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Theory of Stimulated Concentration Scattering*

N. Bloembergen,[†] W. H. Lowdermilk,[‡] M. Matsuoka, and C. S. Wang
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

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From the general formulation of the coupling of a laser wave and a scattered light wave with density, temperature, and concentration fluctuations in a binary fluid mixture, an expression for the gain g_c of stimulated concentration scattering is derived. It is shown that this gain is usually much smaller than the gain for stimulated Brillouin scattering g_B. However, in gaseous mixtures at relatively low pressures with a large difference in polarizability as well as in mass between the two components, g_c can become larger than g_B. A large difference in polarizabilities increases the coupling of light to the concentration fluctuations, while a large difference in mass produces a pronounced increase in damping of a sound wave. The calculated values for g_c/g_B are compared with experimental results.

I. INTRODUCTION

Spontaneous light scattering from fluids has a long history. The spectral triplet in the scattered light spectrum, consisting of a central (Rayleigh) peak and a Brillouin doublet, is well known.[1,2] The low-lying excitations of the medium involved in these scattering processes are the thermal diffusion and the acoustical phonon modes, respectively. In a binary mixture of fluids the Rayleigh cross section for the central component can be very much enhanced, because the contribution from concentration fluctuations can be larger than that from temperature fluctuations. There are, of course, many other types of excitations which contribute to the scattered light spectrum. Examples are rotational motions or librations of anisotropic molecules (inelastic Rayleigh wing scattering) and vibrational excitations or optical phonon modes (Raman scattering). All of these spontaneous scattering processes have been studied with renewed vigor and much greater precision by means of gas-laser beams during the past decade.[2,3]

In principle there are stimulated scattering processes associated with each spontaneous process.[4] The intensity in a scattered mode can be amplified exponentially with a gain coefficient proportional to the incident laser intensity. If this gain coefficient is larger than the unavoidable (linear) absorption and spontaneous scattering losses, some preferred scattered light modes may build up to very high intensities. Usually the stimulated process with the lowest threshold is dominant and may deplete the laser intensity before other processes can be stimulated. Due to differences in a transient response it is sometimes possible to excite two or more stimulated processes with a high intensity laser pulse. Since the response of low-lying hydrodynamic excitations is slow, they are best stimulated in relatively long laser pulses. The results of a steady-state gain theory are valid in the limit that the spectral width of the laser is smaller than the spontaneous linewidth divided by the gain coefficient.

Stimulated Brillouin and Raman scattering are most frequently observed, and their relative steady-state and transient characteristics have been studied in detail. Stimulated Rayleigh wing scattering in liquids from anisotropic molecules is also well established.[4]

Stimulated scattering associated with the sharp central Rayleigh peak is more difficult to demonstrate experimentally without ambiguity. It is characterized by a small frequency shift and is usually difficult to stimulate by the short pulses from Q-switched lasers. The thermal Rayleigh scattering from temperature fluctuations induced by absorption has been demonstrated convincingly,[5,6] and the thermal scattering induced by the electrocaloric effect in a nonabsorbing fluid has been discussed in several papers by Fabelinskii and co-workers.[6]

Two experiments have been reported which claim to have demonstrated stimulated concentration scattering. One of these was concerned with a binary mixture of liquids,[7] the other with a mixture of gases.[8] It is the purpose of this paper to present a systematic investigation, analyzing the relative importance of the stimulated scattering from density, temperature, and concentration fluctuations. In Sec. II we present the relevant dynamical equations of a fluid mixture and discuss their range of validity. In Sec. III the coupling mechanisms with the electromagnetic fields are analyzed. The concentration scattering can easily be made to dominate the thermal scattering, but the ever present Brillouin scattering usually has a much higher gain. The steady-state solutions for stimulated concentration and Brillouin scattering from a binary fluid mixture are given in Sec. IV. It is shown in Sec. V that the stimulated concentration scattering can become dominant only in selected situations, e.g., in a binary gas mixture at relatively low pressure with two components with large differences in mass and polarizability. Numerical calculations on the competition between stimulated Brillouin and concentration scattering are compared with recent experimental results.[7-9] The agreement is satisfactory, but our calculations show some doubt on the correctness of the interpretation that stimulated concentration scattering was responsible for the earlier observations.[7,8]

II. REVIEW OF THE DYNAMICAL EQUATIONS IN A FLUID MIXTURE

Consider a mixture of two fluids.[10] Let there be N_1 molecules of mass m_1 and N_2 molecules of mass m_2 per unit volume. The chemical potentials of the two species are μ_1 and μ_2, respectively. The differential free energy may then be expressed as

$$dF = -S\,dT - P\,dV + \mu_1 dN_1 + \mu_2 dN_2 \ . \tag{1}$$

The mass density is

$$\rho = N_1 m_1 + N_2 m_2 = N[c' m_1 + (1-c')m_2] \ , \tag{2}$$

where N is the total number of particles per unit volume and c' is the relative number concentration of the first species. It is related to the relative mass concentration c by

$$c = c'[c' + (1-c')(m_2/m_1)]^{-1} \tag{3}$$

and

$$\frac{\partial c}{\partial c'} = \left(\frac{\partial c'}{\partial c}\right)^{-1} = \frac{m_1 m_2}{[m_1 c' + m_2(1-c')]^2} = \frac{[m_2 c + (1-c)m_1]^2}{m_1 m_2} \ . \tag{4}$$

If pressure, temperature, and mass concentration are taken as independent variables, the total differential of the Gibbs free energy per unit mass may be written as

$$d\Phi = -s\,dT + v\,dP + \mu\,dc \ , \tag{5}$$

where the chemical potential of the mixture per unit mass μ has been introduced:

$$\mu = (\mu_1/m_1) - (\mu_2/m_2) \ . \tag{6}$$

The diffusion current may be expressed as

$$\vec{\mathrm{i}} = \alpha \nabla\mu - \beta\nabla T \ , \tag{7}$$

where the last term represents the thermal diffusion. The heat current is given by

$$\vec{\mathrm{q}} = \left(\mu + \frac{\beta T}{\alpha}\right)\vec{\mathrm{i}} - \kappa\nabla T \ . \tag{8}$$

The last term represents the heat current in the absence of diffusion. These convection equations are valid if the relative variation of the thermodynamic quantities over a mean free path of the molecules is small.

The chemical potential μ is expanded as a function of P, T, and c and the coefficients of diffusion, thermal diffusion, and barodiffusion are introduced by the following relations:

$$D=\frac{\alpha}{\rho}\left(\frac{\partial\mu}{\partial c}\right)_{T,P}, \quad \chi=\frac{\kappa}{\rho c_P},$$

$$\frac{\rho K_T D}{T}=\alpha\left(\frac{\partial\mu}{\partial T}\right)_{c,P}+\beta; \quad \kappa=\gamma-\frac{\beta^2 T}{\alpha}, \tag{9}$$

$$K_P=P\left(\frac{\partial V}{\partial c}\right)_{P,T}\bigg/\left(\frac{\partial\mu}{\partial c}\right)_{P,T}=-P\left(\frac{\partial\rho}{\partial c}\right)_{P,T}\bigg/\rho^2\left(\frac{\partial\mu}{\partial c}\right)_{P,T}.$$

For a dilute gas, obeying the ideal-gas law, the chemical potentials of the individual species have the form

$$\mu_1=k_B T\ln c'+\psi_1(T), \quad \mu_2=k_B T\ln(1-c')+\psi_2(T), \tag{10}$$

where the ψ's are functions of temperature only. With these relations one finds that

$$\left(\frac{\partial\mu}{\partial c}\right)_{T,P}=\frac{k_B T}{c(1-c)[m_2 c+(1-c)m_1]} \tag{11}$$

and

$$K_P\left(\frac{\partial c'}{\partial c}\right)=\frac{N(m_2-m_1)c'(1-c')}{\rho}. \tag{12}$$

The fundamental hydrodynamic equations for the two component fluid mixture, which express the conservation of mass, momentum, energy, and number of particles of individual species, may be written in the following forms:

(i) continuity equation (conservation of mass)

$$\frac{\partial\rho}{\partial t}+\operatorname{div}(\rho\vec{V})=0; \tag{13}$$

(ii) Navier-Stokes equation (conservation of momentum)

$$\frac{\partial V}{\partial t}+(\vec{V}\cdot\operatorname{grad})\vec{V}=-\frac{1}{\rho}\operatorname{grad}P+\frac{\eta}{\rho}\nabla^2\vec{V}+\frac{1}{\rho}\left(\tfrac{1}{3}\eta+\zeta\right)\operatorname{grad}\operatorname{div}\vec{V}; \tag{14}$$

(iii) thermal diffusion equation (conservation of energy)

$$\frac{\partial T}{\partial t}-\frac{K_T}{c_P}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}\frac{\partial c}{\partial t}+\frac{T}{c_P}\left(\frac{\partial s}{\partial P}\right)_{T,P}\frac{\partial P}{\partial t}=\chi\nabla^2 T; \tag{15}$$

(iv) concentration diffusion equation (conservation of particle number of individual species)

$$\frac{\partial c}{\partial t}=D\left[\nabla^2 c+\frac{K_T}{T}\nabla^2 T+\frac{K_P}{P}\nabla^2 P\right]. \tag{16}$$

In this macroscopic thermodynamic approach the transport coefficients are regarded as constants, to be obtained experimentally, which describe the properties of a continuous medium. In a microscopic approach the macroscopic conservation laws are derived from the Boltzmann equation, according to the Chapman-Enskog procedure. The transport coefficients are then obtained in terms of molecular parameters. When only binary collisions are taken into account the following expressions are valid in a mixture of dilute gases[11]:

$$D=\frac{3}{8N\sigma_{12}^2}\left(\frac{Tk_B(m_1+m_2)}{2m_1m_2}\right)^{1/2}$$

$$=2.628\times10^{-3}\frac{[T^3(M_1+M_2)/2M_1M_2]^{1/2}}{P\sigma_{12}^2}$$

(rigid sphere)

$$=2.628\times10^{-3}\frac{[T^3(M_1+M_2)/2M_1M_2]^{1/2}}{P\sigma_{\mathrm{LJ}\,12}^2\,\Omega_{12}^{11}(T_{12}^*)}$$

(Lennard-Jones pot.) , (17)

$$\eta=\frac{\eta_1\eta_2}{[c'\eta_2^{1/2}+(1-c')\eta_1^{1/2}]^2}, \tag{18}$$

$$\eta_i=\frac{1}{4\sigma_i^2}\left(\frac{k_B m_i T}{\pi}\right)^{1/2}=2.6693\times10^{-5}\frac{(M_iT)^{1/2}}{\sigma_i^2}$$

(rigid sphere)

$$=2.6693\times10^{-5}\frac{(M_iT)^{1/2}}{\sigma_{\mathrm{LJ}\,i}^2\,\Omega^{(22)}(T^*)}$$

(Lennard-Jones pot.) ,

$$K'_P=\frac{c'(1-c')N(m_2-m_1)}{\rho}. \tag{19}$$

Here σ_i and σ_{ij} are molecular diameters in the rigid-sphere model, σ_{LJi} and σ_{LJij} are parameters describing the Lennard-Jones interaction potential, and $\Omega^{(ij)}(T_{12}^*)$ are Chapman-Cowling integrals as a function of the reduced temperature.

For very dilute gases the equations lose their validity, because the variation of the dynamical variables over a mean free path becomes large. The dimensionless constant, which is characteristic for the transition from the hydrodynamic to the kinetic regime, may be written in the form[12]

$$y=(8\pi)^{1/2}N\sigma^2/k=\lambda/\pi^{3/2}\bar{l}, \tag{20}$$

where λ is the wavelength of periodic variations and $\bar{l}=1/\sqrt{2}\,\pi N\sigma^2$ is the mean free path. For $y>3$ the hydrodynamic equations are valid. To be sure that we are in the hydrodynamic regime, we have calculated the parameter y for various gases in Table I.

TABLE I. Gas parameters for a rigid-sphere model at $T = 300\,°\mathrm{K}$. σ is hard-sphere collision diameter of the molecule in angstroms. M is molecular weight. $\bar{l}$ is mean free path in microns. η is the shear viscosity. P is the pressure in atmospheres.

	σ(Å)	M	$\eta\times10^5$ g/sec cm	$\bar{l}$	y
H_2	2.731	2.016	8.986	$0.1123/P$	$0.5548P$
He	2.174	4.003	19.821	$0.1770/P$	$0.3520P$
Xe	4.916	131.3	23.372	$0.0346/P$	$1.800P$
SF_6	6.323[a]	146.05	13.974	$0.0209/P$	$2.978P$

[a] Calculated from the measured value of η.

III. COUPLING WITH THE ELECTROMAGNETIC FIELD

In the presence of an electric field the differential free energy per unit mass has to be augmented by terms due to variations in the electric field and the dielectric constant and takes on the form

$$dF = -S\,dT + \mu_0 dc + P\rho^{-2} d\rho - \frac{\epsilon \vec{E}\cdot d\vec{E}}{4\pi\rho} - \frac{E^2 d\epsilon}{8\pi\rho}\,. \tag{21}$$

Here ϵ must be regarded as a function of the variables T, c, and ρ. It can be shown that the force per unit volume for an uncharged dielectric is changed in the presence of an electric field by an amount[13]

$$\rho\nabla\left[\frac{1}{8\pi}E^2\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,c}\right] - \frac{E^2}{8\pi}\left(\frac{\partial\epsilon}{\partial c}\right)_{\rho,T}\nabla c - \frac{E^2}{8\pi}\left(\frac{\partial\epsilon}{\partial T}\right)_{c,\rho}\nabla T\,.$$

The last two terms are usually negligible compared to the first term. The effect of electrostriction is therefore to add a term

$$\frac{1}{8\pi}\nabla\left(E^2\frac{\partial\epsilon}{\partial\rho}\right)$$

to the right-hand side of Eq. (14). For an isotropic fluid without macroscopic flow, so that the nonlinear hydrodynamic term $(\vec{V}\cdot\nabla)\vec{V}$ may be ignored, the combination of Eqs. (13) and (14) leads to a small amplitude sound-wave equation in a linearized form

$$\frac{\partial^2\rho}{\partial t^2} = \nabla^2 P - \frac{\rho_0}{8\pi}\nabla^2\left[\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,c}E^2\right] + \frac{1}{\rho_0}\left(\frac{4}{3}\eta + \zeta\right)\nabla^2\left(\frac{\partial\rho}{\partial t}\right). \tag{22}$$

In this equation ρ may be expressed in terms of the independent variables P, T, and c by means of the equation of state.

From Eq. (21) it is clear that the entropy per unit mass in the presence of an electric field is changed by an amount

$$\frac{E^2}{8\pi\rho}\left(\frac{\partial\epsilon}{\partial T}\right)_{P,c}\,.$$

In a nonabsorbing dielectric the thermal diffusion equation requires a correction term

$$\frac{T}{8\pi\rho c_P}\left(\frac{\partial\epsilon}{\partial T}\right)_{P,c}\frac{\partial E^2}{\partial t}\,.$$

In the presence of an optical absorption coefficient α_{opt}, one has to add another term, so that the thermal diffusion equation becomes

$$\frac{\partial T}{\partial t} + \frac{T}{c_P}\left(\frac{\partial S}{\partial P}\right)_{T,c}\frac{\partial P}{\partial t} - \frac{K_T}{c_P}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}\frac{\partial c}{\partial t} = \chi\nabla^2 T - \frac{T}{8\pi\rho c_P}\left(\frac{\partial\epsilon}{\partial T}\right)_{P,c}\frac{\partial E^2}{\partial t} + \alpha_{\mathrm{opt}}\frac{c_0 n E^2}{8\pi\rho c_P}\,. \tag{23}$$

In a similar manner the concentration diffusion equation has to be augmented, because the chemical potential per unit mass is changed by an amount

$$\frac{1}{8\pi\rho}\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T}E^2\,.$$

Instead of Eq. (16), the concentration diffusion equation becomes

$$\frac{\partial c}{\partial t} = D\left\{\nabla^2 c + \frac{K_T}{T}\nabla^2 T + \frac{K_P}{P}\nabla^2 P - \left[8\pi\rho\left(\frac{\partial\mu}{\partial c}\right)_{T,P}\right]^{-1}\nabla^2\left[\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T}E^2\right]\right\}. \tag{24}$$

To these three equations the wave equation for the electromagnetic field in the isotropic medium must be added,

$$\nabla^2 E - \frac{\epsilon}{c_0^2}\frac{\partial^2 E}{\partial t^2} = \frac{1}{c_0^2}\frac{\partial^2}{\partial t^2} \times E\left[\left(\frac{\partial\epsilon}{\partial P}\right)_{T,c}P + \left(\frac{\partial\epsilon}{\partial T}\right)_{P,c}T + \left(\frac{\partial\epsilon}{\partial c}\right)_{T,P}c\right]. \tag{25}$$

Solutions to the set of four simultaneous second-order differential equations (22) – (25) may be found in the parametric linearized approximation, in which the laser field

$$E_L(\vec{r}, t) = \tfrac{1}{2}E_L e^{ik_L z - i\omega_L t} + cc$$

is considered as a constant parameter. The scattered light is represented by a backward wave with amplitude E_s, frequency ω_s, and wave number k_s,

$$E_s(\vec{r}, t) = \tfrac{1}{2}E_s e^{-ik_s z - i\omega_s t} + cc\,.$$

Assume for the pressure, concentration, and temperature variations solutions of the form

$$P(\vec{r}, t) = \tfrac{1}{2}P_1 e^{+ikz - i\omega t} + cc\,,$$
$$c(\vec{r}, i) = \tfrac{1}{2}c_1 e^{+ikz - i\omega t} + cc\,, \tag{26}$$
$$T(\vec{r}, t) = \tfrac{1}{2}T_1 e^{+ikz - i\omega t} + cc\,.$$

Substitute these expressions into Eqs. (22)–(25) and ignore all terms higher than linear in the four small variables E_s, P_1, c_1, and T_1. With the phase and frequency matching conditions (momentum and energy conservation between the waves), $k = k_L + k_s$, $\omega = \omega_L - \omega_s$, a secular determinant is obtained which gives a general dispersion relation. Unfortunately this relation is too complicated to afford physical insight and it will not be written out explicitly. For the special case $E_L = E_s = 0$, absence of the electromagnetic field, the relation must of course reduce to the description of sound waves in a fluid mixture.[10] Numerous papers have been devoted to the description of stimulated thermal and Brillouin scattering of light in a single-component fluid where $c_1 = 0, \partial\epsilon/\partial c = 0$.[14–16]

The interest in this paper is directed toward the concentration scattering in a nonabsorbing gaseous mixture. A solution for this case will be presented in Sec. IV, after some explicit expressions for the coupling coefficients $\partial\epsilon/\partial P$ and $\partial\epsilon/\partial c$ have been given.

For a substance obeying the Clausius-Mosotti relation,

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N[c'\alpha_1 + (1 - c')\alpha_2] ,$$

where α_1 and α_2 are the polarizabilities of the two-molecular species, one readily obtains with the aid of Eqs. (2)–(4)

$$P\left(\frac{\partial\epsilon}{\partial P}\right)_{c,T} = \rho\left(\frac{\partial\epsilon}{\partial\rho}\right)_{c,T} = \rho\left(\frac{\partial\epsilon}{\partial\rho}\right)_{c',T} = \frac{1}{3}(\epsilon - 1)(\epsilon + 2) \tag{27}$$

and

$$\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T} = \left(\frac{\partial\epsilon}{\partial c'}\right)_{N,T}\frac{\partial c'}{\partial c} = \frac{4\pi}{9}\,\frac{(\epsilon + 2)^2 m_1 m_2 N}{[m_2 c + (1 - c)m_1]^2}\,(\alpha_1 - \alpha_2) \ . \tag{28}$$

For a gas with a small optical density one may put $(\epsilon + 2)/3 \sim 1$.

It should be noted that the coupling to the concentration can only become comparable to the density coupling for $\alpha_1 \gg \alpha_2$.

IV. STIMULATED CONCENTRATION AND BRILLOUIN SCATTERING

In a nonabsorbing gaseous mixture the coupling of the temperature with the electric field and the concentration may be ignored, $\alpha_{\text{opt}} = 0$, $\partial\epsilon/\partial T = 0$, and $K_T = 0$, in Eqs. (23)–(25). The temperature Eq. (23) may be combined with the sound-wave equation. For small thermal conductivity χ, this leads to a sound wave propagating with the adiabatic velocity $v_s = \gamma v_T$ instead of the isothermal velocity v_T, and an additional thermal damping term.[10] Here $\gamma = c_P/c_V$ is the ratio of the specific heats at constant pressure and volume, respectively. The sound-wave equation may thus be written in the form

$$\begin{aligned}\frac{\partial^2 P}{\partial t^2} + v_s^2\left(\frac{\partial\rho}{\partial c}\right)_{P,T}\frac{\partial^2 c}{\partial t^2} &= v_s^2\nabla^2 P \\ &+ \left[\frac{1}{\rho_0}\left(\frac{4}{3}\eta + \zeta\right) + \chi(\gamma - 1)\right]\frac{\partial}{\partial t}(\nabla^2 P) \\ &- (8\pi)^{-1}\rho_0\left(\frac{\partial\epsilon}{\partial\rho}\right)_{T,c} v_s^2\,\nabla^2 E^2 \\ &- \frac{\rho_0}{4\pi(\epsilon + 2)}E^2\left(\frac{\partial\epsilon}{\partial\rho}\right)^2\nabla^2 P \ .\end{aligned} \tag{29}$$

The last term arises from the gradient of $\partial\epsilon/\partial\rho$ in Eq. (22), as evaluated by means of Eq. (27). This term was inadvertently omitted by Wang.[17] It leads to an additional contribution of the intensity-dependent Brillouin shift.[17]

The Stokes wave equation (25) is reduced to the form

$$\nabla^2 E_s - \frac{\epsilon(\omega_s)}{c_0^2}\frac{\partial^2 E_s}{\partial t^2} = \frac{1}{c_0^2}\left(\frac{\partial\epsilon}{\partial P}\right)_{c,T}\frac{\partial^2(PE_L)}{\partial t^2} + \frac{1}{c_0^2}\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T}\frac{\partial^2(cE_L)}{\partial t^2} \ . \tag{30}$$

The concentration equation (24) takes the form

$$\begin{aligned}\frac{\partial c}{\partial t} &= D\left[\nabla^2 c + \frac{K_P}{P_0}\nabla^2 P\right] \\ &- \left[8\pi\rho_0\left(\frac{\partial\mu}{\partial c}\right)_{T,P}\right]^{-1} D\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T}\nabla^2 E^2 \\ &- \left[8\pi\rho_0\left(\frac{\partial\mu}{\partial c}\right)_{T,P}\right]^{-1} DE^2\nabla^2\left(\frac{\partial\epsilon}{\partial c}\right)_{P,T} \ .\end{aligned} \tag{31}$$

The last term may be evaluated by means of Eq. (28) in terms of $\nabla^2 P_1$ and $\nabla^2 c_1$. It corresponds to an intensity-dependent frequency shift of the stimulated concentration scattering, analogous to a similar term in Eq. (29) for the Brillouin scattering.

The set of three coupled equations (29)–(31) for E_s, P_1, and c_1 may now be solved by the same procedure as followed by Herman and Gray[15] for the case of thermal Brillouin scattering in a one-component fluid, where the three variables were E_s, P_1 or ρ_1, and T_1.

Since the characteristic relaxation times for diffusion and acoustic damping are assumed to be short, compared to the laser pulse duration, we may look for a steady-state solution for E_s. The imaginary part of the wave vector of the Stokes wave due to the driving terms on the right side of Eq. (30) determines the amplitude spatial gain constant of the Stokes wave. We thus solve the two inhomogeneous equations (29) and (31) for P_1^* and c_1^* in terms of E_s and substitute into Eq. (30), using the "ansatz" (26). One thus finds the power gain constant for combined stimulated Brillouin-concentration scattering,

$$G_{B,c}=\operatorname{Im}-\frac{|E_L|^2\omega_s}{16\pi c_0 n}\left[(Dk^2+i\omega)\frac{\gamma_e^2 v_s^2 k^2}{P_0}+\frac{\gamma_e v_s^2\omega^2(\partial\rho/\partial c)_{P,T}(\partial\epsilon/\partial c)_{P,T}Dk^2}{P_0\rho_0(\partial\mu/\partial c)_{P,T}}\right.$$
$$\left.+\frac{(\omega_B^2-\omega^2+i\omega\eta' k^2/\rho_0)Dk^2(\partial\epsilon/\partial c)_{P,T}^2}{\rho_0(\partial\mu/\partial c)_{P,T}}-\frac{Dk^4K_P\gamma_e v_s^2(\partial\epsilon/\partial c)_{P,T}}{P_0}\right]$$
$$\times\left[\left(\omega_B^2-\omega^2+i\omega\eta'\frac{k^2}{\rho_0}\right)(Dk^2+i\omega)+\frac{v_s^2\omega^2Dk^2K_P(\partial\rho/\partial c)_{P,T}}{P_0}\right]^{-1}. \tag{32}$$

The following abbreviations have been used:

$$\omega_B^2=\left(v_s^2-\frac{\gamma_e^2|E_L|^2}{4\pi\rho_0(\epsilon+2)}\right)k^2\,,$$
$$\gamma_e=\rho_0\left(\frac{\partial\epsilon}{\partial\rho}\right)_{c,T}=\tfrac{1}{3}(\epsilon-1)(\epsilon+2)\,, \tag{33}$$
$$\eta'=\tfrac{4}{3}\,\eta+\zeta+\rho_0\chi(\gamma-1)\,,$$
$$\omega=\omega_L-\omega_s,\quad k_L=k+k_s,\quad \omega_s=c_0k_s/n\,.$$

The expression (32) shows large resonant values of the gain in the vicinity of $\omega=\omega_B$ (stimulated Brillouin gain) and in the vicinity of $\omega\simeq 0$ (stimulated concentration gain). The latter may be nearly uncoupled from the Brillouin gain and is approximately given by

$$G_c=\frac{\omega_s k^2D(\partial\epsilon/\partial c)_{P,T}^2|E_L|^2}{16\pi nc_0\rho_0(\partial\mu/\partial c)_{P,T}}\;\frac{\omega}{\omega^2+D^2k^4}\;. \tag{34}$$

It assumes a maximum value for a small stokes shift $\omega=Dk^2$. We may write $G_{c,\max}=g_cI_L$, where $I_L=c_0n|E_L|^2/8\pi$ is the laser intensity, and the gain coefficient for stimulated concentration scattering is given by

$$g_c=\frac{k_s(\partial\epsilon/\partial c)_{P,T}^2}{4c_0n^3\rho_0(\partial\mu/\partial c)_{P,T}}\;. \tag{35}$$

The resonance at $\omega=\omega_B$ leads to the usual stimulated Brillouin gain with the maximum gain factor given by

$$G_{B,\max}=\frac{\omega_s|E_L|^2\rho_0(\partial\epsilon/\partial\rho)^2\omega_B}{32\pi c_0nv_s^2\Gamma}=g_BI_L\,, \tag{36}$$

where

$$g_B=k_s\rho_0\left(\frac{\partial\epsilon}{\partial\rho}\right)^2\Big/2c_0n^3kv_s\eta_T \tag{37}$$

and

$$\Gamma=\frac{k^2\eta_T}{2\rho_0}=\frac{k^2}{2\rho_0}\left\{\frac{4}{3}\eta+\zeta+\kappa\left(\frac{1}{c_V}-\frac{1}{c_P}\right)\right.$$
$$\left.+\left[Dv_s^2\Big/\rho\left(\frac{\partial\mu}{\partial c}\right)_{P,T}\right]\left(\frac{\partial\rho}{\partial c}\right)_{P,T}^2\right\}. \tag{38}$$

In a binary mixture the sound wave has an extra damping term [last term of Eq. (38)] due to the coupling with the concentration fluctuation.[18] This extra damping depends on $(\partial\rho/\partial c)_{P,T}^2$, and consequently the sound wave is heavily damped in a mixture with a large difference of component masses. The threshold of stimulated Brillouin scattering is increased by mixing. The ratio of the gain constants for stimulated concentration and Brillouin scattering is

$$\frac{g_c}{g_B}=\frac{kv_s\eta_T(\partial\epsilon/\partial c)_{P,T}^2}{2\rho_0^3(\partial\epsilon/\partial\rho)_{c,T}^2(\partial\mu/\partial c)_{P,T}}\;. \tag{39}$$

From Eqs. (38) and (28) it follows that a large difference in polarizability and a large difference in mass of the two components is favorable to make this ratio appreciable. Furthermore, the total density or pressure should be kept low, because the ratio is inversely proportional to the density. This is a consequence of the fact that g_c is proportional to the density, but g_B increases proportional to the square of the density, as the acoustic damping constant is inversely proportional to the density.[19]

For a gaseous mixture Eq. (39) can be simplified with the aid of Eqs. (11), (27), and (28) to

$$\frac{g_c}{g_B}=\frac{kv_s\eta_T}{2Nk_BT}\;\frac{c'(1-c')(\alpha_1-\alpha_2)^2}{[\alpha_1c'+(1-c')\alpha_2]^2} \tag{40}$$

with η_T given by Eq. (38).

V. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENT

If one substitutes typical values for a liquid mixture into Eq. (39), the ratio is found to be very small compared to unity. For example, a mixture of n-hexane (58% weight concentration) and nitrobenzene (42%) gives $g_c/g_B\sim 1.25\times10^{-5}$. This throws doubt on the interpretation of the experiment de-

TABLE II. Comparison of the concentration and Brillouin gain coefficients in a mixture of SF_6 and He at total pressure 10 atm.

He c'	$\eta \times 10^4$ mix (g/cm sec)	$v_s \times 10^{-4}$ (cm/sec)	$\Delta\nu_B$ (cm^{-1})	$\eta_T \times 10^4$ (g/cm sec)	g_c/g_B	$g_B \times 10^{10}$ (cm/W)	$g_c \times 10^{10}$ (cm/W)
0	1.397	1.509	0.0145	2.474	0	53.352	0
0.1	1.444	1.608	0.0154	5.821	0.0076	17.405	0.1325
0.2	1.492	1.723	0.0165	9.305	0.0295	8.137	0.2396
0.3	1.542	1.859	0.0179	12.923	0.0734	4.220	0.3096
0.4	1.596	2.025	0.0194	16.646	0.1568	2.255	0.3535
0.5	1.652	2.233	0.0214	20.449	0.30	1.191	0.3686
0.6	1.711	2.507	0.0241	24.392	0.596	0.5935	0.3534
0.7	1.773	2.895	0.0278	27.932	1.142	0.2711	0.3097
0.8	1.839	3.509	0.0337	31.035	2.310	0.1037	0.2396
0.9	1.908	4.731	0.0454	31.898	5.067	0.0262	0.1327
0.95	1.945	6.088	0.0584	28.495	7.030	0.0100	0.0703
0.98	1.967	7.635	0.0733	20.461	5.444	0.0053	0.0287
1	1.982	10.194	0.0979	4.626	0	0.0086	0

scribed in Ref. 7. Near the critical point in a binary mixture, where $\partial\mu/\partial c \to 0$, the concentration gain could become large. The diffusion constant D approaches zero at the same time. The correlation length and correlation time for the concentration fluctuations becomes very long, $\sim 10^{-3}$ sec. The steady-state analysis breaks down for solid-state laser pulses, and even for gas-laser beams it would be difficult to keep the required coherence for such long times. A transient analysis must be made and the experimental difficulties would be further enhanced by the large spontaneous critical opalescence, although amplification of this spontaneous emission at high intensities may well be detectable.

Even for gaseous mixtures it is difficult to obtain a ratio g_c/g_B comparable to unity. It should be kept in mind that the total pressure cannot be decreased arbitrarily, because the parameter y in Eq. (20) would become too small and the kinetic regime would take over. Also the required path length to obtain appreciable over-all gain would be too long.

In Table II we have calculated numerical values of the constants which appear in g_c and g_B as a function of helium concentration, for a gaseous mixture of SF_6 and He at 10 atm total pressure and $T = 300$ °K. The diffusion constant $D = 0.037\,47$ cm^2/sec and viscosity are calculated from Eqs. (17) and (18), using the tabulated Lennard-Jones potential parameters (Ref. 11). The adiabatic sound velocity is calculated using the expression $v_s = [(c'\gamma_1 + (1-c')\gamma_2)k_B T/(c'm_1 + (1-c')m_2)]^{1/2}$. The high-frequency specific-heat ratios for He and SF_6 are taken to be $\gamma_1 = 1.667$ and $\gamma_2 = 1.333$.[20] η_T, the

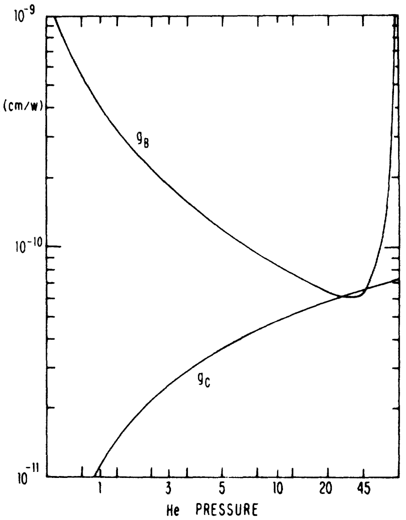

FIG. 1. Backward Brillouin and concentration gain coefficients as functions of He partial pressure (in atm) keeping the partial pressure of SF_6 at 5 atm.

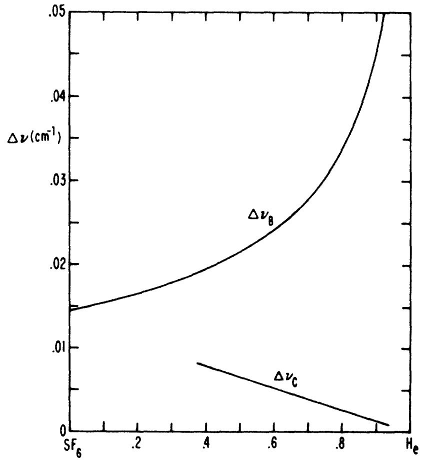

FIG. 2. Stokes frequency shift of the backward scattered light from a mixture of SF_6 and He as a function of He concentration, starting with five atmosphere SF_6.

TABLE III. Comparison of the concentration and Brillouin gain coefficients in a mixture of Xe and He at total pressure 10 atm.

He c'	$\eta\times10^4$ mix (g/cm sec)	$v_s\times10^{-4}$ (cm/sec)	Δ_{ν_B} (cm-1)	$\eta_T\times10^4$ (g/cm sec)	g_c/g_B	$g_B\times10^{10}$ (cm/W)	$g_c\times10^{10}$ (cm/W)
0	2.337	1.779	0.0171	5.453	0	16.830	0
0.1	2.296	1.872	0.0180	10.372	0.0157	6.890	0.1078
0.2	2.257	1.981	0.0190	15.254	0.0541	3.546	0.1916
0.3	2.219	2.113	0.0203	20.082	0.1279	1.968	0.2516
0.4	2.183	2.274	0.0218	24.824	0.2586	1.112	0.2876
0.5	2.147	2.478	0.0238	29.428	0.4853	0.6173	0.2996
0.6	2.112	2.751	0.0264	33.800	0.8855	0.3247	0.2875
0.7	2.078	3.138	0.0301	37.745	1.6262	0.1547	0.2516
0.8	2.044	3.755	0.0361	40.677	3.1129	0.0615	0.1914
0.9	2.012	4.984	0.0479	40.322	6.3119	0.0170	0.1073
0.95	1.996	6.117	0.0587	34.871	7.821	0.0073	0.0569
0.98	1.986	7.792	0.0748	24.347	5.731	0.0041	0.0235
1	1.982	10.193	0.0978	4.624	0	0.0086	0

gain coefficient g_B, and the ratio g_c/g_B are calculated from Eqs. (37), (38), and (40), respectively.

We have also calculated the gain coefficients g_B and g_c for a mixture of five atmospheres of SF_6 as a function of the additional helium pressure. The results are plotted in Fig. 1. It is seen that stimulated concentration scattering may be expected to dominate when the concentration of helium is around 0.85. The gain ratio becomes larger mainly because the damping of sound wave increases and the Brillouin gain becomes smaller. Thus, in order to be able to see the stimulated concentration scattering one has to increase the laser power from the value used in obtaining the stimulated Brillouin scattering. The expected frequency behavior of the stimulated back scattered light has been plotted in Fig. 2. The frequency shift should increase for the stimulated Brillouin scattering when helium is added to SF_6. As the concentration gain becomes larger than the Brillouin gain one would see a sudden decrease in the frequency shift.

The numerical results for mixtures of helium and xenon gas are given in Table III. These results should be compared with the data reported in Ref. 8. The experiment in Ref. 8 was done for a Xe and He mixture with He concentration $c'=0.9$. At this concentration the Brillouin shift should be 0.0479 cm^{-1} instead of 0.055 cm^{-1} reported. According to Table III the gain ratio at a total pressure of 3 atm should be $g_c/g_B=21$ in contrast to $g_c/g_B=0.1$ as estimated in Ref. 8. The observed concentration shift 0.033 ~ 0.042 cm^{-1} agrees with the value $\Delta\nu_c=Dk^2/2\pi c=0.032$ cm^{-1}. At a higher total pressure the stimulated Brillouin should take over the stimulated concentration scattering as suggested in Ref. 8; however, this should not occur at a total pressure as low as 4 atm. In conclusion, the theoretical calculations presented in this paper are in partial agreement with the observation in Ref. 8; however, the agreement is not conclusive. Further experimental investigation of the stimulated concentration scattering as a function of concentration and total pressure of the mixture is required. Preliminary observations on SF_6-He mixture[9] have shown that the onset of stimulated concentration scattering can occur at a rather high total pressure. It is clear that in problems relating to the propagation of intense light beams in the atmosphere, stimulated concentration scattering may be ignored.

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Phase-Matched Critical Total Reflection and the Goos-Haenchen Shift in Second-Harmonic Generation*

H. Shih and N. Bloembergen†

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

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It is well established that a totally reflected light beam of finite diameter undergoes a lateral displacement, known as the Goos-Haenchen shift. The theory for the corresponding effect in nonlinear optics is presented. The special phase-matched case, in which both the fundamental and the second harmonic are at critical total reflection, is shown to have a characteristic radiation pattern. Since the finite beam diameter is taken into account, divergencies of earlier theories are eliminated.

I. INTRODUCTION

When a light beam is totally reflected, there is no net power flux normal to the boundary into the less dense medium. There is, however, a nonvanishing component of the Poynting vector tangential to the boundary. The fields decay exponentially normal to the boundary in the less dense medium, but this decay of the evanescent field becomes infinitely slow at the critical angle, for which total reflection first occurs. There is a singularity in $\vec{k}$ space, as the normal component k_z in the less dense medium changes from small positive values through zero to pure imaginary values. An accurate description of the phenomenon of critical total reflection must consider explicitly the finite diameter of the light beam and integrate properly over a distribution in $\vec{k}$ space around the critical point. This problem in linear optics has been discussed by many authors[1] and was solved in a rather complete form by Artman.[2] The field distribution of the fundamental light beam, of width w_0 in the less dense optical medium for critical total reflection, is shown in Fig. 1. The transverse component of the Poynting vector corresponds to a lateral displacement of the reflected beam. This displacement has been observed experimentally and is known as the Goos-Haenchen shift.[3,4]

It is the purpose of this paper to extend these considerations to the domain of nonlinear optics, in particular, to the case of harmonic generation of light by a totally reflected fundamental beam. The theory of total reflection of parametrically generated light has been given by Bloembergen and