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HYDRODYNAMICAL FIELD FLUCTUATIONS IN A NON-EQUILIBRIUM QUASI-STATIONARY STATE DUE TO A TEMPERATURE GRADIENT

II. APPLICATION TO LIGHT SCATTERING*

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Within the general theory of hydrodynamical field fluctuations in a system at non-equilibrium due to a temperature gradient, the problem of light scattering on fluctuations in number density is discussed. The effect of the gradient as well as fluctuations in sound velocity and heat conductivity on the Rayleigh–Brillouin spectrum is analyzed. The presence of the temperature gradient and fluctuations modifies the scattered-light spectrum leading to asymmetry in the heights of the Brillouin lines.

1. Introduction

Rayleigh's theory of light scattering can be formulated with sufficient accuracy within the framework of classical field theory: the electromagnetic field of the light wave, on entering the medium, interacts with the electric charges of the atoms (in the case of atomic systems) or with those of the constituent atoms of the molecules (in that of molecular systems). As a result of this interaction the atomic (molecular) systems become secondary sources of light. The electromagnetic waves thus generated in the atoms (molecules) interfere mutually giving rise to scattered light, emerging from the medium in all directions. Maxwell's equations show that if all the regions of the medium possessed the same optical properties, only forward-scattered light would

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emerge since all the other components would cancel out mutually. In reality, however, light scattering systems are dynamical systems, with properties determining those of the scattered light that vary with time differently throughout various regions of the medium. In a sample at thermodynamical equilibrium, the differences are due to spontaneous fluctuations – quite random phenomena of the nature of local perturbations affecting the momentary and local magnitudes of the physical quantities describing the system.

Smoluchowski [1] and Einstein [2] were the first to proceed to an interpretation of light scattering on the basis of thermal fluctuations in continuous media. They succeeded in expressing the scattered light intensity in terms of averages of the squared fluctuations in density and concentration – measures of the local optical inhomogeneities of the medium – which, in turn, can be expressed in terms of macroscopic thermodynamical functions, such as isothermal compressibility and osmotic pressure. This provided the foundations of the fluctuational theory of light scattering. The phenomenological approach proved to be very fruitful, especially when it comes to explaining the frequency distribution of the scattered light. On the basis of spectral analysis Brillouin [3] and Mandelshtam [4] predicted the existence of two lines in the scattered spectrum disposed symmetrically with respect to the Rayleigh line (unshifted in frequency compared with the frequency of the incident light beam). The presence of the Brillouin doublet is due to light scattering on density fluctuations, propagating throughout the medium in the form of acoustic waves. These theoretical considerations were confirmed by Gross in 1930 [5].

The further development of the fluctuational theory of light scattering was fundamentally influenced by Onsager's hypothesis [6], stating that, as the system returns to thermodynamical equilibrium, the fluctuations of the dynamical quantities vanish in accordance with the same relaxational equations as those obeyed by macroscopic processes.

The central role in the phenomenon of light scattering belongs to fluctuations in electric permittivity. These fluctuations are affected by various processes, the evolution of which occurs on various time and space scales. Obviously, they are also dependent on parameters of a thermodynamical nature, like temperature and pressure. This permits the separate experimental investigation of individual processes by applying the appropriate technique in each case. In atomic systems, the predominant contribution comes from fluctuations in density of the order of 1000 Å in size, thus considerably bigger than the distances separating the atoms. They cause collective motions of great numbers of atoms accessible to a description in terms of macroscopic equations in accordance with the hypothesis of Onsager. These collective motions encompass intervals of time and regions of space much greater than those typical for microscopic (atomic, molecular) processes. Hence, the variations of the quantities characterizing the collective motion of the atoms occur in times much longer than the times between successive collisions of the atoms. Landau and Placzek [7] were the first to propose a description of light scattering involving quantities specific to hydrodynamics and thermodynamics. Because of the imperfection of the light sources then available, spectral analysis investigations of light scattering by atomic (gaseous) systems were by no means a popular line of research. It was only the coming of lasers that gave a new impulse to experiments of this type. New spectroscopic techniques were evolved [8, 9]. Also, numerous theoretical papers appeared on light scattering from liquid systems in the hydrodynamical range [10–14].

Rapid developments took place, moreover, in the molecular approach to light scattering in liquids. The work of Born [15], Yvon [16], Fixman [17] and others (see ref. [18]) made light scattering a highly effective method for studying the parameters characterizing atoms and molecules as well as their interactions.

At the same time, attempts were made to fill the gap between the studies of microscopic phenomena by methods of neutron scattering and studies in the hydrodynamical range involving light scattering. This led to the arisal of generalized hydrodynamics, dealing with the thermodynamical coefficients as functions of the wave vector $\boldsymbol{k}$ and the transport coefficients as functions of $\boldsymbol{k}$ and frequency ω [19–21]. At the intersection of these two levels, in molecular liquids, there can occur an exchange of energy between the internal degrees of freedom and those related with translational motion. This leads to the presence of an additional line – the Mountain peak [21] – in the spectrum of scattered light. In comparison with the Rayleigh line, it is much broader and its height is lower, making it observable as a continuous background extending between the Rayleigh line and the Brillouin doublet. This additional component causes divergences from the Lorentzian shape of the lines; moreover, the Landau – Placzek formula [7]

$$\frac{I_c}{2I_B} = \gamma - 1 , \tag{1}$$

expressing the relation between the intensity of the central line I_c, that of the doublet I_B, and the Poisson coefficient $\gamma = C_p/C_V$, ceases to be valid.

In recent years, papers have appeared bearing on light scattering by media in a state of stationary non-equilibrium due to a temperature gradient or a flow velocity gradient [22–26]. In these cases the mechanism of the effect is related with fluctuations about stationarity as the latter evolves slowly towards complete thermodynamical equilibrium.

The earliest research in this field made use of the linear response method

[22–24]. Nonetheless, most papers apply the traditional method of hydrodynamical fluctuations [25, 26]; a few are based on kinetic theory, or the Kadanoff–Swift theory of bonded modes [27–29]. Grabert [30] applies the Fokker–Planck equation, which, with certain additional assumptions concerning the stochastic forces, leads to the method of Langevin.

The aim of the present paper is to derive the correlation function of fluctuations in number density within the framework of our earlier [31] general theory of the correlation theory of hydrodynamic fields in simple systems and to apply the function thus derived to the phenomenon of light scattering. The system under consideration is in a state of non-equilibrium caused by the application of a temperature gradient. The system is assumed to evolve slowly to the state of equilibrium so that we are justified in dealing with the momentary intermediate states as quasi-stationary.

2. The intensity of light scattered on density fluctuations

We consider a non-magnetic, non-conducting and non-absorbing medium. The electric field of the incident plane wave is of the form

$$\boldsymbol{E}(\boldsymbol{r}, t) = \boldsymbol{E}_0 \exp[\mathrm{i}(\boldsymbol{k}_0 \cdot \boldsymbol{r} - \omega_0 t)] , \tag{2}$$

with $\boldsymbol{E}_0$ the amplitude, $\boldsymbol{k}_0$ the wave vector, and ω_0 the frequency. The momentary electric permittivity is

$$\varepsilon(\boldsymbol{r}, t) = \varepsilon_0 + \delta\varepsilon(\boldsymbol{r}, t) , \tag{3}$$

where $\delta\varepsilon(\boldsymbol{r}, t)$ is a fluctuation of the permittivity in the point $\boldsymbol{r}$ at the moment of time t. The time-dependent form of the scattered light intensity at the point of observation, distant by $\boldsymbol{R}$ from the medium (we are interested in the isotropic part only, cf. refs. [18, 32]) is

$$I(\boldsymbol{k}, t) = \frac{I_0(t)\, \omega_0^4}{16\pi^2 R^2 \varepsilon_0^2 c^4} \langle \delta\varepsilon_k(0)\, \delta\varepsilon_k^*(t) \rangle (1 + \cos^2\Theta) , \tag{4}$$

where $\langle \delta\varepsilon_k(0)\, \delta\varepsilon_k^*(t) \rangle$ is the stochastic correlation function of fluctuations in permittivity of the medium, $I_0(t)$ the incident light intensity, Θ the scattering angle, whereas $\boldsymbol{k}$ is now the difference in wave vectors between the incident and the scattered wave. In simple atomic fluids at thermodynamical equilibrium, the electric permittivity is in general a function of the density ρ_0 (or the number of atoms n_0) and temperature T_0, i.e., $\varepsilon_0(n_0, T_0)$. The local values of the number density and the temperature are

$$n(\boldsymbol{r}, t) = n_0 + \delta n(\boldsymbol{r}, t), \qquad T(\boldsymbol{r}, t) = T_0 + \delta T(\boldsymbol{r}, t). \tag{5}$$

On expanding the electric permittivity fluctuations in series in the fluctuations $\delta n(\boldsymbol{r}, t)$ and $\delta T(\boldsymbol{r}, t)$ and rejecting all but the first-order terms, we obtain

$$\delta\varepsilon(\boldsymbol{r}, t) = \left(\frac{\partial \varepsilon}{\partial n}\right)_T \delta n(\boldsymbol{r}, t) + \left(\frac{\partial \varepsilon}{\partial T}\right)_n \delta T(\boldsymbol{r}, t). \tag{6}$$

Experiment shows that in most cases $(\partial\varepsilon/\partial T)_n \simeq 0$, so that only the fluctuations in number density remain. On insertion of (6) into (4) we have

$$I(\boldsymbol{k}, t) = \frac{I_0(t)\, \omega_0^4}{16\pi^2 R^2 \varepsilon_0^2 c^4} \left(\frac{\partial \varepsilon}{\partial n}\right)_T^2 \langle \delta n_k(0)\, \delta n_k(t)\rangle (1 + \cos^2\Theta). \tag{7}$$

For the integral (total) scattering into a given direction, eq. (7) leads to the Einstein–Smoluchowski expression [32]

$$I = \frac{I_0 \omega_0^4}{16\pi^2 R^2 \varepsilon_0^2 c^4 V} \left(\frac{\partial \varepsilon}{\partial n}\right)_{T_0}^2 k_B T_0 n_0^2 \chi_T (1 + \cos^2\Theta). \tag{8}$$

Here V is the scattering volume and

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T_0} \tag{9}$$

the isothermal compressibility of the medium. For a perfect gas $\chi_T = V/k_B T_0 n_0$.

It will be remembered [8] that the spectrum of light scattered on fluctuations in number density expressed within the framework of classical hydrodynamics is the sum of three Lorentzians: the central component is referred to as the Rayleigh line whereas the two others constitute the Brillouin doublet (often referred to as the Stokes line and anti-Stokes line in accordance with Raman terminology). The central line is concentrated at $\omega = 0$ and has a half width of $D_T k^2$. The two Brillouin lines are disposed symmetrically with respect to $\omega = 0$ and are concentrated at $\pm c_s k$ with half widths Γk^2, where D_T is the thermal diffusion coefficient, c_s the adiabatic velocity of sound, and Γ the damping coefficient of acoustic waves.

The form in general use for the description of the spectral distribution of fluctuations in number density (i.e., by way of (7)) of scattered light (cf. ref.

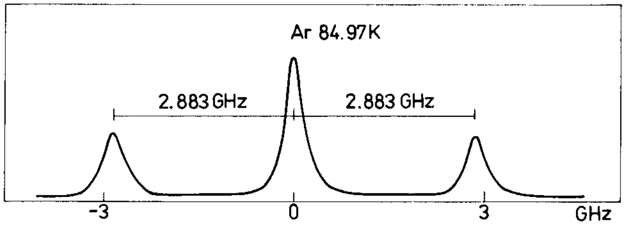

Fig. 1. The spectrum of light scattered by liquid argon ($T = 84.97\ K$, $\Theta = 90°14'$, $\lambda = 5145$ Å).

[32]) is

$$\langle \delta n_k\, \delta n_k^* \rangle = R_k(\omega) + B_{+k}(\omega) + B_{-k}(\omega) ,$$
$$R_k(\omega) = k_B T_0 \chi_T n_0^2 \left(1 - \frac{1}{\gamma}\right) \frac{2 D_T k^2}{\omega^2 + (D_T k^2)^2} , \tag{10}$$
$$B_{\pm k}(\omega) = k_B T_0 \chi_T n_0^2 \frac{1}{2\gamma} \frac{\Gamma k^2}{(\omega \pm c_s k)^2 + (\frac{1}{2}\Gamma k^2)^2} .$$

For the integral intensity, eqs. (10) go over into the Landau–Placzek formula (1).

The spectrum of isotropic light scattering resulting from the above expressions is, in principle, in good agreement with experiment. Fig. 1 shows the Rayleigh line and Brillouin doublet for liquid argon as recorded by Benedek et al. [33].

3. The correlation function of fluctuations in number density in the hydrodynamical range in the presence of a temperature gradient

In an earlier paper [31] we considered an immobile ($\langle v \rangle = 0$) atomic fluid consisting of a great number of identical elements – atoms. No exchange of energy is assumed to occur between the internal and translational degrees of freedom (cf. ref. [30]). We now produce a temperature gradient in the system imposing conditions in which the temperature changes linearly from point to point and the gradient is so weak that the system at every moment of time is in a weakly non-equilibrium quasi-stationary state. The system tends to complete equilibrium, but this requires a time much longer than all the microscopic relaxation times. It thus fulfils the conditions for Bogoliubov hierarchisation of relaxation times and lies within the hydrodynamical region where it can be described in terms of a normal distribution function. It is now dependent on time by way of functions defining the hydrodynamic fields, namely, the scalar fields of number density n and energy density e and the vectorial field of momentum density $\boldsymbol{g}$. We assume these hydrodynamical quantities to fluctuate throughout the medium giving rise to local momentary inhomogeneities in regions of the order of 1000 Å involving transport and dissipation. This motion of great numbers of atoms is accessible to a description in terms of the macroscopic laws of hydrodynamics and thermodynamics. To determine the scattered-light spectrum, one has to calculate the fluctuation correlation functions of hydrodynamic fields. In our earlier paper [31] we have proposed these correlation functions in a form taking into account the greatest possible number of contributions:

i) the effect of a temperature gradient on the viscosity coefficients η and ζ as well as on the heat conductivity coefficient κ and sound velocity c_s;

ii) fluctuations of the velocity of sound and the coefficient of heat conductivity;

iii) calculating the contributions with an accuracy up to terms quadratic in $\boldsymbol{q}$ (the quantity providing a measure of the gradient).

As stated above, the correlation function of fluctuations in number density plays the chief role in the study of light scattering by systems of atoms. In our case it is of the following form (where the notation is that of ref. [31]):

$$\langle \delta n_k\, \delta n_k^* \rangle = \frac{1}{|D(k, q, \omega)|^2} \times \sum_{k', k'', n', l} [\alpha_{12}(\boldsymbol{k}')\, \alpha_{12}^*(\boldsymbol{k}'')\, \beta_{n', l} - \alpha_{13}(\boldsymbol{k}')\, \alpha_{13}^*(\boldsymbol{k}'')\, \beta_{T, n', l}]\,, \quad (11)$$

where

$$\begin{aligned}
\alpha_{12}(\boldsymbol{k}') &= -n_0(s + \gamma D_T k^2)\delta(\boldsymbol{k}' - \boldsymbol{k}) \\
&\quad + \mathrm{i}\,\frac{\delta \tilde{T}}{2}\, n_0 \left(\frac{\partial \gamma D_T k^2}{\partial T}\right)^2 \left\{\left[1 + 2\,\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} + \boldsymbol{q})) \right. \\
&\quad \left. - \left[1 - 2\,\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} - \boldsymbol{q}))\right\} \\
&\quad + \mathrm{i}\,\frac{\delta \tilde{T}}{6}\, n_0 (1 + 1) \left(\frac{\partial \gamma D_T k^2}{\partial T}\right) \left\{\left[\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} + \boldsymbol{q})) \right. \\
&\quad \left. + \left[\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} - \boldsymbol{q}))\right\} \\
&\quad + \frac{(\delta \tilde{T})^2}{12}\, n_0 \left(\frac{\partial^2 \gamma D_T k^2}{\partial T^2}\right) \left(\frac{q}{k}\right)^2 \\
&\quad \times [2\delta(\boldsymbol{k}' - \boldsymbol{k}) + \delta(\boldsymbol{k}' - (\boldsymbol{k} + 2\boldsymbol{q})) - \delta(\boldsymbol{k}' - (\boldsymbol{k} - 2\boldsymbol{q}))]\,, \qquad (12)
\end{aligned}$$

$$\alpha_{13}(\boldsymbol{k}') = -\alpha n_0 c_T^2 k^2 \delta(\boldsymbol{k}' - \boldsymbol{k}) + \mathrm{i}\,\frac{\delta\tilde{T}}{2}\,\alpha n_0(1 + 1)\left(\frac{\partial c_T^2 k^2}{\partial T}\right)$$
$$\times \left\{\left[1 + 2\,\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} + \boldsymbol{q}))\right.$$
$$\left. - \left[1 - 2\,\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} + \left(\frac{q}{k}\right)^2\right]\delta(\boldsymbol{k}' - (\boldsymbol{k} - \boldsymbol{q}))\right\}, \qquad (13)$$

whereas $\beta_{n',l}$ and $\beta_{T,n',l}$ are correlation functions of the stochastic parts of the equations of motion of the fluctuations in velocity (momentum) and temperature (energy),

$$\beta_{n',0} = 2k_B T_0 m n_0 D_V(\boldsymbol{k} + n'\boldsymbol{q})^4 \delta(\omega - \omega')$$
$$+ k_B(\delta\tilde{T})^2 m n_0\left(\frac{\partial D_V}{\partial T}\right)(\boldsymbol{k} + n'\boldsymbol{q})^4\delta(\omega - \omega'), \qquad (14)$$

$$\beta_{n',\pm1} = \mp k_B\delta\tilde{T}\left[2\eta\left(1 + \frac{\partial \ln \eta}{\partial \ln T}\right)(\boldsymbol{k} + n'\boldsymbol{q})^2[\boldsymbol{k} + (n' \pm 1)\boldsymbol{q}]^2\right.$$
$$+ (\zeta - \tfrac{2}{3}\eta)\left(1 + \frac{\partial \ln (\zeta - \frac{2}{3}n)}{\partial \ln T}\right)$$
$$\left.\times (\boldsymbol{k} + n'\boldsymbol{q})^2[\boldsymbol{k} + (n' \pm 1)\boldsymbol{q}]^2\right]\delta(\omega' - \omega), \qquad (15)$$

$$\beta_{n',\pm2} = \frac{(\delta\tilde{T})^2}{2}\,k_B\left[2\left(\frac{\partial n}{\partial T}\right)(\boldsymbol{k} + n'\boldsymbol{q})^2[\boldsymbol{k} + (n' \pm 2)\boldsymbol{q})^2\right.$$
$$\left. + \left(\frac{\partial(\zeta - \frac{2}{3}n)}{\partial T}\right)(\boldsymbol{k} + n'\boldsymbol{q})^2[\boldsymbol{k} + (n' \pm 2)\boldsymbol{q}]^2\right]\delta(\omega' - \omega), \qquad (16)$$

$$\beta_{T,n',0} = 2k_B T_0 \kappa(\boldsymbol{k} + n'\boldsymbol{q})^2\delta(\omega' - \omega)$$
$$+ k_B\kappa(\delta\tilde{T})^2\left(1 + 2\,\frac{\partial \ln \kappa}{\partial \ln T}\right)(\boldsymbol{k} + n'\boldsymbol{q})\delta(\omega' - \omega), \qquad (17)$$

$$\beta_{T,n',\pm1} = \left[\mp\mathrm{i}k_B T_0\kappa\delta\tilde{T}\left(2 + \frac{\partial \ln \kappa}{\partial \ln T}\right)(\boldsymbol{k} + n'\boldsymbol{q})[\boldsymbol{k} + (n' \pm 1)\boldsymbol{q}]\right.$$
$$\left.\mp \mathrm{i}\cdot\tfrac{3}{4}k_B\kappa\,\frac{(\delta\tilde{T})^3}{T_0}\left(\frac{\partial \ln \kappa}{\partial \ln T}\right)(\boldsymbol{k} + n'\boldsymbol{q})(\boldsymbol{k} + (n' \pm 1)\boldsymbol{q})\right]\delta(\omega' - \omega), \qquad (18)$$

$$\beta_{T,n',\pm2} = -\tfrac{1}{2}k_B\kappa(\delta\tilde{T})^2\left(1 + 2\,\frac{\partial \ln \kappa}{\partial \ln T}\right)(\boldsymbol{k} + n'\boldsymbol{q})[\boldsymbol{k} + (n' \pm 2)\boldsymbol{q}]\delta(\omega' - \omega). \qquad (19)$$

To determine $D(\boldsymbol{k}, s, \boldsymbol{q})$, one has to solve the dispersion relation $D(\boldsymbol{k}, s, \boldsymbol{q}) = 0$ with respect to $s = -\mathrm{i}\omega$ and factorize the polynomial. On restricting ourselves to terms in q^2, we get

$$|D(\boldsymbol{k}, \omega, \boldsymbol{q})|^{-2} = |D(\boldsymbol{k}, \omega)|^{-2}[1 - F(\omega, \boldsymbol{k})] , \tag{20}$$

where

$$|D(\boldsymbol{k}, \omega)|^2 = [\omega^2 + (D_{\mathrm{T}}k)^2][(\omega + c_{\mathrm{s}}k)^2 + (\Gamma k^2)^2][(\omega - c_{\mathrm{s}}k)^2 + (\Gamma k^2)^2] . \tag{21}$$

The function $F(\omega, \boldsymbol{k})$ occurring in (20) is moreover dependent on the thermodynamical parameters D_{V}, D_{T} and c_{s} of the medium. Since we are interested in how the function $F(\omega, \boldsymbol{k})$ affects the scattered light spectrum, the only values of relevance to us are those for the frequencies corresponding to the individual lines:

$$\begin{aligned} &\omega = 0 \qquad &&\text{Rayleigh line } F(\omega, k) \to f_{\mathrm{R}} , \\ &\omega \pm c_{\mathrm{s}}k \qquad &&\text{Stokes and anti-Stokes Brillouin lines,} \\ & &&F(\omega, k) \to f_{\mathrm{B}} \quad \text{or} \quad f_{\mathrm{B'}} . \end{aligned} \tag{22}$$

On transforming (20) appropriately and using the preceding notation, we obtain

$$\begin{aligned} |D(\boldsymbol{k}, \omega, \boldsymbol{q})|^{-2} = {} & \frac{1 - f_{\mathrm{R}}}{(c_{\mathrm{s}}k)^4[\omega^2 + (D_{\mathrm{T}}k^2)^2]} + \frac{1 - f_{\mathrm{B}}}{4(c_{\mathrm{s}}k)^4[(\omega - c_{\mathrm{s}}k)^2 + (\Gamma k^2)^2]} \\ & + \frac{1 - f_{\mathrm{B'}}}{4(c_{\mathrm{s}}k)^4[(\omega + c_{\mathrm{s}}k)^2 + (\Gamma k^2)^2]} , \end{aligned} \tag{23}$$

on neglecting the insignificant terms that appear in calculating (20) for $\omega = 0$ and $\omega = \pm c_{\mathrm{s}}k$, respectively. Each of the functions f_{R}, f_{B} and $f_{\mathrm{B'}}$ can be expressed as the sum of components, independent of the parameter $\boldsymbol{q}$, dependent linearly $(\boldsymbol{k} \cdot \boldsymbol{q}/k^2)$ on $\boldsymbol{q}$, and quadratically $(\boldsymbol{k} \cdot \boldsymbol{q}/k^2)^2$ on $\boldsymbol{q}$:

$$f_i = f_{i,0} + f_{i,1} + f_{i,2} . \tag{24}$$

Their explicit form is rather bulky and is to be found in appendix B of our paper [31], whereas the significant part of the spectrum comes from the greatest components:

$$f_{\mathrm{R},0} = -\tfrac{1}{4}(\gamma^2 + 2\gamma - 3)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)^2 + \tfrac{1}{2}(\gamma - 1)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)\left(\frac{D_\mathrm{V}k^2}{c_\mathrm{s}k}\right) - \tfrac{1}{4}\left(\frac{D_\mathrm{V}k^2}{c_\mathrm{s}k}\right)^2 , \tag{25}$$

$$f_{\mathrm{R},1} = \frac{1}{2}\,\frac{\delta\tilde{T}}{T_0}\left\{\left[8 + \left(\frac{16}{\gamma - 1} + 16\right)\left(\frac{\Gamma k^2}{c_\mathrm{s}k}\right)^2 - 2(\gamma + \gamma - 1)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)\right]\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln T}\right) + T_{0\alpha}\left[-8 + \frac{16}{\gamma - 1}\left(\frac{\Gamma k^2}{c_\mathrm{s}k}\right) - 2\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)\right]\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln n}\right)\right\}\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} , \tag{26}$$

$$f_{\mathrm{R},2} = \frac{1}{2}\left(\frac{\delta\tilde{T}}{T_0}\right)\frac{1}{\gamma^2}\left[8(\gamma^2 + 2 + 2\gamma^2 + 6\gamma - 4)\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln T}\right)^2 + 24(T_0\alpha)^2\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln n}\right)^2\right]\left(\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}\right)^2 , \tag{27}$$

$$f_{\mathrm{B},0} = -\tfrac{1}{16}(\gamma^2 + 2\gamma - 3)\left(\frac{D_\mathrm{T}k}{c_\mathrm{s}k}\right)^2 + \tfrac{1}{8}(\gamma - 1)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)\left(\frac{D_\mathrm{V}k^2}{c_\mathrm{s}k}\right) - \frac{1}{16}\left(\frac{D_\mathrm{V}k}{c_\mathrm{s}k}\right)^2 , \tag{28}$$

$$f_{\mathrm{B}',0} = f_{\mathrm{B},0} , \tag{29}$$

$$\begin{aligned} f_{\mathrm{B},1} = \frac{\delta\tilde{T}}{T_0}\,\frac{1}{\gamma}\Bigg\{\Bigg[&4(1 + \gamma - 1)\left(\frac{c_\mathrm{s}k}{\Gamma k^2}\right) \\ &+ (\gamma - 1)(\gamma^2 - 2\gamma + 1 + \gamma^3 - 3\gamma^2 + 3\gamma - 1)\left(\frac{D_\mathrm{T}}{\Gamma}\right)\left(\frac{D_\mathrm{V}}{\Gamma}\right) \\ &+ \frac{\gamma - 1}{64}(3\gamma^3 - 129\gamma + \gamma^3 - \gamma^2 - 137\gamma - 383)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right) \\ &+ (1 + \gamma - 1)\left(\frac{\Gamma k^2}{c_\mathrm{s}k}\right)\Bigg]\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln T}\right) \\ &+ \Bigg\{4\left(\frac{c_\mathrm{s}k}{\Gamma k^2}\right) + \left(\frac{\Gamma k^2}{c_\mathrm{s}k}\right) + 8(\gamma - 1)\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right) \\ &- \tfrac{1}{2}(\gamma - 1)\left[\left(\frac{\Gamma k^2}{c_\mathrm{s}k}\right) + 2\left(\frac{D_\mathrm{T}k^2}{c_\mathrm{s}k}\right)\right](\gamma^2 + 2\gamma - 3)\left(\frac{D_\mathrm{T}}{\Gamma}\right)^2\Bigg\} \\ &\times T_0\alpha\left(\frac{\partial \ln c_\mathrm{s}}{\partial \ln n}\right)\Bigg\}\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2} , \end{aligned} \tag{30}$$

$$f_{\mathrm{B}',1} = \frac{\delta\tilde{T}}{T_0}\,\frac{1}{\gamma}\left(\left[4(1+\gamma-1)\left(\frac{c_{\mathrm{s}}k}{\Gamma k^2}\right)\right.\right.$$
$$+(\gamma-1)(\gamma^2-2\gamma+1+\gamma^3-3\gamma^2+3\gamma-1)\left(\frac{D_{\mathrm{T}}}{\Gamma}\right)\left(\frac{D_{\mathrm{V}}}{\Gamma}\right)$$
$$+\frac{\gamma-1}{64}(3\gamma^3-129\gamma+\gamma^3-\gamma^2-137\gamma-639)\left(\frac{D_{\mathrm{T}}k^2}{c_{\mathrm{s}}k}\right)$$
$$\left.+(1+\gamma-1)\left(\frac{\Gamma k^2}{c_{\mathrm{s}}k}\right)\right]\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln T}\right)$$
$$+\left\{4\left(\frac{c_{\mathrm{s}}k}{\Gamma k^2}\right)+\left(\frac{\Gamma k^2}{c_{\mathrm{s}}k}\right)-8(\gamma-1)\left(\frac{D_{\mathrm{T}}k^2}{c_{\mathrm{s}}k}\right)\right.$$
$$\left.+\tfrac{1}{2}(\gamma-1)\left[\left(\frac{\Gamma k^2}{c_{\mathrm{s}}k}\right)+2\left(\frac{D_{\mathrm{T}}k^2}{c_{\mathrm{s}}k}\right)\right](\gamma^2+2\gamma-3)\left(\frac{D_{\mathrm{T}}}{\Gamma}\right)^2\right\}$$
$$\left.\times\, t_0\alpha\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln n}\right)\right)\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}\,, \tag{31}$$

$$f_{\mathrm{B},2} = \left(\frac{\delta\tilde{T}}{T_0}\right)^2\frac{1}{\gamma^2}\left[6(\gamma^2+\gamma^2-1)\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln T}\right)^2\right.$$
$$+12(\gamma+\gamma-1)T_0\alpha\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln T}\right)\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln n}\right)$$
$$\left.+6(T_0\alpha)^2\left(\frac{\partial\ln c_{\mathrm{s}}}{\partial\ln n}\right)^2\right]\left(\frac{\boldsymbol{k}\cdot\boldsymbol{q}}{k^2}\right)^2, \tag{32}$$

$$f_{\mathrm{B}',2} = f_{\mathrm{B},2}\,. \tag{33}$$

One sees that the corrections to the Brillouin lines differ just slightly as to their absolute values, and this only in the linear parts of the respective expressions. The underlinings applied above have the following meaning in accordance with ref. [31]:

------- terms related with the temperature gradient;

______ terms related with fluctuations of the transport coefficients and isothermal sound velocity;

=\=\=\=\=\= cross-terms; whereas terms due to the fundamental hydrodynamic field fluctuations are not underlined.

With regard to eq. (2) et seq., the correlation function (11) takes the form

$$\langle\delta n_k\,\delta n_k^*\rangle = R_k(\omega)+B_{+k}(\omega)+B_{-k}(\omega)\,, \tag{34}$$

the Rayleigh component being

$$R_k(\omega) = k_B T_0 \chi_T n_0^2 \left(1 - \frac{1}{\gamma}\right) \frac{2D_T k^2}{\omega^2 + (D_T k^2)^2} \times [1 - A - B(\hat{k}\cdot\hat{q}) + C(\hat{k}\cdot\hat{q}) + D(\hat{q}\cdot\hat{q})] , \quad (35)$$

and the Brillouin components

$$B_{+k}(\omega) = k_B T_0 \chi_T n_0^2 \frac{1}{2\gamma} \frac{\Gamma k^2}{(\omega + c_s k)^2 + (\frac{1}{2}\Gamma k^2)^2} \times [1 - A' + B'(\hat{k}\cdot\hat{q}) + C'(\hat{k}\cdot\hat{q})^2 + D'(\hat{q}\cdot\hat{q})] , \quad (36)$$

$$B_{-k}(\omega) = k_B T_0 \chi_T n_0^2 \frac{1}{2\gamma} \frac{\Gamma k^2}{(\omega - c_s k)^2 + (\frac{1}{2}\Gamma k^2)^2} \times [1 - A' + B''(\hat{k}\cdot\hat{q}) + C'(\hat{k}\cdot\hat{q})^2 + D'(\hat{q}\cdot\hat{q})] . \quad (37)$$

The vectors $\hat{k}$ and $\hat{q}$ are unit vectors. In (35)–(37) we have made use of the following notation:

$$\begin{aligned} A &= (1 + a) f_{R,0} , \\ B &= (1 + a) f_{R,1} \lambda , \\ C &= [(f_2'' - a f_2)(1 - f_{R,0}) - (1 - a) f_{R,2}] \lambda^2 , \\ D &= (f_2''' - a f_2')(1 - f_{R,0}) \lambda^2 , \end{aligned} \quad (38)$$

$$\begin{aligned} A' &= (1 + b) f_{B,0} , \\ B' &= (1 + b) f_{B',1} \lambda , \\ C' &= \{(h f_2 + f_2'')(1 - f_{B,2}) + [h f_2 (b - c) - f_2'' d](1 - f_{B,0}) - b f_{B,2}\} \lambda^2 , \\ D' &= [h^2 f_2' (1 + b - c) + f_2''' (1 - d)](1 - f_{B,0}) \lambda^2 , \end{aligned} \quad (39)$$

and

$$B'' = (1 - b) f_{B,1} \lambda , \quad (40)$$

whereas

$$\begin{aligned} a &= \frac{1}{\gamma - 1} \left(\frac{\gamma D_T k^2}{c_s k}\right)^2 \left(\frac{D_V}{D_T}\right) , \qquad b = \left(\frac{\gamma D_T k^2}{c_s k}\right)^2 \left(\frac{D_V}{\Gamma}\right) , \\ c &= (\gamma - 1) \frac{D_T}{\Gamma} , \qquad d = \frac{D_V}{\Gamma} , \\ \lambda &= \frac{q}{k} , \qquad h = \left(\frac{\gamma D_T k^2}{c_s k}\right) , \end{aligned} \quad (41)$$

and the functions f_2, f_2', f_2'' and f_3''' of eqs. (38)–(41) are as follows:

$$\begin{aligned} f_2 = {} & \left(\frac{\delta\tilde{T}}{T_0}\right)^2 \left(\tfrac{19}{3} + \tfrac{2}{3}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right) + \left(\tfrac{32}{3} + \tfrac{2}{3}\right)\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right) \\ & + \left(\tfrac{343}{9} + \tfrac{39}{9}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^2 \\ & + \left(\frac{\delta\tilde{T}}{T_0}\right)^2 \left(\tfrac{13}{30} + \tfrac{11}{30}\right)\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^2 , \end{aligned} \tag{42}$$

$$\begin{aligned} f_2' = {} & \left(\frac{\delta\tilde{T}}{T_0}\right)^2 \left[2\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right) - \left(1 - 2 - \frac{\delta\tilde{T}}{T_0}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^2 \right. \\ & - \frac{\delta\tilde{T}}{T_0}\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^2 \\ & + \frac{\delta\tilde{T}}{T_0}\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^3 + \frac{\delta\tilde{T}}{T_0}\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)^3 + \left(\frac{\partial^2 \ln D_{\mathrm{T}}}{\partial (\ln T)^2}\right) \\ & \left. - \frac{\delta\tilde{T}}{T_0}\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)\left(\frac{\partial^2 \ln D_{\mathrm{T}}}{\partial (\ln T)^2}\right) - \frac{\delta\tilde{T}}{T_0}\left(\frac{\partial \ln D_{\mathrm{V}}}{\partial \ln T}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)\left(\frac{\partial^2 \ln D_{\mathrm{T}}}{\partial (\ln T)^2}\right) \right] , \end{aligned} \tag{43}$$

$$\begin{aligned} f_2'' = {} & \frac{\delta\tilde{T}}{T_0}\left[(1 + 3)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right)^2 + 24(1 + 1)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right) \right. \\ & + \left(\frac{\delta\tilde{T}}{T_0}\right)^2 \left(\tfrac{1}{4} + \tfrac{3}{4}\right)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right)^2 \\ & \left. + 12(1 + 1)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right) \right] , \end{aligned} \tag{44}$$

$$f_3''' = 4\left(\frac{\delta\tilde{T}}{T_0}\right)^2 \left[(1 - 1)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right) - (1 - 1)\left(\frac{\partial \ln D_{\mathrm{T}}}{\partial \ln T}\right)\left(\frac{\partial \ln c_{\mathrm{s}}}{\partial \ln T}\right) \right] . \tag{45}$$

In most cases $a, b \ll 1$ and one is justified in simplifying the expressions:

$$\begin{aligned} & A \approx f_{\mathrm{R},0} , \qquad B \approx f_{\mathrm{R},1}\lambda , \\ & C \approx [(f_2'' + af_2) - f_{\mathrm{R},2}]\lambda^2 , \qquad D \approx (f_2''' - af_2')\lambda^2 , \end{aligned} \tag{46}$$

$$\begin{aligned} & A' \approx f_{\mathrm{B},0} , \qquad B' \approx f_{\mathrm{B}',1}\lambda , \qquad B'' \approx f_{\mathrm{B},1}\lambda , \\ & C' \approx (hf_2 + f_2' - hf_2 c - f_2'' d)\lambda^2 , \qquad D' \approx f_2'''\lambda^2 . \end{aligned} \tag{47}$$

The preceding simplification is well founded physically and will be essential to our further considerations enabling us to write the expressions in compact form with a view to detailed analysis.

4. Discussion and conclusions

For a detailed analysis of the expressions (34) et seq., derived above, it is convenient to rewrite eqs. (35)–(37) as follows:

$$R_k(\omega) = k_B T_0 \chi_T n_0^2\left(1 - \frac{1}{\gamma}\right) \frac{2D_T k^2}{\omega^2 + (D_T k^2)^2}\{1 - A_1(0) - A_2(\nabla T)\cos\beta + [A_3(\nabla T) + A_4(\nabla T)]\cos^2\beta + A_5(\nabla T)\}\,, \tag{48}$$

$$B_{\pm k}(\omega) = k_B T_0 \chi_T n_0^2 \frac{1}{2\gamma} \frac{\Gamma k^2}{(\omega \pm c_s k)^2 + (\frac{1}{2}\Gamma k^2)^2} \times \{1 - \tfrac{1}{4}A_1(0) \pm [A_6(\nabla T) + A_7(\nabla T)]\cos\beta + [A_3(\nabla T) + A_4(\nabla T)]\cos^2\beta + A_5(\nabla T)\}\,, \tag{49}$$

where $\cos\beta = \hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{q}}$ is the cosine of the angle between the temperature gradient ∇T and the scattering vector (the latter is the difference between the wave vectors of the incident wave and scattered wave observed). The terms A_i, $i = 1, 2, \ldots, 7$, have the form

$$\begin{aligned}
A_1(0) &= -\tfrac{1}{4}(\gamma^2 + 2\gamma - 3)\left(\frac{D_T k}{c_s}\right)^2 + \tfrac{1}{2}(\gamma - 1)\left(\frac{D_T k}{c_s}\right)\left(\frac{D_V k}{c_s}\right) - \frac{1}{4}\left(\frac{D_V k}{c_s}\right)^2, \\
A_2(\nabla T) &= \frac{4}{c_s}[1 + (1 + \alpha t)^2]\left(\frac{\partial c_s}{\partial T}\right)\left(\frac{q}{k}\right)\nabla T\,, \\
A_3(\nabla T) &= \frac{24}{c_s}\frac{1}{\delta\tilde{T}}\left(\frac{\partial c_s}{\partial T}\right)\left(\frac{q}{k}\right)^2(\nabla T)^2\,, \\
A_4(\nabla T) &= \frac{48}{c_s}\frac{1}{\delta\tilde{T}}\left(\frac{\partial c_s}{\partial T}\right)\left(\frac{q}{k}\right)^2(\nabla T)^2\,, \\
A_5(\nabla T) &= \frac{4}{T_0 c_s \delta\tilde{T}}\left(\frac{\partial c_s}{\partial T}\right)\left[1 - \frac{T_0}{D_T}\left(\frac{\partial D_T}{\partial T}\right)\right]\left(\frac{q}{k}\right)^2(\nabla T)^2\,, \\
A_6(\nabla T) &= \frac{4}{\Gamma k}\frac{1}{(\gamma + 1)}\left(\frac{\partial c_s}{\partial T}\right)[1 + (1 + \alpha t)^2]\left(\frac{q}{k}\right)\nabla T\,, \\
A_7(\nabla T) &= \frac{4}{\Gamma k}\left(\frac{\partial c_s}{\partial T}\right)[1 + (1 + \alpha t)^2]\left(\frac{q}{k}\right)\nabla T\,.
\end{aligned} \tag{50}$$

By eq. (50), we have

$$A_4(\nabla T) = 2A_3(\nabla T)\,,$$
$$A_6(\nabla T) = \left(1 - \frac{1}{\gamma}\right)A_7(\nabla T)\,. \tag{51}$$

Eqs. (50) are contributions to the scattered light spectrum due to the temperature gradient and the fluctuations in sound velocity and thermal conductivity coefficient. One readily notes that on omission of the temperature gradient eqs. (48) and (49) go over into (10) provided that we moreover neglect $A_1(0)$ — a very small term resulting from the inclusion of higher-order solutions of the dispersion equation. The latter correlation, however, modifies the Landau–Placzek expressions (eq. (10)) and the total scattered intensity, which takes the form

$$\frac{R_k}{2B_k} = \frac{(1-1/\gamma)[1-A_1(0)]}{(1/\gamma)[1-\frac{1}{4}A_1(0)]} = \frac{4[\gamma - 1 - A_1(0)\,(\gamma-1)]}{4 - A_1(0)}\,, \tag{52}$$

$$R_k + 2B_k = k_B T_0 \chi_T n_0^2\left[1 - A_1(0)\left(1 - \frac{1}{\gamma} + \frac{1}{4\gamma}\right)\right]. \tag{53}$$

A comparison of (48), (49) with expressions (10) leads to the conclusion that the line shapes are unaffected by these corrections; they remain Lorentzian, and only their heights undergo modifications in each point of the spectrum. The corrections $A_2(\nabla T)$, $A_6(\nabla T)$ and $A_7(\nabla T)$ are linearly dependent on ∇T, whereas $A_3(\nabla T)$, $A_4(\nabla T)$ and $A_5(\nabla T)$ are quadratic in ∇T. The latter three corrections affect all three lines identically by way of the factor $[A_3(\nabla T) + A_4(\nabla T)]\cos^2\beta + A_5(\nabla T)$. Thus the whole spectrum undergoes a modification by this factor albeit with no differences between the modifications experienced by the individual lines.

Table I gives a detailed discussion of the expressions (48) and (49) in relation to the angle β between the temperature gradient and the scattering vector (the difference between the wave vectors of the incident and scattered light waves).

The most essential corrections seem to be $A_6(\nabla T)$ and $A_7(\nabla T)$. Being functions of the temperature gradient vector, they are direction dependent and lead to asymmetry in the heights of the Brillouin components. The matter has first been discussed in 1979 by Procaccia et al. [22] and independently by Kirkpatrick et al. [26] and dealt with from different points of view (see the review article of Schmitz [34]). In our approach, based on the general fluctuation theory of hydrodynamical fields in systems involving a temperature

Table I
Dependence of the Rayleigh and Brillouin lines on the angle between the temperature gradient and the scattering vector.

cos β	The expressions for $R_k(\omega)$ and $B_{\pm k}(\omega)$ [a]
1 $\quad \overset{\nabla T}{\underset{k}{\rightrightarrows}}$	$R_k(\omega) = \tilde{\tilde{R}}_k(\omega)\,[1 - A_1(0) - A_2(\nabla T) + A_3(\nabla T) + A_4(\nabla T) + A_5(\nabla T)]$, $B_{\pm k}(\omega) = \tilde{\tilde{B}}_{\pm k}(\omega)\,[1 - \frac{1}{4}A_1(0) \pm A_6(\nabla T) \pm A_7(\nabla T) + A_3(\nabla T) + A_4(\nabla T) + A_5(\nabla T)]$,
0 $\quad \nabla T \uparrow \underset{k}{\rightarrow}$	$R_k(\omega) = \tilde{\tilde{R}}_k(\omega)\,[1 - A_1(0) + A_5(\nabla T)]$, $B_{\pm k}(\omega) = \tilde{\tilde{B}}_{\pm k}(\omega)\,[1 - \frac{1}{4}A_1(0) + A_5(\nabla T)]$,
−1 $\quad \overset{\nabla T}{\underset{k}{\leftrightarrows}}$	$R_k(\omega) = \tilde{\tilde{R}}_k(\omega)\,[1 - A_1(0) + A_2(\nabla T) + A_3(\nabla T) + A_4(\nabla T) + A_5(\nabla T)]$, $B_{\pm k}(\omega) = \tilde{\tilde{B}}_{\pm k}(\omega)\,[1 - \frac{1}{4}A_1(0) \mp A_6(\nabla T) \mp A_7(\nabla T) + A_3(\nabla T) + A_4(\nabla T) + A_5(\nabla T)]$.

[a] For simplicity, we use the following notation:

$$\tilde{\tilde{R}}_k(\omega) = k_B T_0 \chi_T n_0^2 (1 - 1/\gamma)\, \frac{(2D_T k^2)}{[\omega^2 + (D_T k^2)^2]}\,, \quad \tilde{\tilde{B}}_{\pm k}(\omega) = k_B T_0 \chi_T n_0^2 (1/2\gamma)\, \frac{\Gamma k^2}{[(\omega \pm c_s k)^2 + (\frac{1}{2}\Gamma k^2)^2]}\,.$$

gradient [31], we distinguish two mechanisms of the asymmetry: one related with the temperature gradient only, $A_6(\nabla T)$, and the other related with the gradient as well as the fluctuations in transport coefficients and sound velocity, $A_7(\nabla T)$. The asymmetry of the Brillouin lines is shown schematically in fig. 2 (for the sake of clarity, we have omitted $A_1(0)$, the terms A_3, A_4 and A_5 related with the square of the gradient, as well as the term A_2 of no effect on the Brillouin lines, in this way rendering more strongly the role of A_6 and A_7 responsible for the asymmetry).

By analogy with eqs. (52) and (53) we can write Landau–Placzek type formulae that hold as well when a temperature gradient exists in the system. Let us put $\cos\beta = 1$ and restrict ourselves to a linear dependence on ∇T. We

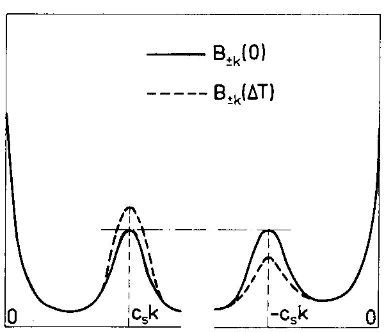

Fig. 2. The scattered light spectrum from atomic systems. Continuous graph ——— standard Brillouin spectrum, dashed graph ------- Brillouin spectrum with temperature gradient imposed on the system.

thus obtain

$$\frac{R_k}{B_{\pm k}} = \frac{(1-1/\gamma)[1-A_1(0)-A_2(\nabla T)]}{(1/2\gamma)[1-\frac{1}{4}A_1(0)\pm A_6(\nabla T)\pm A_7(\nabla T)]}\,,$$

$$\frac{B_{+k}}{B_{-k}} = \frac{1-\frac{1}{4}A_1(0)+A_6(\nabla T)+A_7(\nabla T)}{1-\frac{1}{4}A_1(0)-A_6(\nabla T)-A_7(\nabla T)}\,, \tag{54}$$

$$R_k + B_{+k} + B_{-k} = k_B T_0 \chi_T n_0^2\left[1 - A_1(0)\left(1-\frac{1}{\gamma}+\frac{1}{4\gamma}\right) - A_2(\nabla T)\left(1-\frac{1}{\gamma}\right)\right].$$

Obviously, eqs. (54) reduce to (52), (53) in the absence of the gradient. The above equations show that the corrections A_6 and A_7 causing asymmetry of the Brillouin lines (the ratio B_{+k}/B_{-k} provides a measure of the asymmetry) have no effect on the Rayleigh line (dependent on ∇T by A_2) or the integral scattering (for a given direction of observation).

The expression

$$\frac{B_{+k}-B_{-k}}{B_{+k}+B_{-k}} = \frac{A_6(\nabla T)+A_7(\nabla T)}{1-\frac{1}{4}A_1(0)}\cos\beta \tag{55}$$

is sometimes used as a measure of the Brillouin lines asymmetry (in (55), we have omitted terms quadratic in ∇T). Beysens et al. [35, 36] and Kiefte et al. [37] have carried out experimental studies of eq. (55) versus ∇T for various values of the angle β. Similar measurements have also been performed by Schmitz and Cohen [38] on the basis of their theory, which comprises effects of absorption and reflection of acoustic waves as well as spatial inhomogeneities caused by the temperature gradient.

All in all, the temperature dependence of the parameters characterizing the medium, as well as the very presence of a temperature gradient, act in a manner to modify perceptibly the spectrum of scattered light giving rise to asymmetry in the Brillouin lines due to correlations between the fluctuations in density and the dissipative flow of Joule heat caused by the temperature gradient. A method of calculation similar to ours has been applied in refs. [25, 26], and especially in ref. [23], albeit on a much more modest scale. The authors of refs. [25, 26] apply the method of fluctuational hydrodynamics and arrive at the correlation function of density fluctuations. They restrict themselves, however, to the influence of the temperature gradient on the sound velocity, viscosity coefficient, and heat conductivity coefficient, but neglect the fluctuations of these quantities. Moreover, they restrict themselves to solving the equation of dispersion to the second order of perturbation calculus. Also, the correlation functions of the stochastic parts of their hydrodynamical equations are presented more intuitively than it would result strictly from calculation. Tremblay et al. [23] have applied a calculation technique resembling ours involving Langevin's formalism; however, like the authors of refs. [25, 26], they fail to take into consideration fluctuations in sound velocity and heat conductivity coefficient. Our approach [31], in fact, appears to be more thorough and of a higher degree of generality.

A suggestion put forward in certain papers [22–26] concerning the interpretation of the asymmetry in the Brillouin lines seems to be of interest. The mechanism invoked is that of a flow of Joule heat caused by the gradient of temperature: thus, a given point of the medium receives more phonons from warmer regions than from colder ones. Hence, depending on the geometry chosen in experiment, one of the Brillouin lines is taller than the other.

Recently, the number of papers dealing with various aspects of hydrodynamical fluctuations and heat conductivity in simple atomic systems also involving the presence of a temperature gradient has increased notably [39–43], proving the importance of the problems under consideration and the growing interest in the subject.

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