order to facilitate comparison with the results given by Cohen *et al.*,⁸ we also introduced the quantity

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

The complex roots of \underline{K} can be obtained as the roots of \underline{K}_{II} , i. e., in the present case from

$$\text{Det} \begin{bmatrix} K_{33} - \lambda & K_{34} \\ K_{43} & K_{44} - \lambda \end{bmatrix} = 0 , \quad (24)$$

yielding

$$\begin{aligned}
 \lambda_{3,4} = & \frac{1}{2} \left[D_T(\gamma - 1) + D\rho^2 c_0^2 \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \Phi^2 \right. \\
 & \left. + \frac{(\frac{4}{3}\eta + \xi)}{\rho} \right] k^2 \pm ikc_0 \\
 = & \Gamma k^2 \pm ikc_0 , \quad (25)
 \end{aligned}$$

where Γ denotes the coefficient of k^2 in the previous line. The advantage of the scheme presented here is, we think, the ease with which one obtains the appropriate eigenvalues once the hydrodynamic matrix \underline{K} has been evaluated.

The elements of the eigenvector matrix will now be obtained using the scheme discussed in Sec. V. In the present case the matrix \underline{V} , correct to terms of order k , can be written as

$$\underline{V} = \begin{bmatrix} V_{11}^I & V_{12}^I & V_{13}^{(1)} & V_{13}^{(1)*} \\ V_{21}^I & V_{22}^I & V_{23}^{(1)} & V_{23}^{(1)*} \\ 0 & 0 & V_{33}^{II} & V_{33}^{II*} \\ x & x & x & x \end{bmatrix} . \quad (26)$$

Here V_{ij}^I and V_{ij}^{II} are elements of the eigenvectors of \underline{K}_I and \underline{K}_{II} , respectively. One easily obtains

$$\underline{V}^I = \begin{bmatrix} \left[\frac{\lambda_1 - Dk^2}{\lambda_1 - \lambda_2} \right]^{1/2} & \left[\frac{\lambda_2 - Dk^2}{\lambda_2 - \lambda_1} \right]^{1/2} \\ \left[\frac{\lambda_2 - Dk^2}{\lambda_2 - \lambda_1} \right]^{1/2} & - \left[\frac{\lambda_1 - Dk^2}{\lambda_1 - \lambda_2} \right]^{1/2} \end{bmatrix} \quad (27)$$

and

$$V_{33}^{\text{II}} = \frac{1}{\sqrt{2}} - \frac{i[\Gamma - (\frac{4}{3}\eta + \xi)/\rho]k}{c_0 2\sqrt{2}} \quad (28)$$

Furthermore, the elements $V_{ij}^{(1)}$ are given by the general formula (12), i. e., in the present case

$$V_{13}^{(1)} = \frac{-i \left[D_T \left(\frac{\partial v}{\partial T} \right)_{p,c} + D \frac{k_T}{T} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \Phi \right] \left(\frac{\rho T}{\chi_s c_p} \right)^{1/2} k}{c_0 \sqrt{2}} \quad (29)$$

and

$$V_{23}^{(1)} = \frac{-i \left\{ D \Phi \left[\rho \left(\frac{\partial \mu}{\partial c} \right)_{p,T} / \chi_s \right]^{1/2} k \right\}}{c_0 \sqrt{2}} \quad (30)$$

Given the eigenvalues and eigenvectors of \underline{K} one can write down, using Eq. (6), the elements of the

$$\begin{aligned} S_{\beta_3\beta_3}(k, \omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{f=1}^{n+1} \frac{V_{3f}^2}{\lambda_f + i\omega} \\ &= \frac{1}{2\pi} \left(\frac{\Gamma k^2 - \frac{[\Gamma - (\frac{4}{3}\eta + \xi)/\rho](kc_0 + \omega)k}{c_0}}{(\Gamma k^2)^2 + (kc_0 + \omega)^2} + \frac{\Gamma k^2 - \frac{[\Gamma - (\frac{4}{3}\eta + \xi)/\rho](kc_0 - \omega)k}{c_0}}{(\Gamma k^2)^2 + (kc_0 - \omega)^2} \right). \end{aligned} \quad (32)$$

On the other hand the "cross correlations" $S_{\beta_1\beta_3}(k, \omega)$ and $S_{\beta_2\beta_3}(k, \omega)$ contribute only non-Lorentzian terms, for example,

$$\begin{aligned} S_{\beta_1\beta_3}(k, \omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{f=1}^{n+1} \frac{V_{1f} V_{3f}}{\lambda_f + i\omega} \\ &= \frac{-1}{2\pi} \frac{\left[D_T \left(\frac{\partial v}{\partial T} \right)_{p,c} + D \frac{k_T}{T} \left(\frac{\partial \mu}{\partial c} \right)_{p,T} \Phi \right] \left(\frac{\rho T}{\chi_s c_p} \right)^{1/2} k}{2c_0} \left(\frac{(kc_0 + \omega)}{(\Gamma k^2)^2 + (kc_0 + \omega)^2} + \frac{(kc_0 - \omega)}{(\Gamma k^2)^2 + (kc_0 - \omega)^2} \right). \end{aligned} \quad (33)$$

The normal-mode decomposition of the light scattering spectrum can now be completed by insertion of the quantities $S_{\beta_i\beta_j}(k, \omega)$ in Eq. (2) together with the elements of the inverse of the transformation matrix $\underline{Q}(k)$, so as to obtain the $S_{\alpha_i\alpha_j}(k, \omega)$ which on substitution in Eq. (1) yields $S_\epsilon(k, \omega)$.

VII. CONCLUSION

The general treatment given here implies that, even for a fluid with an arbitrary number of components, both the Lorentzian and non-Lorentzian contributions to the shifted lines can always be readily obtained. Although the contributions to the unshifted peak are generally more difficult to obtain, the real symmetric matrix determining the nonpropagating modes can be extracted in a straightforward manner. The fact that this real symmetric matrix has a dimension lower by 2 than the full hydrodynamic matrix allows one, for example, to obtain analytic expressions for the nonpropagating modes in a three-component fluid.

spectral density matrix of the β variables, each of which contributes to the spectrum. The central peak is due to contributions from $S_{\beta_1\beta_1}(k, \omega)$, $S_{\beta_1\beta_2}(k, \omega)$, and $S_{\beta_2\beta_2}(k, \omega)$, and we give as an example

$$\begin{aligned} S_{\beta_1\beta_1}(k, \omega) &= \frac{1}{\pi} \operatorname{Re} \sum_{f=1}^{n+1} \frac{V_{1f}^2}{\lambda_f + i\omega} \\ &= \frac{1}{\pi} \left[\frac{(\lambda_1 - Dk^2)}{\lambda_1 - \lambda_2} \frac{\lambda_1}{\lambda_1^2 + \omega^2} \right. \\ &\quad \left. + \frac{(\lambda_2 - Dk^2)}{\lambda_2 - \lambda_1} \frac{\lambda_2}{\lambda_2^2 + \omega^2} \right] \end{aligned} \quad (31)$$

[terms of order $(a/b)^2$ have been neglected]. The contributions to the shifted lines are of two types, Lorentzian and non-Lorentzian. The element $S_{\beta_3\beta_3}(k, \omega)$ contains both types

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APPENDIX A: EIGENVALUES OF THE HYDRODYNAMIC MATRIX

It is the purpose of this appendix to establish the statements made in Sec. IV regarding the accuracy of the roots $p_I(\lambda)$ and $p_{\text{II}}(\lambda)$ relative to the exact roots of $p(\lambda)$. It can easily be shown that $R(\lambda)$, as defined by Eq. (9) has the following form:

$$R(\lambda) = r_0 \lambda^{n-1} + r_1 \lambda^{n-2} + \dots + r_{n-1}, \quad (\text{A1})$$

where $r_0 = O(a^2)$, $r_1 = O(a^3)$, ..., $r_{n-1} = O(a^{n+1})$. Denoting the roots of $p_I(\lambda)$ by $\lambda_1^I, \lambda_2^I, \dots, \lambda_{n-1}^I$ we can write $p(\lambda)$ as

$$p(\lambda) = (\lambda_1^I - \lambda)(\lambda_2^I - \lambda) \dots (\lambda_{n-1}^I - \lambda)p_{II}(\lambda) + R(\lambda). \quad (\text{A2})$$

Introducing $\lambda'_i = \lambda_i - \lambda_i^I$ as the difference between the real roots of $p(\lambda)$ and the similarly ordered roots of $p_I(\lambda)$, we can write for a specific root λ_i that

$$p(\lambda_i) = (\lambda_1^I - \lambda_i)(\lambda_2^I - \lambda_i) \dots (\lambda_{n-1}^I - \lambda_i) \times (\lambda_{n-1}^I - \lambda_i)p_{II}(\lambda_i) + R(\lambda_i) = 0. \quad (\text{A3})$$

The factors $(\lambda_j^I - \lambda_i)$ for $j \neq i$ are of order a , $p_{II}(\lambda_i)$ can readily be established as of order b^2 , and $R(\lambda_i)$ is of order a^{n+1} . Thus one can immediately write that

$$\lambda'_i = O[(a^2/b^2)a]. \quad (\text{A4})$$

Hence the difference between the exact real roots and the corresponding roots of $p_I(\lambda)$ is no more than of order $(a/b)^2 a$, that is the real roots of \underline{K} are given, correct to terms of order k^2 , by the roots of the real symmetric matrix \underline{K}_I .

We now consider the complex roots. Since $\lambda_1^I, \dots, \lambda_{n-1}^I$ are the roots of the matrix \underline{K}_I , from the theory of polynomials¹¹ we know that

$$\sum_{i=1}^{n-1} \lambda_i^I = \sum_{i=1}^{n-1} a_{ii}. \quad (\text{A5})$$

Analogously, denoting the roots of $p_{II}(\lambda)$ by λ_n^{II} and λ_{n+1}^{II} , we have

$$\lambda_n^{II} + \lambda_{n+1}^{II} = 2 \operatorname{Re} \lambda_n^{II} = a_{nn} + a_{n+1, n+1}. \quad (\text{A6})$$

Furthermore, application of the same theorem to the exact roots yields

$$\sum_{i=1}^{n+1} \lambda_i = \sum_{i=1}^{n+1} a_{ii}. \quad (\text{A7})$$

Combining Eqs. (A5)–(A7) one obtains

$$\sum_{i=1}^{n-1} (\lambda_i - \lambda_i^I) = 2(\operatorname{Re} \lambda_n^{II} - \operatorname{Re} \lambda_n). \quad (\text{A8})$$

But in the previous paragraph of this appendix we established that the left-hand side of Eq. (A8) is of order $(a/b)^2 a$. Hence the error in the real part of the complex roots is of order $(a/b)^2 a$, so that the real part of the imaginary roots of \underline{K} is given, correct up to terms of order k^2 by the real part of the roots of \underline{K}_{II} .

We still have to consider the imaginary part of the complex roots. We resort to the result of the theory of polynomials¹¹ that the sum of the products of the zeros of the characteristic polynomial, taken two at a time, is equal to the sum of all principal minors of order 2. Denoting the difference be-

tween the imaginary part of the complex roots of $p(\lambda)$ and the imaginary part of the roots of $p_{II}(\lambda)$ by θ , i. e.,

$$\lambda_n = \lambda_n^{II} + O[(a^2/b^2)a] + i\theta, \quad \text{and taking into account that } \lambda_{n+1} = \lambda_n^*$$

it is not difficult to establish that the sum of the products of the roots of $p(\lambda)$ taken two at a time can be written as $O(a^2) + (b + \theta)^2$, where we have recognized that, neglecting terms of order $(a/b)^2 b$, the imaginary part of λ_n^{II} is equal to b . The sum of all principal minors of order 2 can, from inspection of \underline{K} , be seen to be equal to $O(a^2) + b^2$. Thus according to the theorem stated above we have

$$O(a^2) + (b + \theta)^2 = O(a^2) + b^2.$$

Hence θ must be of order $(a/b)^2 b$ and the complex part of the imaginary roots of \underline{K} is given correct up to terms of order k by the imaginary part of the roots of \underline{K}_{II} .

APPENDIX B: EIGENVECTORS OF THE HYDRODYNAMIC MATRIX

The purpose of this appendix is to establish the validity of the assertions made in Sec. V, regarding the accuracy of the approximate eigenvectors of \underline{K} . Rather than develop the argument for a general case, we shall, for the sake of clarity, indicate the procedure for a three-dimensional matrix. The procedure involves solution of the exact eigenvector equations and comparison, term by term, with the approximate eigenvectors.

We first consider the eigenvector \underline{V}_1 corresponding to the real eigenvalue λ_1 , which is determined by the set of equations

$$\begin{bmatrix} a_{11} - \lambda_1 & a_{12} & 0 \\ a_{12} & a_{22} - \lambda_1 & b \\ 0 & -b & a_{33} - \lambda_1 \end{bmatrix} \begin{bmatrix} V_{11} \\ V_{21} \\ V_{31} \end{bmatrix} = 0. \quad (\text{B1})$$

The exact eigenvalue $\lambda_1 = \lambda_1^I + \lambda_1'$, with $\lambda_1^I = a_{11}$ and $\lambda_1' = O[(a^2/b^2)a]$. From the set of Eq. (B1) one obtains

$$V_{21} = (\lambda_1'/a_{12}) V_{11} = [O(a^2/b^2)]V_{11}$$

and

$$V_{31} = [b/(a_{33} - \lambda_1)] V_{21} = [O(a/b)]V_{11}. \quad (\text{B2})$$

The normalization condition for the eigenvectors, given in Ref. 6, Eq. (19), reads in the present case $V_{11}^2 + V_{21}^2 - V_{31}^2 = 1$. Inserting Eqs. (B2) in this equality yields $V_{11}^2 = 1 + O(a^2/b^2) + \dots$, so that

$$V_{11} = 1 + O(a^2/b^2) + \dots. \quad (\text{B3})$$

But in the present case, $V_{11}^I = 1$, and thus, as already claimed in Sec. V we have

$$V_{11} = V_{11}^I + O(a^2/b^2) + \dots. \quad (\text{B4})$$

Furthermore, combining Eqs. (B2) and (B3) one

gets

$$\begin{aligned} V_{21} &= O(a^2/b^2) + \dots, \\ V_{31} &= O(a/b) + \dots \end{aligned} \quad (\text{B5})$$

We now turn to the eigenvectors corresponding to the complex eigenvalues. Again one starts from the set of Eqs. (B1), now featuring a complex eigenvalue, say $\lambda_2 = \lambda_2^{\text{II}} + \lambda_2'$ where

$$\lambda_2^{\text{II}} = \frac{1}{2}(a_{22} + a_{33}) + i[b^2 - \frac{1}{4}(a_{22} - a_{33})^2]^{1/2}$$

and

$$\lambda_2' = O[(a^2/b^2)a] + iO[(a^2/b^2)b].$$

For the eigenvector elements the following relations hold:

$$\begin{aligned} V_{12} &= \frac{a_{12}}{\lambda_2 - a_{11}} V_{22} = \left[-\frac{ia_{12}}{b} + O\left(\frac{a^2}{b^2}\right) + \dots \right] V_{22}, \\ V_{32} &= \frac{-b}{\lambda_2 - a_{33}} V_{22} = \left[i - \frac{a_{22} - a_{33}}{2b} + iO\left(\frac{a^2}{b^2}\right) + \dots \right] V_{22}. \end{aligned} \quad (\text{B6})$$

Using the normalization requirement, which now reads $V_{12}^2 + V_{22}^2 - V_{32}^2 = 1$, one obtains $V_{22}^2 = \frac{1}{2} + iO(a/b) + O(a^2/b^2) + \dots$, where the term $O(a/b)$

can be shown to be equal to $-(a_{22} - a_{33})/4b$; thus,

$$V_{22} = \frac{1}{\sqrt{2}} - \frac{i(a_{22} - a_{33})}{b4\sqrt{2}} + O\left(\frac{a^2}{b^2}\right) + \dots \quad (\text{B7})$$

But the first two terms on the right-hand side of Eq. (B7) together form exactly V_{22}^{I} , thus

$$V_{22} = V_{22}^{\text{II}} + O(a^2/b^2) + \dots \quad (\text{B8})$$

From Eqs. (B6) and (B7) it follows that

$$\begin{aligned} V_{32} &= \frac{i}{\sqrt{2}} - \frac{(a_{22} - a_{33})}{b4\sqrt{2}} + iO\left(\frac{a^2}{b^2}\right) + \dots \\ &= V_{32}^{\text{II}} + iO\left(\frac{a^2}{b^2}\right) + \dots \end{aligned} \quad (\text{B9})$$

and

$$\begin{aligned} V_{12} &= -\frac{ia_{12}}{b\sqrt{2}} + O\left(\frac{a^2}{b^2}\right) + \dots \\ &= V_{12}^{(1)} + O\left(\frac{a^2}{b^2}\right) + \dots \end{aligned} \quad (\text{B10})$$

This completes the proof, for the special case of a three-dimensional hydrodynamic matrix, of the statements made in Sec. V regarding the approximate eigenvectors of the hydrodynamic matrix.

*NATO Science Fellow 1971-72.

¹Present address: Departement Scheikunde, Dienst voor Thermodynamika Vrije, Universiteit Brussel, 1050 Brussels, Belgium.

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Electronic-Recombination Coefficient of $^3\text{He}_2^+$ Compared to $^4\text{He}_2^+$ †

A. Wayne Johnson and J. B. Gerardo

Sandia Laboratories, Albuquerque, New Mexico 87115

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The electronic-recombination coefficient of $^3\text{He}_2^+$ is shown to be $(1.23 \times 10^{-8} + 5.04 \times 10^{-10}p) \text{ cm}^3 \text{ sec}^{-1}$, compared to that of $^4\text{He}_2^+$, which is $(1.15 \times 10^{-8} + 3.86 \times 10^{-10}p) \text{ cm}^3 \text{ sec}^{-1}$, where p is the gas pressure in Torr.

Since the electronic-recombination coefficient of helium molecular ions (He_2^+) has been shown to be larger^{1,2} than previously expected, the earlier theoretical models used to calculate this coefficient are not satisfactory. Although collisional stabilization of autoionizing levels of He_2^+ may be the dom-

inant mechanism in the recombination process,² no firm theoretical analysis of this mechanism has been presented. Thus, to date, the mechanisms which account for the electronic recombination of He_2^+ are not fully understood. We have obtained electronic-recombination coefficients of $^3\text{He}_2^+$ and