in terms of the jump frequency $\nu = 6D/d^2$ and spectral densities $I^{(q)}$ defined by

$$I^{(q)} = \sum_k g_{kk}^{(q)} - \tfrac{1}{4} \sum_{j,k} g_{jk}^{(q)}. \qquad \text{(C4a)}$$

The first sum is over all sites but one, and the second is over all *nearest neighbor pairs* (j, k), not including that one. In terms of the polar coordinates of the vectors to the special site, the functions $g_{jk}^{(q)}$ are given by

$$g_{jk}^{(1)} = \sin\theta_j \sin\theta_k \cos\theta_j \cos\theta_k \cos(\varphi_j - \varphi_k)/r_j^3 r_k^3,$$

$$g_{jk}^{(2)} = \sin^2\theta_j \sin^2\theta_k \cos(2\varphi_j - 2\varphi_k)/r_j^3 r_k^3. \qquad \text{(C4b)}$$

We have evaluated Eq. (C4:) for a magnetic field aligned along the c axis, including terms arising from sites no more distant than the third-neighbor distance. This results in the values $I^{(1)} = 0.341$, $I^{(2)} = 2.564$, and

$$(T_1^{-1})_{\text{inter}} = 0.361\gamma^4\hbar^2\nu/(b^6\omega^2) \qquad \text{(C5)}$$

expressed in terms of the intramolecular proton distance b for comparison with Eq. (46). An additive combination of $(T_1^{-1})_{\text{inter}}$ and $(T_1^{-1})_{\text{intra}}$ would yield $(T_1)_{\text{total}} = 0.675(T_1)_{\text{intra}}$; since our estimate of $(T_1^{-1})_{\text{inter}}$ is likely a lower bound, we adopt as a working equation $(T_1)_{\text{total}} = 0.6(T_1)_{\text{intra}}$ for Table IV.

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Light Scattering from Binary Solutions[*]

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The spectrum of the light scattered by a binary solution is calculated from thermodynamic fluctuation theory and the linearized hydrodynamic equations appropriate to a two-component fluid. The spectrum consists of three peaks. Expressions are obtained for the positions and widths of the two-side, Brillouin peaks. In general the central, unshifted Rayleigh peak is found to consist of a superposition of two Lorentzians that involve the combined dynamical effects of heat conduction and diffusion. The condition is stated under which it is possible to separate the central peak simply into two contributions, one arising from diffusion and one from thermal conduction. For many binary systems this separation is justified. In these cases measurement of the spectrum of the scattered light should prove to be an attractive alternative means of measuring the diffusion coefficient of binary solutions.

I. INTRODUCTION

In recent years there has been considerable interest in studying the spectral distribution of light scattered from fluid systems. Although the spectrum of the scattered light is confined to a narrow range of frequencies it is now possible to investigate the spectrum using a gas laser and an optical mixing system.[1] In this article we are concerned with the spectrum arising from a binary solution, away from its critical point. Our motivation for addressing this problem is twofold. First, we wish to investigate the kinds of information that may be obtained from binary solution Brillouin scattering. Second, we wish to provide an analysis that can be used as a reference point for investigations of more complicated situations, i.e., light scattering from multicomponent solutions or solutions where exchange of energy between internal modes[2,3] and/or where chemical reactions occur.[4]

The intensity of the scattered light is related to the space–time Fourier transform of the auto-correlation function of the local dielectric constant. To calculate this quantity we used the approach suggested by Landau and Placzek.[5] The space and time response of the system to a deviation from the equilibrium state is calculated using (i) linearized hydrodynamic equations to determine the modes by which the system returns to equilibrium as well as the relative amplitudes for each mode and (ii) thermodynamic fluctuation theory to provide

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[1] A. T. Forrester, J. Opt. Soc. Am. **51**, 253 (1961). H. Z. Cummins, N. Knable, and Y. Yeh, Phys. Rev. Letters **12**, 150 (1964); S. S. Alpert, Y. Yeh, and E. Lipworth, *ibid.* **14**, 486 (1965); N. C. Ford and G. B. Benedek, *ibid.* **15**, 649 (1965); J. B. Lastovka and G. B. Benedek, *ibid.* **17**, 1039 (1966).

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[5] L. Landau and G. Placzek, Physik Z. Sowjetunion **5**, 172 (1934). For more details of the method see, for example, R. Pecora, J. Chem. Phys. **40**, 1604 (1964), R. D. Mountain, Rev. Mod. Phys. **38**, 205 (1966), or J. A. McLennan, Helv. Phys. Acta **40**, 645 (1967).

initial values for the correlation functions. We include all hydrodynamic effects appropriate to a two-component fluid.

As might be expected the spectrum we calculate consists of three components; an unshifted central (Rayleigh) component and two shifted Brillouin components. The shifted Brillouin doublet arises from pressure fluctuations at constant entropy. These fluctuations have a frequency spectrum associated with sound waves or phonons with the adiabatic speed of sound

$$c_0=[(\partial p/\partial \rho)_{s,c}]^{1/2}, \tag{1.1}$$

where p, ρ, s, and c are respectively the pressure, density, entropy, and concentration of the mixture. Two lines are observed because the sound waves propagate in opposite directions at the speed c_0. These lines are broadened by the dissipative processes in the solution which lead to sound absorption.

The central Rayleigh component contains the combined effects of entropy (or temperature) fluctuations at constant pressure and concentration fluctuations. An important conclusion of our analysis is that, in general, the effects of heat conduction and diffusion on the width of the Rayleigh component cannot be separated in a simple way. The cross effects between energy transport and diffusion that are present in a binary fluid result in a more complicated structure for the Rayleigh line. These cross effects are well known in nonequilibrium thermodynamics[6] as the Dufour effect (a concentration gradient inducing heat flow) and Soret effect (a temperature gradient inducing a diffusion flux).

We point out the conditions under which a simple separation of the effects of heat conduction and diffusion occur. Many binary systems satisfy these conditions so that light scattering will be useful for the determination of diffusion coefficients.

II. LIGHT-SCATTERING FORMALISM

In thermodynamic fluctuation theory the random thermal motion of molecules in a fluid is considered to produce fluctuations in a set of complete, local thermodynamic variables. These fluctuations result in local variations in the dielectric constant and therefore in scattering of light. The intensity of the scattered light is given by the expression[7]

$$I(\mathbf{R}_0, \mathbf{k}, \omega)=I_0(Nk_0^4/32\pi^3R_0^2)\sin^2\Phi S(\mathbf{k}, \omega), \tag{2.1}$$

where $\mathbf{k}$ is the *change* in wave vector and ω the *change* (measured in radians per second) in frequency of the light upon scattering, R_0 is the distance from the origin to the point of observation, Φ is the angle between the electric vector of the incident intensity I_0 and $\mathbf{R}_0$. The relationship between the magnitudes of $\mathbf{k}$ and the incident wave vector $\mathbf{k}_0$ is

$$k=2nk_0\sin(\theta/2), \tag{2.2}$$

where n is the average index of refraction of the medium and θ is the scattering angle. In Eq. (2.1) $S(\mathbf{k}, \omega)$ is the generalized structure factor

$$S(\mathbf{k},\omega)=2\operatorname{Re}\int_0^\infty dt\int d\mathbf{r}d\mathbf{r}'$$
$$\times\langle\delta\epsilon(\mathbf{r}+\mathbf{r}', t)\delta\epsilon(\mathbf{r}', 0)\rangle\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)], \tag{2.3}$$

where $\delta\epsilon(\mathbf{r}, t)$ is the fluctuation in the local dielectric constant at the point $\mathbf{r}$ at time t. In terms of Fourier–Laplace transforms

$$S(\mathbf{k},\omega)=2\operatorname{Re}\langle\hat{\epsilon}(\mathbf{k}, i\omega)\epsilon(-\mathbf{k})\rangle, \tag{2.4}$$

where

$$\hat{\epsilon}(\mathbf{k}, z)=\int_0^\infty dt\int d\mathbf{r}\delta\epsilon(\mathbf{r}, t)\exp[i\mathbf{k}\cdot\mathbf{r}-zt] \tag{2.5}$$

and

$$\epsilon(\mathbf{k})=\int d\mathbf{r}\delta\epsilon(\mathbf{r}, 0)\exp(i\mathbf{k}\cdot\mathbf{r}). \tag{2.6}$$

The caret is used to indicate a Laplace-time transform. If only k is indicated as a variable, the time-independent initial value is implied. The angular bracket $\langle\cdots\rangle$ indicates an average over the initial states of the system. Our basic concern is to compute $S(\mathbf{k}, \omega)$ for a two-component solution.

We begin by relating the fluctuations in the local dielectric constant to fluctuations in the local thermodynamic quantities such as the pressure, concentration, and temperature:

$$\delta\epsilon(\mathbf{r}, t)=(\partial\epsilon/\partial p)_{T,c}\delta p(\mathbf{r}, t)$$
$$+(\partial\epsilon/\partial T)_{p,c}\delta T(\mathbf{r}, t)+(\partial\epsilon/\partial C)_{p,T}\delta C(\mathbf{r}, t). \tag{2.7}$$

We shall use the linearized hydrodynamic equations to describe the time dependence of the fluctuations. For this system these equations are the continuity equation[8]

$$(\partial\rho/\partial t)+\rho_0\operatorname{div}\mathbf{v}=0, \tag{2.8}$$

the longitudinal part of the Navier–Stokes equation

$$\rho_0(\partial\mathbf{v}/\partial t)=-\operatorname{grad}p+\eta_s\nabla^2\mathbf{v}$$
$$+(\tfrac{1}{3}\eta_s+\eta_v)\operatorname{grad}\operatorname{div}\mathbf{v}, \tag{2.9}$$

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[6] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland Publ. Co., Amsterdam, 1962), Chap. 11, p. 278 *et. seq.*

[7] L. Landau and E. Lifshitz, *Electrodynamics of Continuous Media* (Addison–Wesley Publ. Co., Inc., Reading, Mass., 1960), Chap. 14.

[8] L. Landau and E. Lifshitz, *Fluid Mechanics* (Addison–Wesley Publ. Co., Inc., Reading, Mass., 1959), Chap. 6. The heat-flux vector introduced here differs from that of Ref. 6, p. 26 by a term $h\mathbf{i}$, where h is the difference of the partial specific enthalpies of the components and $\mathbf{i}$ is the diffusion flux of one of the components.

the diffusion equation

$$\partial C/\partial t = D[\nabla^2 c + (k_T/T_0)\nabla^2 T + (k_p/p_0)\nabla^2 p], \quad (2.10)$$

and the energy transport equation

$$\rho_0 C_p \frac{\partial T}{\partial t} - \rho_0 k_T \left(\frac{\partial \mu}{\partial c}\right)_{p,T} \frac{\partial c}{\partial t} + \rho_0 T_0 \left(\frac{\partial S}{\partial p}\right)_{T,c} \frac{\partial p}{\partial t} = \kappa \nabla^2 T. \quad (2.11)$$

In these equations T is the temperature; μ the chemical potential of the mixture[9]; C_p the specific heat at constant pressure, $\mathbf{v}$ the mass velocity, k_p the thermodynamic quantity

$$k_p = -\frac{(p_0/\rho_0^2)(\partial\rho/\partial c)_{p,T}}{(\partial\mu/\partial c)_{p,T}}.$$

Equilibrium values are denoted by a subscript zero. Other quantities appearing in these equations are the transport coefficients: κ is the thermal conductivity, η_s and η_v are the shear and volume viscosities, respectively, D is the diffusion coefficient, and k_T is the thermal diffusion ratio.

Next, we must express Eqs. (2.8)–(2.11) in terms of the variables that have been chosen to characterize the local state of the fluid. For a binary system we must choose three such state variables. While any three independent variables will suffice for the calculation certain choices will prove a good deal more convenient than others. The criterion we shall use to select the three state variables (x_1, x_2, x_3) is that the probability of a fluctuation $w(x_1, x_2, x_3)$ is statistically independent; i.e., $w(x_1, x_2, x_3) = h_1(x_1)h_2(x_2)h_3(x_3)$.[9a] The Boltzmann principle gives the probability w as

$$w \propto \exp(\Delta S_T/k_B), \quad (2.12)$$

where ΔS_T is the change in entropy of system plus surroundings caused by the fluctuation. If for convenience we choose our system to contain one gram of solution then[10]

$$\Delta S_T/k_B = -(1/2k_BT_0)[\delta s\delta T - \delta V\delta p + \delta\mu\delta c]. \quad (2.13)$$

It is easy to show that the Gaussian approximation $\langle\delta T\delta p\rangle \neq 0$ and $\langle\delta s\delta c\rangle \neq 0$. Hence the two obvious candidate choices (T, p, c) and (p, s, c) do not satisfy our criterion of statistical independence.

If we consider the set of variables (ϕ, p, c), where

$$\phi = T - (T_0\alpha_T/C_p\rho_0)p; \quad [\delta\phi = \delta T - (T_0\alpha_T/C_p\rho_0)\delta p], \quad (2.14)$$

then it is easily shown in the Gaussian approximation that

$$\frac{\Delta S_T}{k_B} = -\frac{1}{2k_BT_0}\left[\frac{C_p}{T_0}(\delta\phi)^2 + \frac{\beta_s}{\rho_0}(\delta p)^2 + \left(\frac{\partial\mu}{\partial c}\right)_{p,T}(\delta c)^2\right]. \quad (2.15)$$

In these equations α_T is the isothermal expansion coefficient, β_s is the adiabatic compressibility

$$\beta_s = \frac{1}{\rho_0}\left(\frac{\partial\rho_0}{\partial p}\right)_{s,c} = \frac{\beta_T}{\gamma}, \quad (2.16)$$

where $\gamma = C_p/C_v$ and β_T is the isothermal compressibility. The set of variables (ϕ, p, c) is the unique linear combination of the variables (T, p, c) which is a statistically independent set. We express fluctuations in the local dielectric constant, in terms of spatial Fourier transforms, as

$$\epsilon(\mathbf{k}, t) = \left(\frac{\partial\epsilon}{\partial p}\right)_{\phi,c} p(\mathbf{k}, t) + \left(\frac{\partial\epsilon}{\partial\phi}\right)_{p,c} \phi(\mathbf{k}, t) + \left(\frac{\partial\epsilon}{\partial c}\right)_{\phi,p} c(\mathbf{k}, t). \quad (2.17)$$

The probability distribution obtained by substituting Eq. (2.15) in Eq. (2.12) will be used to obtain the quantities $\langle|p(\mathbf{k})|^2\rangle$, $\langle|\phi(\mathbf{k})|^2\rangle$ and $\langle|c(\mathbf{k})|^2\rangle$. Since k^{-1} is much greater than the range of molecular correlations this is an acceptable procedure. Near the critical point this breaks down as the range of molecular correlations is comparable to k^{-1}. Also, the expansions used to obtain Eq. (2.15) are of doubtful validity near the critical point.[11]

Our next task is to use Eqs. (2.8)–(2.11) to obtain $p(\mathbf{k}, t)$, $\phi(\mathbf{k}, t)$ and $c(\mathbf{k}, t)$ in terms of the initial fluctuations $p(\mathbf{k})$, $\phi(\mathbf{k})$, $c(\mathbf{k})$.

III. CALCULATION OF THE CORRELATION FUNCTION MATRIX

We now rewrite the linearized hydrodynamic equations (2.8)–(2.11) in terms of the variables p, ϕ, c, and $\psi = \operatorname{div}\mathbf{v}$. In terms of Fourier–Laplace transforms this set of equations, in matrix form, is

$$M\cdot\hat{N}(\mathbf{k}, z) = T\cdot N(\mathbf{k}), \quad (3.1)$$

where $\hat{N}(\mathbf{k}, z)$ is a column vector with elements

$$\hat{c}(\mathbf{k}, z), \hat{p}(\mathbf{k}, z), \hat{\phi}(\mathbf{k}, z), \hat{\psi}(\mathbf{k}, z).$$

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[9] For one gram of solution $\mu = \mu_1/m_1 - \mu_2/m_2$, where m_1 and m_2 are the masses and μ_1 and μ_2 are the chemical potentials of the two species. See Ref. 8, p. 221.

[9a] *Note added in proof:* P. C. Jordan and J. R. Jordan [J. Chem. Phys. **45**, 2492 (1966)] describe a scheme for choosing variables. Some of the results of the present paper are quoted there. We wish to thank the referee for calling our attention to this work.

[10] L. Landau and E. Lifshitz, *Statistical Physics* (Addison–Wesley Publ. Co., Inc., Reading, Mass., 1958), Chap. 12. We have assumed that fluctuations in ψ are not correlated with fluctuations in the thermodynamic variables. Since $\partial\epsilon/\partial\psi = 0$ we have not included the probability of a fluctuation in ψ in Eqs. (2.12)–(2.15).

[11] M. E. Fisher, J. Math. Phys. **5**, 944 (1964).

The 4×4 matrix M has the form

$$M=\begin{bmatrix} z(\partial\rho/\partial c)_{p,T} & z/c_0^2 & z(\partial\rho/\partial T)_{p,c} & \rho_0 \\ 0 & -k^2/\rho_0 & 0 & z+bk^2 \\ z+Dk^2 & Dk^2[(k_p/p_0)+(k_T\alpha_T/\rho_0C_p)] & Dk^2(k_T/T_0) & 0 \\ -z(k_T/C_p)(\partial\mu/\partial c)_{p,T} & \chi k^2(T_0\alpha_T/\rho_0C_p) & z+\chi k^2 & 0 \end{bmatrix} \tag{3.2}$$

and the 4×4 matrix T has the form

$$T=\begin{bmatrix} (\partial\rho/\partial c)_{p,T} & c_0^{-2} & (\partial\rho/\partial T)_{p,c} & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ -(k_T/C_p)(\partial\mu/\partial c)_{p,T} & 0 & 1 & 0 \end{bmatrix}. \tag{3.3}$$

We have introduced

$$\chi=\kappa/\rho_0C_p \tag{3.4}$$

and

$$b=(\tfrac{4}{3}\eta_s+\eta_v)/\rho_0.$$

The solution of Eq. (3.1) is straightforward and the algebraic details will not be included here. The general structure of the solutions is

$$\hat{N}_i(\mathbf{k},z)=[\det(M(\mathbf{k},z))]^{-1}\sum_j P_{ij}(\mathbf{k},z)N_j(\mathbf{k}), \tag{3.5}$$

where the P_{ij} are algebraic fuuctions. We are interested in correlation functions of the form $\langle\hat{N}_i(\mathbf{k},z)N_j(-\mathbf{k})\rangle$. From Eq. (3.5) it follows that

$$\langle\hat{N}_i(\mathbf{k},z)N_j(-\mathbf{k})\rangle =[P_{ij}(\mathbf{k},z)/\det(M)]\langle\,|N_j(\mathbf{k})\,|^2\rangle \tag{3.6}$$

as we have assumed that the $\{N_i\}$ are statistically independent.

An expression for the correlation functions is obtained by taking the inverse Laplace transform of Eq. (3.6):

$$\langle N_i(\mathbf{k},t)N_j(-k)\rangle=\frac{\langle\,|N_j(\mathbf{k})\,|^2\rangle}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega e^{i\omega t}P_{ij}(\mathbf{k},i\omega)}{\det(M(\mathbf{k},i\omega))}. \tag{3.7}$$

In order to perform this inversion we must obtain the roots of $\det(M)$. We seek approximate roots of $\det(M)$ considering as small the dimensionless parameters $(\chi k/c_0)$, (bk/c_0), and (Dk/c_0). In typical experiments $k\simeq10^5$ cm^{-1}, $c_0\simeq10^5$ cm/sec so that these quantities are on the order of 10^{-2}, 10^{-2}, and 10^{-4}, respectively. To lowest order the roots of $\det(M)=0$ are $z=0$, 0, $\pm ic_0k$.

In the next approximation when linear terms in the small quantities are retained one obtains

$$\det(M(\mathbf{k},z))=-c_0^2(z+z_1)(z+z_2) \times(z-ic_0k+\Gamma k^2)(z+ic_0k+\Gamma k^2). \tag{3.8}$$

The roots related to the two propagating modes are

$$z=\pm ic_0k-\Gamma k^2 \tag{3.9}$$

with

$$\Gamma=\frac{1}{2}\left\{\frac{(4/3)\eta_s+\eta_v}{\rho_0}+\chi(\gamma-1)+\frac{Dc_0^2}{\rho_0^2(\partial\mu/\partial c)_{p,T}} \times\left[\left(\frac{\partial\rho}{\partial c}\right)_{p,T}+\frac{k_T}{C_p}\left(\frac{\partial\rho}{\partial T}\right)_{p,c}\left(\frac{\partial\mu}{\partial c}\right)_{p,T}\right]^2\right\}. \tag{3.10}$$

The roots z_1 and z_2 related to the nonpropagating modes are

$$z_1=\tfrac{1}{2}[\chi k^2+\mathfrak{D}k^2]+\tfrac{1}{2}\{[\chi k^2+\mathfrak{D}k^2]^2-4\chi Dk^4\}^{1/2} \tag{3.11}$$

and

$$z_2=\tfrac{1}{2}[\chi k^2+\mathfrak{D}k^2]-\tfrac{1}{2}\{[\chi k^2+\mathfrak{D}k^2]^2-4\chi Dk^4\}^{1/2}, \tag{3.12}$$

where

$$\mathfrak{D}=D[1+(k_T^2/T_0C_p)(\partial\mu/\partial c)_{p,T}]. \tag{3.13}$$

These roots which determine the modes by which a two-component system responds to deviations from thermal equilibrium have been previously obtained by Martin.[12]

We are now in a position to take the inverse Laplace transform indicated in Eq. (3.7). To terms linear in the

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[12] P. Martin in *Statistical Mechanics of Equilibrium and Non-Equilibrium*, J. Meixner, Ed. (North-Holland Publ. Co., Amsterdam, 1965), p. 124.

designated small quantities one finds[13]

$$\langle p(\mathbf{k},t)p(-k)\rangle/\langle|p(\mathbf{k})|^2\rangle=\exp(-\Gamma k^2t)\cos(c_0kt) \tag{3.14}$$

$$\frac{\langle\phi(\mathbf{k},t)\phi(-\mathbf{k})\rangle}{\langle|\phi(\mathbf{k})|^2\rangle}=\left(\frac{z_1-Dk^2}{z_1-z_2}\right)\exp(-z_1t)+\left(\frac{z_2-Dk^2}{z_2-z_1}\right)\exp(-z_2t) \tag{3.15}$$

$$\frac{\langle c(\mathbf{k},t)c(-\mathbf{k})\rangle}{\langle|c(\mathbf{k})|^2\rangle}=\left(\frac{z_2-Dk^2}{z_2-z_1}\right)\exp(-z_1t)+\left(\frac{z_1-Dk^2}{z_1-z_2}\right)\exp(-z_2t), \tag{3.16}$$

$$\frac{\langle\phi(\mathbf{k},t)c(-\mathbf{k})\rangle}{\langle|c(\mathbf{k})|^2\rangle}=\frac{Dk^2k_T(\partial\mu/\partial c)_{p,T}}{C_p(z_1-z_2)}[\exp(-z_1t)-\exp(-z_2t)]=\frac{\langle c(\mathbf{k},t)\phi(-\mathbf{k})\rangle}{\langle|\phi(\mathbf{k})|^2\rangle}\left(\frac{c_p}{T_0(\partial\mu/\partial c)_{p,T}}\right). \tag{3.17}$$

With these results and use of Eqs. (2.4) and (2.16) we obtain our final expression for $S(\mathbf{k},\omega)$:

$$\begin{aligned}S(\mathbf{k},\omega)={}&\left(\frac{\partial\epsilon}{\partial p}\right)_{\phi,c}^2\frac{k_BT_0\rho_0}{\beta_s}\left(\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega+c_0k)^2}+\frac{\Gamma k^2}{(\Gamma k^2)^2+(\omega-c_0k)^2}\right)\\&+\left(\frac{\partial\epsilon}{\partial c}\right)_{p,\phi}^2\left(\frac{k_BT_0}{(\partial\mu/\partial c)_{p,T}}\right)\left(\frac{2}{z_2-z_1}\right)\left(\frac{(z_2-Dk^2)z_1}{z_1^2+\omega^2}+\frac{(z_1-Dk^2)z_2}{z_2^2+\omega^2}\right)\\&+\left(\frac{\partial\epsilon}{\partial\phi}\right)_{c,p}^2\left(\frac{k_BT_0^2}{C_p}\right)\left(\frac{2}{z_2-z_1}\right)\left(\frac{(Dk^2-z_1)z_1}{z_1^2+\omega^2}-\frac{(Dk^2-z_2)z_2}{z_2^2+\omega^2}\right)\\&+\left(\frac{\partial\epsilon}{\partial\phi}\right)_{p,c}\left(\frac{\partial\epsilon}{\partial c}\right)_{p,\phi}\left(\frac{2k_BT}{C_p}\right)\left(\frac{2Dk^2k_T}{z_1-z_2}\right)\left(\frac{z_1}{z_1^2+\omega^2}-\frac{z_2}{z_2^2+\omega^2}\right).\end{aligned} \tag{3.18}$$

We have replaced the equilibrium averages appearing in Eqs. (3.15)–(3.18) by their $k\rightarrow0$ limit. These averages have been computed from Eqs. (2.12) and (2.15).

It is interesting to observe that the last term in Eq. (3.19) is of purely dynamical origin and is unexpected from thermodynamic fluctuation theory considerations.[14] This term does not effect the intensity ratio of the Rayleigh and Brillouin components as the integrated intensity is zero.

Finally we note that it is possible to show from elementary thermodynamic considerations that

$$\begin{gathered}(\partial\epsilon/\partial c)_{p,\phi}=(\partial\epsilon/\partial c)_{p,T},\\(\partial\epsilon/\partial\phi)_{p,c}=(\partial\epsilon/\partial T)_{p,c},\\\left(\frac{\partial\epsilon}{\partial p}\right)_{\phi,c}=\left(\frac{\partial\epsilon}{\partial p}\right)_{s,c}=\left(\frac{\partial\epsilon}{\partial p}\right)_{T,c}+\frac{T_0\alpha_T}{\rho_0C_p}\left(\frac{\partial\epsilon}{\partial T}\right)_{p,c}.\end{gathered} \tag{3.19}$$

This relates the dielectric constant derivatives to measurable quantities.

IV. DISCUSSION

The spectrum associated with a binary solution consists of three peaks. The two Brillouin peaks are centered at frequencies $\omega=\pm c_0k$ and have a Lorentzian shape with width Γk^2. The central peak consists of the superposition of two Lorentzians with amplitudes involving many parameters. The complex structure of the expression describing the central Rayleigh peak is a direct consequence of the coupling between diffusion and heat flow that exists in binary systems. In general, the central peak cannot be simply considered as the superposition of two Lorentzians, the first arising from thermal conduction and the second from diffusion.

There are, however, a number of conditions, met by a wide variety of binary systems, that result in a simplified expression for the central component line shape. The implication is that in these cases it will be possible to obtain information about a specific transport coefficient from the width of the central line.

We wish to mention that precisely the same expression for the spectrum of the central peak is obtained if one considers a uniform pressure system where only concentration and temperature fluctuations take place. In this case one uses the hydrodynamic Eqs. (2.10) and (2.11) with the pressure terms absent.

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[13] In order to satisfy the initial condition $\langle p(\mathbf{k},0)\psi(-\mathbf{k})\rangle=0$ one must take small terms, which have been neglected in Eq. (3.14), into account. This changes $\cos(c_0kt)$ to $\cos(c_0kt-\varphi)$ where the phase angle φ is a small quantity. A nonzero value of φ leads to non-Lorentzian terms in the Brillouin components. See L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) **24**, 419 (1963), C. J. Montrose, V. A. Solovyev, and T. A. Litovitz, J. Acoust. Soc. Am. **43**, 117 (1968) for discussion of this point. Such terms were not included here since the effect of them is usually too small to be observed in systems which do not exhibit internal relaxation processes.

[14] G. A. Miller, J. Phys. Chem. **71**, 2305 (1967).

The ratio J of the intensity of the central peak i_c to that of the two Brillouin peaks $2i_B$ is

$$J=i_c/2i_B=\frac{[k_BT_0/(\partial\mu/\partial c)_{p,T}](\partial\epsilon/\partial c)^2{}_{p,T}+(k_BT_0^2/C_p)(\partial\epsilon/\partial T)^2{}_{p,c}}{(k_BT_0\rho_0/\beta_s)(\partial\epsilon/\partial p)^2{}_{T,c}} \tag{4.1}$$

Miller[14] has recently obtained this value of J from thermodynamic arguments. He points out the interesting possibility of using measured values of J to obtain activity coefficients.

There is one reported measurement of linewidths of Brillouin components in binary solutions. Fabelinskii *et al.*, have measured the widths and positions of the Brillouin doublets in the system t-butyl-alcohol/H_2O at 21°C for a number of concentrations.[15] The splittings were used to obtain a hypersound velocity v. The widths are not interpreted on the basis of Eq. (3.10) but rather are used to estimate the dispersion of v on the basis of a frequency-dependent volume viscosity.[16]

In certain situations the general expression for $S(\mathbf{k},\omega)$ will simplify. For example, as the solute concentration becomes small the diffusion constant D approaches a finite value and the thermal diffusion ratio k_T tends to zero.[8] In this case the widths of the Brillouin peaks approaches

$$\Gamma\to\frac{1}{2}\left[\frac{(4/3)\eta_s+\eta_v}{\rho_0}+\chi(\gamma-1)+\frac{Dc_0^2}{\rho_0^2}\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}^2\right] \tag{4.2}$$

and $z_1\rightarrow\chi k^2$, $z_2\rightarrow Dk^2$. The *central* part of the spectrum now has the form

$$S(\mathbf{k},\omega)^{\text{cen}}=\left(\frac{\partial\epsilon}{\partial c}\right)_{p,T}^2\left(\frac{k_BT_0}{(\partial\mu/\partial c)_{p,T}}\right)\left(\frac{2Dk^2}{(Dk^2)^2+\omega^2}\right)+\left(\frac{\partial\epsilon}{\partial T}\right)_{c,p}^2\left(\frac{k_BT_0}{C_p}\right)^2\left(\frac{2\chi k^2}{(\chi k^2)^2+\omega^2}\right). \tag{4.3}$$

Since in the limit $k_T\rightarrow 0$ heat conduction and diffusion are uncoupled the central Rayleigh line consists of the superposition of two Lorentzians with widths which are directly proportional to the thermal diffusivity χ and the diffusion coefficient D. In this limiting case it may be possible to resolve the two components of the central peak and hence obtain an experimental determination of D and χ.

For many binary solutions one finds $\chi\gg D$. Under these circumstances $z_1\approx\chi k^2$ and $z_2\approx Dk^2$. The central part of the spectrum has the form of Eq. (4.3) Since $\chi\gg D$ the part arising from diffusion appears as a sharp narrow peak superimposed over a much broader peak arising from heat conduction. Assuming reasonable values for the factors multiplying the two Lorentzian contributions it may frequently be possible to assign the measured central peak solely to diffusion. Many binary solutions satisfy the condition $\chi\gg D$, and it is probably on this class of systems that experiments can most profitably be performed.

Recently Fabelinskii *et al.*[17] measured the width of the central peak in the binary solutions carbon disulfide/acetone and n-propanol/bromoform. These authors attribute the entire central peak to diffusion and for the n-propanol/bromoform system report the variation of the diffusion constant with concentration. The reported values of D are of the order of 10^{-5} cm^2/sec. One may easily estimate χ for these solutions using measured values of λ for the pure components and empirical combination rules.[18] One finds that χ is of the order of 10^{-3} cm^2/sec so that the condition $\chi\gg D$, is easily met. In an analogous experiment Dubin, Lunacek, and Benedek[19] determined the diffusion constant of a number of biologically interesting macromolecules [$D\approx 10^{-7}$ cm^2/sec] by measuring the width of the central Rayleigh line. These experiments indicate that for a wide class of systems light scattering provides a practical alternative to the complicated conventional methods for measuring diffusion coefficients.

We may also consider the opposite case where the mixture has a very high heat capacity and hence temperature variations may be neglected. In this case the width of the Brillouin peaks approaches

$$\Gamma\to\frac{1}{2}\left[\frac{(4/3)\eta_s+\eta_v}{\rho_0}+\frac{DC_0^2}{\rho_0}\left(\frac{\partial c}{\partial\mu}\right)_{p,T}\left(\frac{\partial\rho}{\partial c}\right)_{p,T}^2\right] \tag{4.4}$$

and $z_1\rightarrow 0$, $z_2\rightarrow Dk^2$. The *central* part of the spectrum has the form

$$S(\mathbf{k},\omega)^{\text{cen}}=\left(\frac{\partial\epsilon}{\partial c}\right)_{p,T}\left(\frac{k_BT_0}{(\partial\mu/\partial c)_{p,T}}\right)\left(\frac{2Dk^2}{(Dk^2)^2+\omega^2}\right). \tag{4.5}$$

In this approximation $(\partial\epsilon/\partial p)_{c,s}\approx(\partial\epsilon/\partial\rho)_{c,T}$ and c_0 may be replaced by the isothermal speed of sound. Exactly the same spectrum is obtained if one begins by considering a uniform temperature system so that the temperature system so that the temperature terms are absent in the hydrodynamic equations.

We wish to call attention to the work of Blum[20] on light scattering from multicomponent systems. He considers the problem of calculating the spectrum of light scattered by multicomponent fluid. The binary system is examined by way of illustration.

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[16] For a discussion of the consequences of including frequency dependence in η_v see Ref. 2 and I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968), Chap. 6.

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