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Stimulated Thermal Rayleigh Scattering in Liquids

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In a previous calculation of the gain factor for stimulated thermal scattering, it has been assumed that the dielectric constant is insensitive to changes in temperature. In our treatment such an approximation has not been made and it is shown that this additional contribution gives rise to a correction of up to 6% to the stimulated thermal Rayleigh peak for liquids commonly used in such experiments. The inadequacy of the Lorentz-Lorenz relation in estimating the magnitude of this correction is also discussed.

In a recent paper by Herman and Gray,[1] the gain factor for the stimulated thermal Rayleigh peak has been calculated. The density and temperature are taken as independent thermodynamic variables and it is assumed that the dielectric constant is insensitive to changes in temperature, i.e.,

$$\left(\frac{\partial\epsilon}{\partial T}\right)_\rho \delta T \ll \left(\frac{\partial\epsilon}{\partial\rho}\right)_T \delta\rho ,$$

where $\delta\rho$ and δT are the rise in density and temperature, respectively, ϵ is the dielectric constant of the medium. This assumption is common in the literature and generally quite valid. Stimulated thermal Rayleigh scattering, however, is one physical situation where this approximation is not so good. As a guide to future attempts to obtain quantitative agreement between theory and experiment we set down a more exact theoretical treatment. It is true that for most liquids

$$R \equiv \left(\frac{\partial\epsilon}{\partial T}\right)_\rho \Big/ \left(\frac{\partial\epsilon}{\partial\rho}\right)_T \simeq 10^{-4} ;$$

however, in the final expression for the stimulated thermal Rayleigh gain it is not R but R times a quantity of order 10^3 that appears and as a result the term that has been ignored previously is not negligibly small. In most cases this additional term would change the gain of the stimulated thermal Rayleigh peak by 3 to 6%. In some recent experiments,[2] I_2 has been used as a coloring agent to study stimulated thermal scattering. In these cases there exists large discrepancies between theory and experiment with regard to the onset of thermal Rayleigh scattering. The treatment presented here does not account for such discrepancies.

In this paper a derivation of the gain factor, including both contributions to the change in dielectric constant, is given. In the limit when $R \to 0$ our result reduces to Herman and Gray's[1] result. It is shown that for $R \simeq 0.6 \times 10^{-4}\,\mathrm{g\,cm^{-3}\,{}^\circ K^{-1}}$ for benzene (we compute this value of R from existing experimental data in the literature[3]) the additional term changes the gain of the stimulated thermal Rayleigh peak by about 5% from Herman and Gray's result.[1] It should be pointed out that Mack's[4] data leads to a value for $R = 1.34 \times 10^{-4}\,\mathrm{g\,cm^{-3}\,{}^\circ K^{-1}}$ which gives a change of 13% from Herman and Gray's[1] value. This estimate is too high because Mack made use of the Lorentz-Lorenz relation which is inadequate for the liquids discussed.

We are interested in calculating the power gain per unit length G, which is related to the imaginary part of the nonlinear susceptibility $\chi_{NL}(\omega_S)$ through the relation $G = 4\pi k_S \operatorname{Im}\chi_{NL}(\omega_S)$, where the subscript S refers to the scattered wave and k is the wave number. To calculate G we start with a set of two coupled equations,[1] one describing the temperature fluctuation $\delta T(t)$, the other describing the density fluctuation $\delta\rho(t)$ [or equivalently in terms of dilatation $\Delta(t) = -\delta\rho(t)/\rho_0$] in an isotropic medium:

$$K\frac{\partial^2 T}{\partial Z^2} - \rho_0 C_v \frac{\partial T}{\partial t} - T_0 F\frac{\partial\Delta}{\partial t} = -\frac{1}{4\pi}n_0 c\alpha E^2 \qquad (1)$$

$$B_T\frac{\partial^2\Delta}{\partial Z^2} + \eta\frac{\partial}{\partial t}\frac{\partial^2\Delta}{\partial Z^2} - \rho_0\frac{\partial^2\Delta}{\partial t^2} - F\frac{\partial^2 T}{\partial Z^2} = -\frac{\gamma^e}{8\pi}\frac{\partial^2}{\partial Z^2}(E^2)\,. \qquad (2)$$

Here ρ_0, T_0 are the equilibrium values of the density and temperature, respectively, C_v the specific heat at constant volume, K the static thermal conductivity, n_0 some average value of the refractive index, $\gamma^e = \rho_0(\partial\epsilon/\partial\rho)_T$ is the electrostrictive coupling constant, α the electromagnetic absorption coefficient, c the speed of light in vacuum, E the total electric field, η the effective viscosity of the medium. The factor $F = \beta B_T \equiv \rho_0 C_v(\gamma - 1)/T_0\beta$, where β is the coefficient of volume expansion, γ is the usual ratio of specific heats and B_T is the isothermal bulk modulus.

The nonlinear polarization is given by

$$P_{NL}(t) = [\delta\epsilon(\rho, T)/4\pi]E(t)$$

$$= \frac{\gamma^e}{4\pi\rho_0}E(t)\delta\rho(t) + \frac{\gamma^T}{4\pi T_0}E(t)\delta T(t), \qquad (3)$$

where $\gamma^T = T_0(\partial\epsilon/\partial T)_\rho$ and it is the latter term involving γ^T that has been completely ignored earlier.[1] As stated above $\delta\rho(t) = -\rho_0\Delta(t)$ and thus P_{NL} can be easily expressed in terms of $\Delta(t)$ rather than $\delta\rho(t)$. Equations (1) and (2) are to be solved simultaneously for $\Delta(t)$ and $\delta T(t)$ to obtain the nonlinear polarization.

Solving Eqs. (1) and (2) for the case of back scattering using the usual steady-state approach[1] we obtain the following expression for the complete gain factor

$$G = \frac{\gamma^e}{8\pi\rho_0}\left(\frac{k^2 k_S |E_L|^2}{\rho_0 C_v}\right)\left(F n_0 c\alpha \times \frac{[\omega(\omega^2 - \omega_B^2) - \frac{1}{2}\Gamma_B\Gamma_R\omega]}{[\omega^2 + (\frac{1}{2}\Gamma_R)^2][(\omega^2 - \omega_B^2)^2 + (\Gamma_B\omega)^2]} + \frac{1}{2}\rho_0 C_v\gamma^e\frac{\Gamma_B\omega}{[(\omega^2 - \omega_B^2)^2 + (\Gamma_B\omega)^2]}\right)$$

$$+ \frac{\gamma^T}{8\pi T_0}\left(\frac{k_S|E_L|^2}{\rho_0^2 C_v}\right)\left(\rho_0 n_0 c\alpha\frac{\omega}{[\omega^2 + (\frac{1}{2}\Gamma_R)^2]} + \frac{1}{2}T_0 F k^2\gamma^e\frac{\omega[\frac{1}{2}\Gamma_R(\omega^2 - \omega_B^2) + \Gamma_B\omega^2]}{[\omega^2 + (\frac{1}{2}\Gamma_R)^2][(\omega^2 - \omega_B^2)^2 + (\Gamma_B\omega)^2]}\right), \qquad (4)$$

where the subscript L refers to the incident (laser) field, $k = k_L + k_S$ and $\omega = \omega_L - \omega_S$. Further $\omega_B = u_1 k$ where $u_1^2 = B^T/\rho_0$, $\Gamma_R = 2Kk^2/\rho_0 C_v$ is the Rayleigh linewidth and $\Gamma_B = \eta k^2/\rho_0$ is the Brillouin linewidth. The term involving $(\gamma^e)^2$ leads to the usual gain at the Stokes frequency for ordinary stimulated Brillouin scattering. The term involving $\gamma^e\gamma^T$ would modify this slightly but numerical computation shows that the correction is of the order of 0.01% so this term can be ignored. Now we concentrate on stimulated thermal scattering (arising from terms involving α) where our theory predicts a non-negligible change from previous results.

For stimulated thermal scattering we can immediately write the gain factor, $G^{(\alpha)}$, from Eq. (4) as follows:

$$G^{(\alpha)} = A\left(\frac{R}{\beta\rho_0}\frac{\omega}{\omega_B^2[\omega^2 + (\frac{1}{2}\Gamma_R)^2]} + \frac{\omega(\omega^2 - \omega_B^2) - \frac{1}{2}\Gamma_B\Gamma_R\omega}{[\omega^2 + (\frac{1}{2}\Gamma_R)^2][(\omega^2 - \omega_B^2)^2 + (\Gamma_B\omega)^2]}\right), \qquad (5)$$

where $A = \dfrac{\gamma^e}{8\pi\rho_0}\left[\dfrac{k^2 k_S|E_L|^2}{\rho_0 C_v}\right]$,

$$R = \frac{(\partial\epsilon/\partial T)_\rho}{(\partial\epsilon/\partial\rho)_T} \equiv \frac{(\partial n/\partial T)_\rho}{(\partial n/\partial\rho)_T}\,. \qquad (6)$$

In actual practice the laser beam has some finite width Γ_L and one should convolute the above frequency spectrum with the laser profile. The convoluted expression for $G^{(\alpha)}$ can be easily derived, but for the purpose of the discussion here it does not add anything, and so we will not write it down. If in Eq. (5) we let $R \to 0$ and neglect the quantity $\frac{1}{2}\Gamma_B\Gamma_R\omega$ in the second term, we immediately regain the result obtained by Herman and Gray for $\Gamma_L = 0$.

For most liquids R is a small quantity but the combination $R/\beta\rho_0$ may not be. To estimate $R/\beta\rho_0$ from existing experimental data we write

$$\frac{R}{\beta\rho_0} = \left[1 + \frac{\kappa_T}{\beta}\left(\frac{(\partial n/\partial T)_p}{(\partial n/\partial p)_T}\right)\right], \qquad (7)$$

TABLE I. Values of $R/\beta\rho_0$ for some liquids. The experimental data in columns 2–5 are from Coumou *et al.* (Ref. 3).

Liquid	$10^3\beta$ ($°\mathrm{C}^{-1}$)	$10^{12}\kappa_T$ ($\mathrm{cm}^2\ \mathrm{dyne}^{-1}$)	$10^5\left(\frac{\partial n}{\partial T}\right)_p$ ($°\mathrm{C}^{-1}$)	$10^{12}\left(\frac{\partial n}{\partial p}\right)_T$ ($\mathrm{cm}^2\ \mathrm{dyne}^{-1}$)	$\frac{R}{\beta\rho_0}\times 100\%$ calculated from Eq. (7)
Carbon disulphide	1.19	94	−81.6	68.2	5.5
Benzene	1.21	95	−63.8	52.3	4.6
n decane	1.04	105	−44.8	46.9	3.6
Methyl ethyl ketone	1.30	108	−51.0	44.2	4.1
Carbon tetrachloride	1.21	106	−58.6	52.8	2.8
n hexadecane	0.90	83	−40.6	39.1	4.2

where $\kappa_T = 1/B_T$ is the isothermal compressibility and p is pressure. Using this expression and the experimental data of Coumou *et al.*[3] we list the values of $R/\beta\rho_0$ for some common liquids in Table I. Since the stimulated thermal Rayleigh peak occurs at $\omega = -\frac{1}{2}\Gamma_R$ (in terms of the frequency of the scattered light at $\omega_S = \omega_L + \frac{1}{2}\Gamma_R$) it is easy to see that in fact $R/\beta\rho_0$ is just the ratio of the first term to the second in Eq. (5) for stimulated thermal Rayleigh scattering, and this ratio is independent of linewidths. The last column in Table I then indicates the percentage error being made by assuming that

$$(\partial\epsilon/\partial\rho)_T\,\delta\rho \gg (\partial\epsilon/\partial T)_\rho\,\delta T\,.$$

The largest value of $R/\beta\rho_0$ quoted in Table I is about 6%. However, there may exist other liquids for which $R/\beta\rho_0$ is even larger. In water, for example,

$$\left(\frac{\partial n}{\partial T}\right)_p = -10.6\times10^{-6}\,°\mathrm{C}^{-1},\ \text{Ref. 5},$$

$$\left(\frac{\partial n}{\partial p}\right)_T = 14.9\times10^{-12}\ \mathrm{cm}^2\ \mathrm{dyne}^{-1},\ \text{Ref. 5},$$

$$\beta = 0.2\times10^{-3}\,°\mathrm{C}^{-1},\ \text{Ref. 4},$$

$$\kappa_T = 45.6\times10^{-12}\ \mathrm{cm}^2\ \mathrm{dyne}^{-1},\ \text{Ref. 6},$$

which leads to $(R/\beta\rho_0)\times100\% \simeq 84$. Although this may represent a rough estimate, it indicates that there may exist other liquids for which $R/\beta\rho_0$ may be quite appreciable. It should perhaps be remarked that a large value of $R/\beta\rho_0$ implies a critical absorption coefficient for the onset of stimulated thermal Rayleigh scattering which is larger than that predicted by Herman and Gray.[1] This may be a clue as to why stimulated thermal Rayleigh scattering has not been observed in water to date. In a recent paper on stimulated thermal Rayleigh scattering, Mack also estimates the value of $(\partial n/\partial T)_\rho$ for various liquids using the following equation, viz,

$$\left(\frac{\partial n}{\partial T}\right)_\rho = \left(\frac{\partial n}{\partial T}\right)_p + \beta\rho_0\left(\frac{\partial n}{\partial \rho}\right)_T\,. \tag{8}$$

He obtains $(\partial n/\partial T)_p$ from experimental data but approximates

$$\left(\frac{\partial n}{\partial \rho}\right)_T \simeq \frac{1}{6n_0\rho_0}(n_0^2-1)(n_0^2+2)$$

according to the Lorentz-Lorenz relation. Since $(\partial n/\partial T)_p$ and $\beta\rho_0(\partial n/\partial\rho)_T$ are of comparable magnitudes but of opposite signs $[(\partial n/\partial T)_p < 0]$, the use of an approximate value for $(\partial n/\partial\rho)_T$ leads to erroneous results for $(\partial n/\partial T)_\rho$ for liquids under consideration. By using Eq. (7) we have avoided the use of Lorentz-Lorenz relation because the latter procedure is inadequate for our analysis.

We conclude that if a quantitative comparison between theory and experiment is to be made, one cannot simply throw away the term arising from γ^T. Even though R is small, $R/\beta\rho_0$ is the parameter of interest which is not negligible.

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Spin Exchange in Collisions between Atoms*

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The work of Glassgold on spin exchange in collisions between atoms is extended to include target polarization. The appropriate averages are taken for spin-exchange collisions which occur in low magnetic fields, but where the incident and scattered beams are selected in a high magnetic field.

INTRODUCTION

An extension of Glassgold's work[1,2] on atomic spin-exchange collisions became necessary in order to understand two types of experiments. The dependence of spin-exchange collisions on target polarization was an important consideration in our study[3] of the feasibility of measuring magnetic resonance of trapped ions by monitoring the spin exchange of an atomic beam scattering from the ions. An additional extension required for interpreting many scattering experiments[4] is the proper averaging over hyperfine states when atoms are selected in high magnetic fields and scattered in a low magnetic field.

SCATTERING FROM A POLARIZED TARGET

If the target has electron spin polarization P, the incident density matrix (I2.10b) (Glassgold's[1] equation numbers will be preceded by I) must be modified. We obtain

$$\rho_{\text{in}} = \tfrac{1}{2} P_1(\alpha) \times [I_2 + P\sigma_z(2)] , \tag{1}$$

where we ignore the target nuclear spin. The cross section for scattering from initial state $|\alpha\rangle$ to final state $\langle\alpha'|$ with no knowledge of the final target state becomes

$$\sigma(\alpha\alpha' ; \theta, P) = \tfrac{1}{2} \operatorname{Tr}\{\mathfrak{F} P_1(\alpha) \times [I_2 + P\sigma_2(2)]\, \mathfrak{F}^\dagger P_1(\alpha) \times I_2\} , \tag{2}$$

where the scattering operator $\mathfrak{F}(\theta)$ is given by (I2.5). If we expand (2), we obtain eight terms which can be evaluated by using the properties of the Pauli spin operators. The cross section is

$$\sigma(\alpha\alpha' ; \theta, P) = \delta_{\alpha\alpha'}[\,|F_d|^2 + P(F_d F_x^* + F_x F_d^*)\langle\alpha|\sigma_z|\alpha\rangle] + |F_x|^2 \textstyle\sum_\mu (1 + P\mu)|\langle\alpha'|\sigma_\mu|\alpha\rangle|^2 , \tag{3}$$

where $F_d(\theta)$ and $F_x(\theta)$ are, respectively, the direct and exchange scattering amplitudes.

We must find the matrix elements of $\sigma_\mu (\mu = 0, \pm 1)$ for the hyperfine states $|\alpha\rangle = |fm\rangle$, where $f = I \pm \frac{1}{2}$ and I is the nuclear spin of the incident atom. Glassgold carries out this evaluation for the square of the matrix elements (I4.3–I4.6). The proper sign for the σ_0 matrix element is obtained from the Landé g factor due to the electron-spin moment

$$\langle fm|\sigma_0|fm\rangle = m g_f , \tag{4}$$

where $g_f = \pm 2/(2I + 1)$ for $f = I \pm \frac{1}{2}$. The cross section becomes