Dispersion of the transport coefficients and modification of the Rayleigh light-scattering triplet in a gas

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The transport equation is used to calculate the eigenvalues (transport coefficients) and the eigenfunctions in two characteristic dispersion frequency ranges. It is shown that changes in the eigenfunctions in dispersion regions modify the spectrum of the triplet of the Rayleigh scattering of polarized light when the gas pressure is varied.

1. INTRODUCTION

The Boltzmann transport equation method is convenient for calculation of the transport coefficients of a gas.[1-3] The problem reduces to determination of the eigenvalues of the linearized Boltzmann collision integral. This method was used in Ref. 4 to study dispersion of the velocity and absorption of sound in a gas with rotational degrees of freedom.

We shall allow for the modification of the eigenvalues (transport coefficients such as the thermal conductivity, thermal diffusivity, and bulk viscosity) and for the hitherto ignored modification of the eigenfunctions of the transport equation in the region of characteristic dispersion frequencies. It is the change in the eigenfunctions that alters the spectrum of the triplet of the Rayleigh scattering of polarized light. In the case of a gas it is convenient to describe the dispersion as the dependence of the transport coefficients on the gas density N, which is equivalent to the usually employed parameter $\omega\tau$, where ω is the frequency and the relaxation time τ depends on the density: $\tau \propto N^{-1}$. Our main result is a demonstration of a new component in the spectrum of the Rayleigh-scattered light in a dispersion region and of the fact that the width of this component proportional to τ^{-1} is governed by slow relaxation of the internal degrees of freedom to translational motion.

2. TRANSPORT COEFFICIENTS OF A GAS WITH INTERNAL DEGREES OF FREEDOM

We consider the eigenvalue problem using the Boltzmann collision integral $\hat{I}_0$ linearized about the equilibrium distribution function $f_0(\Gamma)$. The one-particle function f then becomes

$$f(\mathbf{R},\Gamma)=f_0(\Gamma)[1+\chi(\mathbf{R},\Gamma)],\quad \chi\ll 1,\qquad f_0=\exp\left[-\frac{(\mu-E)}{T}\right],$$

where μ is the chemical potential of the gas, E is the total energy of a molecule, T is the gas temperature, $\mathbf{R}$ is the spatial coordinate, and Γ is the set of all the remaining variables which determine the distribution function f. In the case of a diatomic molecule the set Γ includes not only the velocity vector $\mathbf{v}$, but also the angular momentum vector $\mathbf{M}$ (representing the rotational degrees of freedom) and the energy E (rotational quantum numbers) of the vibrations. In the spatial Fourier representation the eigenvalue problem of the Boltzman transport equation becomes

$$\begin{gathered}(i\mathbf{qv}+\hat{I}_0)\chi_n(\mathbf{q},\Gamma)=\lambda_n\chi_n(\mathbf{q},\Gamma),\\ \chi(\mathbf{q},\Gamma)=\int e^{-i\mathbf{qR}}\chi(\mathbf{R},\Gamma)\,d\mathbf{R}.\end{gathered}\tag{1}$$

Here, $\hat{I}_0$ is the positive definite linearized Boltzmann collision integral.[5]

We can see from Eqs. (1) that the transport equation includes two terms which are in the ratio

$$qv/I_0\sim qv_0/\nu,$$

where $v_0=(T/m)^{1/2}$ is the average thermal velocity and ν is the characteristic frequency of the operator $\hat{I}_0$. The condition $qv_0/\nu\ll 1$ corresponds to the hydrodynamic limit of the transport equation (1). We seek the solution of Eq. (1) by perturbing in the small parameter qv_0/ν. Then, in the first order of perturbation theory, out of five functions with zero eigenvalues $\varphi=1$, $m\mathbf{v}$, and E we can construct linear combinations for which the free-motion operator $i\mathbf{g}\cdot\mathbf{v}$ is diagonal. If we direct the x axis of the adopted coordinate system along $\mathbf{q}$, then the corresponding eigenfunctions χ_i obtained in the first order and the eigenvalues λ_i of the operator $i\mathbf{qv}+\hat{I}_0$ obtained in the second order of perturbation theory can be written as follows:[3]

$$\begin{gathered}
\chi_1=\left(\frac{c_v}{2c_p}\right)^{1/2}\left[1-\left(\frac{c_p}{c_v}\right)^{1/2}\frac{v_x}{v_0}+\frac{1}{c_v^{1/2}}\frac{E-\bar{E}}{\Delta E}\right],\\
\lambda_1=-iqv_0\left(\frac{c_p}{c_v}\right)^{1/2}+\lambda_1^{(2)},\\
\chi_2=\left(\frac{c_v}{2c_p}\right)^{1/2}\left[1+\left(\frac{c_p}{c_v}\right)^{1/2}\frac{v_x}{v_0}+\frac{1}{c_v^{1/2}}\frac{E-\bar{E}}{\Delta E}\right],\\
\lambda_2=iqv_0\left(\frac{c_p}{c_v}\right)^{1/2}+\lambda_2^{(2)},\\
\chi_3=\frac{v_y}{v_0},\quad \lambda_3=\lambda_3^{(2)},\quad \chi_4=\frac{v_z}{v_0},\quad \lambda_4=\lambda_4^{(2)},\\
\chi_5=\left(\frac{c_v}{c_p}\right)^{1/2}\left[\frac{1}{c_v^{1/2}}-\frac{E-\bar{E}}{\Delta E}\right],\quad \lambda_5=\lambda_5^{(2)},\\
\lambda_i^{(2)}=q^2\langle\chi_i v_x|\hat{I}_0^{-1}|\chi_i v_x\rangle,\qquad i=1,\ldots,5,
\end{gathered}\tag{2}$$

where $\bar{E}=c_vT$ and $\Delta E=c_v^{1/2}T$ are the average energy and dispersion of the energy of a molecule, and c_v and c_p are the specific heats of a molecule at constant volume and pressure, respectively, deduced allowing for the internal and translation degrees of freedom. The operator $\hat{I}_0^{-1}$ is the inverse of $\hat{I}_0$ and is defined in the usual way.[1-3]

We shall now use the one-to-one relationship between the hydrodynamic models of the transport equation obtained above and the equations of hydrodynamics,[1-3] which makes it possible to obtain microscopic expressions for the transport coefficients (thermal conductivity, shear and bulk viscosities) allowing for the internal degrees of freedom:

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$$\varkappa = \frac{\rho}{mT^2}\langle v_x(E-c_pT)\,|\hat{I}_0^{-1}|\,v_x(E-c_pT)\rangle,$$

$$\eta = \frac{\rho m}{T}\langle v_x v_y|\hat{I}_0^{-1}|v_x v_y\rangle, \tag{3}$$

$$\zeta = \frac{\rho}{mT}\left\langle\frac{mv^2}{3}-\frac{E}{c_v}\Big|\hat{I}_0^{-1}\Big|\frac{mv^2}{\cdot 3}-\frac{E}{c_v}\right\rangle,$$

where ρ is the density and m is the mass of a molecule.

The advantage of this form of the transport coefficients is that it allows us to separate explicitly the contributions of the various degrees of freedom. It should be pointed out that the vibrational degrees of freedom are described by a scalar parameter E_k and the rotational degrees of freedom by a vector parameter **M**. We shall consider specifically the rotational degrees of freedom and discuss separately the contribution of the vibrational degrees of freedom.

With this in mind it is convenient to write down the collision integral in the form

$$\hat{I}_0=\hat{I}+\Delta\hat{I}, \quad \Delta I \ll I,$$

where the operator $\hat{I}$ describes collisions in which the translational and rotational degrees of freedom are independent, i.e.,

$$w(\Gamma_1\Gamma_2\Gamma_1'\Gamma_2')=w_2(\mathbf{M}_1\mathbf{M}_2\mathbf{M}_1'\mathbf{M}_2')\,w_1(\mathbf{v}_1\mathbf{v}_2\mathbf{v}_1'\mathbf{v}_2').$$

The operator $\Delta\hat{I}$ is responsible for collisions in which the changes in the rotational and translational degrees of freedom are related. In the integral $\hat{I}$ the probability w_1 is governed only by the isotropic component of the interaction potential, which corresponds to the approximation in which the paths of the particles are independent of **M**. The probability w_2 describes collisions involving a change in the angular momentum **M**, averaged over all the paths of the colliding particles. We are essentially dealing here with two types of collisions: resonant exchange of the rotational energy and collisions accompanied by reorientation of the momentum.

Formally, the value of w_2 is obtained from the general expression for w by integration with respect to the variables $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_1'$, and $\mathbf{v}_2'$. The justification for such a separation of the collision integral is provided by recent experimental data on depolarized Rayleigh scattering of light, on the viscomagnetic effect, and on the birefringence in gases,[6] which show that σ_{Mv} (operator $\Delta\hat{I}$) $\ll \sigma_{vv}, \sigma_{MM}$ (operator $\hat{I}$). Here, σ are the cross sections of the various collisions. This form of perturbation theory differs from that used in Ref. 4 because the potential characterized by the parameters $\sigma_{MM} \ll \sigma_{vv}, \sigma_{Mv} \ll \sigma_{vv}$ is nonspherical.

We first consider the microscopic expression for the bulk viscosity ζ. It is clear from Eq. (3) that the expression for ζ represents in fact a sum of matrix elements

$$\sum_\alpha \nu_\alpha^{-1}\left|\left\langle\frac{mv^2}{3}-\frac{E}{c_v}\Big|\chi_\alpha\right\rangle\right|^2,$$

where χ_α are the scalar nonhydrodynamic modes of the operator I_0. Naturally, the main contribution to this sum comes from one term characterized by

$$\chi_\alpha=\chi_6=\left(\frac{2}{3}-\frac{1}{c_v}\right)^{-1/2}\left(\frac{mv^2}{3T}-\frac{E}{c_vT}\right),$$

where E and c_v are the energy and the specific heat of a molecule derived allowing for the rotational degrees of freedom. The appearance of the mode χ_6 is related to activation of the rotational degrees of freedom of a molecule. If we ignore the operator $\Delta\hat{I}$, we obtain an additional law of conservation of the rotational energy of a molecule, which gives rise to the sixth mode χ_6 with zero eigenvalue. The condition that χ_6 be orthogonal to the modes χ_i $(i=1,...,5)$ and its normalization determine the explicit form of this function. The operator $\Delta\hat{I}$ ensures exchange of the rotational and translational energies in collisions, i.e., it gives rise to a nonzero eigenvalue $\Delta\nu_6$ which for the mode χ_6 is

$$\Delta\nu_6=\langle\chi_6|\Delta\hat{I}|\chi_6\rangle=N\langle v\sigma_{Mv}\rangle.$$

The angular brackets in the above equation denote averaging of $v\sigma_{Mv}$ over Maxwellian velocity distribution. In view of the smallness of the quantity $\Delta\nu_6 \ll \nu$ (ν is the gaskinetic collision frequency), the expression for ζ becomes

$$\zeta=\frac{TN}{\Delta\nu_6}\left(\frac{2}{3}-\frac{1}{c_v}\right),$$

which is identical with that obtained in Ref. 6, because the coefficient ζ does not include the contribution of the collisions characterized by a resonant exchange of the internal (rotational or vibrational) energy represented by the cross sections σ_{MM}.

To first order in the ratio $\Delta I/I$ (of order $\Delta\nu/\nu$) the shear viscosity can be described by

$$\eta=\eta_v+\Delta\eta=\frac{\rho m}{T}\Bigg[\sum_{\alpha>5}|\langle v_xv_y|\chi_\alpha(\mathbf{v})\rangle|^2\frac{1}{\nu_\alpha^{v}}$$

$$+\sum_{\alpha>5}|\langle v_xv_y|\Delta\chi_\alpha(\mathbf{M})\rangle|^2\frac{1}{\nu_\alpha^{M}}$$

$$+\sum_{\alpha>5}|\langle v_xv_y|\Delta\chi_\alpha(\mathbf{M},\mathbf{v})\rangle|^2\frac{1}{\nu_\alpha^{Mv}}\Bigg],$$

$$\Delta\chi_\alpha(\mathbf{M},\mathbf{v})=\sum_{\beta>5}\frac{\langle\chi_\alpha(\mathbf{M},\mathbf{v})|\Delta\hat{I}|\chi_\beta(\mathbf{v})\rangle}{\nu_\beta^{v}-\nu_\alpha^{Mv}}\chi_\beta(\mathbf{v}), \tag{4}$$

$$\Delta\chi_\alpha(\mathbf{M})=\sum_{\beta>5}\frac{\langle\chi_\alpha(\mathbf{M})|\Delta\hat{I}|\chi_\beta(\mathbf{v})\rangle}{\nu_\beta^{v}-\nu_\alpha^{M}}\chi_\beta(\mathbf{v}),$$

$$\frac{\Delta\eta}{\eta_v}\sim\left(\frac{\Delta\nu}{\nu^v-\nu^M}\right)^2\frac{\nu^v}{\nu^M}$$

Here, $\chi_\alpha(\mathbf{v})$, $\chi_\alpha(\mathbf{M})$, $\chi_\alpha(\mathbf{M},\mathbf{v})$ are the eigenfunctions of the operator $\hat{I}$, whereas $\nu_\alpha^v, \nu_\alpha^M, \nu_\alpha^{Mv}$ are the corresponding eigenvalues. The order of magnitude of ν_α is given by the following expressions:

$$\nu_\alpha^{v}\propto\sigma_{vv}, \quad \nu_\alpha^{M}\propto\sigma_{MM}, \quad \nu_\alpha^{Mv}\propto\sigma_{vv}.$$

We recall that $\Delta\nu \propto \sigma_{Mv} \ll \sigma_{vv}, \sigma_{MM}$.

In the same order of perturbation theory the thermal conductivity is given by

$$\varkappa=\varkappa_v+\Delta\varkappa_1+\Delta\varkappa_2,$$

$$\begin{aligned}\varkappa_v&=\frac{\rho}{m}\sum_{\alpha}\frac{1}{\nu_\alpha{}^v}\left|\left\langle v_x\left(\frac{mv^2}{2T}-\frac{5}{2}\right)\middle|\chi_\alpha(\mathbf{v})\right\rangle\right|^2,\\ \Delta\varkappa_1&=\frac{\rho}{m}\sum_{\alpha>5}\frac{1}{\nu_\alpha{}^{Mv}}\left|\left\langle v_x\left(\frac{E_{\text{rot}}}{T}-1\right)\middle|\chi_\alpha(\mathbf{M},\mathbf{v})\right\rangle\right|^2,\\ \Delta\varkappa_2&=\frac{\rho}{m}\sum_{\alpha>5}\frac{1}{\nu_\alpha{}^{Mv}}\left|\left\langle v_x\left(\frac{E}{T}-c_p\right)\middle|\Delta\chi_\alpha(\mathbf{M},\mathbf{v})\right\rangle\right|^2.\end{aligned}\tag{5}$$

An allowance is made above for the fact that $c_p^{\text{transl}}=5/2$. In Eq. (5) the first term $\varkappa_v$ is related entirely to translational degrees of freedom, whereas the second ($\Delta\varkappa_1$) and the third ($\Delta\varkappa_2$) represent the rotational degrees of freedom, where $\Delta\varkappa_1$ does not contain the small operator $\Delta\hat{I}$, in contrast to $\Delta\varkappa_2$ which contains this operator. The orders of magnitude of the terms $\Delta\varkappa_1$ and $\Delta\varkappa_2$ are given by

$$\frac{\Delta\varkappa_1}{\varkappa_v}\propto\frac{2}{5}\frac{\nu^v}{\nu^{Mv}},\qquad\frac{\Delta\varkappa_2}{\varkappa_v}\propto\left(\frac{\Delta\nu}{\nu^v-\nu^{Mv}}\right)^2\frac{\nu^v}{\nu^{Mv}}.\tag{6}$$

It should be noted that $\Delta\varkappa_1$ includes only the contributions of the functions which are scalar in $\mathbf{M}$ (dependent on M^2), whereas $\Delta\varkappa_2$ includes harmonics which are anisotropic in $\mathbf{M}$. We shall show later that $\Delta\varkappa_1$ determines the dispersion of the thermal conductivity and can be deduced from the spectrum of the unshifted polarized light scattering, whereas $\Delta\varkappa_2$ is responsible for the change in the thermal conductivity on application of a magnetic field[7,8] (Sentfleben effect).

A similar separation of the transport coefficients [Eqs. (4)–(6)] is possible also in the case of the vibrational degrees of freedom. However, these degrees of freedom do not contribute to the quantities $\Delta\eta$ and $\Delta\varkappa_2$ and, therefore, they are not manifested when a magnetic field is applied.

3. DISPERSION OF THE TRANSPORT COEFFICIENTS

The transport coefficients have been considered so far subject to the condition $qv_0\ll\Delta\nu$, where ν and $\Delta\nu$ are the collision frequencies representing relaxation involving the translational degrees of freedom and the exchange of energy between the translational and internal (rotational) degrees of freedom. This condition implies the absence of the dispersion of sound, since the frequency of sound in a medium $\Omega\approx qv_0$ is much less than the relaxation frequencies ν and $\Delta\nu$. All the other relaxation frequencies $\Delta\nu_k$ which a medium may exhibit (for example, those associated with the conversion of the vibrational electronic energy to the translational degrees of freedom) are assumed to be very small compared with the frequency of sound: $\Delta\nu_k\ll\Omega$. Therefore, only the translational and rotational degrees of freedom can participate in the generation of hydrodynamic modes in the medium and, in particular, in the generation of sound.

It should be stressed that, within the framework of this transport (kinetic) method, the dispersion of the transport coefficients of a Boltzmann gas can be expressed as a function of the density of the gas, which is not true of the hydrodynamic limit $qv_0\ll\nu$, $\Delta\nu_k$.

If one of the relaxation frequencies $\Delta\nu_k$ approaches the frequency of sound, i.e., for $\Delta\nu_k\sim qv_0=\Omega$, the situation changes qualitatively. We now can expect "activation" of a new degree of freedom characterized by a frequency $\Delta\nu_k$, as well as the formation of acoustic modes χ_1 and χ_2. The dispersion of sound associated with the rotational degrees of freedom was discussed in Ref. 4 using the transport equation language, as pointed out already.

In this language a region of dispersion of sound is defined by the condition $|\lambda_1|/\Delta\nu_k\approx 1$, which is equivalent to the usual parameter $\omega\tau\sim 1$ employed in the theory of dispersion, where $\omega=|\lambda_1|=\Omega$, $\tau=1/\Delta\nu_k$. However, there is one other possible dispersion region characterized by $\lambda_5/\Delta\nu_k\approx 1$ or $\Delta\nu_k\sim\lambda_5\sim(qv_0)^2/\nu\ll\Omega$, and related to "activation" of the internal degrees of freedom, which contribute to the thermal conductivity mode χ_5. In this region the thermal conductivity $\varkappa$ or, more exactly, the ratio $\varkappa/c_p$ exhibits dispersion.

We can describe dispersion on the basis of the transport (kinetic) method if we introduce parameters which represent the operative degrees of freedom and which are averaged over the relevant period of motion. As pointed out already, in the case of the rotational degrees of freedom, averaging over the angle of rotation φ of a molecule leaves only the angular momentum vector $\mathbf{M}$. The corresponding parameter for the vibrational degrees of freedom is the vibrational energy E_k averaged over the vibration period.

The scalar parameter E_k can be considered both classically and quantum-mechanically. In the latter case the process of integration with respect to Γ implies summation over the energy levels E_k. The same method is used to allow for the rotational or vibrational degrees of freedom. We consider specifically the dispersion of the transport coefficients due to activation of the vibrational degrees of freedom of a diatomic molecule. In the eigenvalue problem of Eq. (2) we separate the operator $\hat{I}_0$ into two terms:

$$\hat{I}_0=\hat{I}+\Delta\hat{I}_k,$$

the first of which represents independent relaxation involving the translational and vibrational degrees of freedom, whereas the second describes the exchange between them. The characteristic frequencies of the operators $\hat{I}$ and $\Delta\hat{I}_k$ are respectively ν (and ν_k) and $\Delta\nu_k$ and they satisfy the inequality $\nu\gg\Delta\nu_k$. The eigenfrequencies ν and ν_k ($\nu\sim\nu_k$) of the operator $\hat{I}$ represent the times required to establish equilibrium in two subspaces: the subspace of the purely translational degrees of freedom, where ν is the gaskinetic collision frequency, and the subspace of purely vibrational degrees of freedom, where ν_k is the frequency of collisions involving resonant transfer of the vibrational energy. In view of the smallness of $\Delta\nu_k$, representing the exchange of energy between the vibrational and translational degrees of freedom, we can assume that after a time

$$1/\Delta\nu_k>t>1/\nu_k$$

there are two subsystems with independent translational T_t and vibrational T_k temperatures. It follows from the inequality $\Delta\nu_k\ll\nu$ that the operator $\Delta\hat{I}_k$ together with the operator $i\mathbf{q}\cdot\mathbf{v}$ can be regarded as a small correction to $\hat{I}$, and we can use perturbation theory employing the parameter

$$(i\mathbf{q}\mathbf{v}+\Delta\hat{I}_k)/\hat{I}\sim(iqv_0+\Delta\nu_k)/\nu\ll 1.$$

Then, in the zeroth order of perturbation theory the space of the eigenfunctions of the operator $\hat{I}$ with zero eigenvalue consists of five hydrodynamic functions without allowance for the vibrations, $\chi_i^-(1,...,5)$ and of the function $\varphi_k = (E_k - \overline{E}_k)/\Delta E_k$ which describes relaxation of the vibrational energy of the system to the equilibrium value E_k, where $\overline{E}_k = T$ is the average vibrational energy and $\Delta E_k = T$ is the dispersion of the vibrational energy.

We can find the correct hydrodynamic modes in the first order of perturbation theory in terms of the parameter $(iqv_0 + \Delta\nu_k)/\nu$ if we solve the secular equation and find the appropriate eigenvalues in the zeroth subspace, which include six functions. However, among these six functions the shear modes χ_3^- and χ_4^- are unrelated to any other zeroth functions for reasons of symmetry. It therefore follows that the width of these modes $\lambda_3 = \lambda_4$ is governed by Eq. (2) and therefore the shear viscosity η does not exhibit dispersion at any density of the gas when the condition $qv_0 < \nu$ is satisfied. The rest of the system of the coupled equations contains the functions $\chi_1^-, \chi_2^-, \chi_5^-, \varphi_k^-$. Therefore, the complete secular equation is of the fourth order, but it is illuminating to consider this equation in the following two cases. As pointed out already, there are two ranges of gas densities characterized by

$$\Delta\nu_k \sim qv_0, \quad \Delta\nu_k \sim (qv_0)^2/\nu,$$

in which there is a considerable modification of the eigenfunctions and eigenvalues of the eigenvalue problem of the operator $i\mathbf{qv} + \Delta\hat{I}$.

We shall begin with the range of low gas pressures, when

$$qv_0 \gg \Delta\nu_k \sim (qv_0)^2/\nu.$$

In this range the acoustic modes χ_1 and χ_2 are not affected by a vibrational mode φ_k (because of the condition $qv_0 \gg \Delta\nu_k$) so that they remain the eigenfunctions of the investigated secular equation with the eigenvalues λ_1^- and λ_2^- [see Eq. (2)], which ignore the vibrational (rotational) degrees of freedom. The remaining two modes χ_5^- and φ_k^- have the eigenvalues λ_5 and λ_k, which are much smaller than qv_0 and are therefore degenerate to first order in

$$qv_0/\nu \sim (\Delta\nu_k/\nu)^{1/2}.$$

In this case the secular equation can be derived if we include the second order of perturbation theory, i.e., the perturbation operator $\hat{V}$ becomes

$$\hat{V} = \Delta\hat{I} + q^2 v_x \hat{I}^{-1} v_x.$$

The matrix elements of the functions χ_5^- and φ_k^- calculated with the aid of this operator are

$$\langle\chi_5^-|\hat{V}|\chi_5^-\rangle = \frac{1}{c_p^-}\left(\Delta\nu_k + q^2\frac{m}{\rho}\varkappa^-\right),$$

$$\langle\varphi_k|\hat{V}|\varphi_k\rangle = \Delta\nu_k + q^2\frac{m}{\rho}\Delta\varkappa_1,$$

$$\langle\chi_5^-|\hat{V}|\varphi_k\rangle = \langle\varphi_k|\hat{V}|\chi_5^-\rangle = -\Delta\nu_k(c_p^-)^{-1/2},$$

where $\varkappa^-$ and c_p^- are the thermal conductivity and the specific heat derived ignoring the vibrational degrees of freedom, and $\Delta\varkappa_1$ [see Eq. (6)] is the correction to the thermal conductivity associated with the vibrational degrees of freedom.

It therefore follows that the secular equation for this region is

$$\left(\lambda - \frac{\Delta\nu_k}{c_p^-} - q^2\frac{m}{\rho}\frac{\varkappa^-}{c_p^-}\right)\left(\lambda - \Delta\nu_k - q^2\frac{m}{\rho}\Delta\varkappa_1\right) = \frac{\Delta\nu_k^2}{c_p^-}. \qquad (7)$$

This secular equation has two positive roots corresponding to two nonpropagating modes χ_5 and φ_k with the widths λ_5 and λ_k.

Here we give explicit expressions for the eigenfunctions and eigenvalues of Eq. (7) in two limiting cases of high and low gas densities. At low gas densities, i.e., for

$$\Delta\nu_k \ll q^2\frac{m}{\rho}\frac{\varkappa^-}{c_p^-} = \lambda_5^-,$$

we find that

$$\begin{gathered} \chi_5 = \chi_5^-, \quad \lambda_5 = q^2\frac{m}{\rho}\frac{\varkappa^-}{c_p^-} \equiv \lambda_5^-, \\ \varphi_k = \varphi_k^-, \quad \lambda_k = q^2\frac{m}{\rho}\Delta\varkappa_1. \end{gathered} \qquad (8a)$$

At high gas densities, i.e., when

$$\lambda_5^- < \Delta\nu_k \ll qv_0,$$

we obtain

$$\begin{gathered} \chi_5 = \chi_5^+, \quad \lambda_5 = q^2\frac{m}{\rho}\frac{\varkappa^- + \Delta\varkappa_1}{c_p^+} \equiv \lambda_5^+, \\ \varphi_k = \frac{[\chi_5^- - \varphi_k^-(c_p^-)^{1/2}]}{(1+c_p^-)^{1/2}}, \quad \lambda_k = \Delta\nu_k\left(1 + \frac{1}{c_p^-}\right). \end{gathered} \qquad (8b)$$

The plus and minus signs mean that the quantities in question are obtained allowing for and ignoring the vibrational degrees of freedom.

The first limiting case of Eq. (8a) corresponds to two almost independent subsystems with their own temperatures (or energies) and relaxation times λ_5^{-1} and λ_k^{-1}, where $\lambda_5 \sim \lambda_k$. In the second limiting case the coupling between the subsystems is strong, i.e., $\lambda_k \sim \Delta\nu_k \gg \lambda_5$, and the quantity which is conserved is the total energy of the system.

The intermediate range of the gas densities where $\Delta\nu_k \sim \lambda_5^-$ is described by the secular equation

$$\lambda = q^2\frac{m}{\rho}y,$$

which is reduced by the substitution

$$\omega\tau = \frac{\lambda}{\Delta\nu_k},$$

to the usual form of the dispersion of a quantity y as a function of the parameter $\omega\tau$:

$$\left(1 - \frac{\Delta\varkappa_1}{y}\right)\left[1 - \left(\frac{\varkappa^-}{c_p^-}\right)\frac{1}{y}\right] = \frac{c_p^+}{c_p^-}\left[1 - \left(\frac{\varkappa^+}{c_p^+}\right)\frac{1}{y}\right]\frac{1}{\omega\tau}. \qquad (9)$$

The dependence of y on $\omega\tau$ is plotted in Fig. 1 for $k^+/c_p^+ > \varkappa^-/c_p^-$. When this condition is satisfied, there are no intersections of the roots of the secular equation (7). We can see from Fig. 1 that in fact the quantity experiencing the dispersion is not the thermal conductivity $\varkappa$ itself, but its ratio to the specific heat, which reduces to the dispersion of the thermal diffusivity $\varkappa/\rho c_p$. The total change in the value

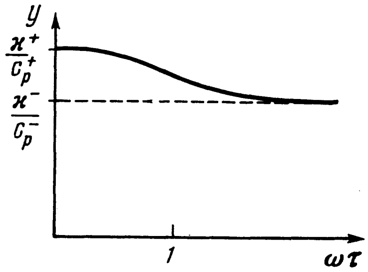

FIG. 1. Dependence of the quantity $y = \varkappa/c_p$ on the parameter $\omega\tau$.

of y in the dispersion region Δy can be estimated from Eq. (6):

$$\Delta y=\frac{\varkappa^+}{c_p{}^+}-\frac{\varkappa^-}{c_p{}^-}\sim\frac{\varkappa^-}{c_p{}^-}\frac{1}{c_p{}^+}\left(\frac{\nu^v}{\nu^{Mv}}-1\right). \qquad (10)$$

When the gas density is increased still further, the condition $qv_0 \sim \Delta\nu_k$ is then satisfied and we now have to allow for the dispersion of sound. In this range of pressures the secular equation is known[4,9] to reduce to the following third-order equation:

$$[\lambda^2+(qu_-)^2]\lambda=[\lambda^2+(qu_+)^2]\Delta\nu_k\left(1+\frac{1}{c_v{}^-}\right), \qquad (11)$$

where u_- and u_+ are the respective values of the velocity of sound derived ignoring and accounting for the vibrational degrees of freedom. In this range of the gas densities the perturbation operator $\hat{V}$ is

$$\hat{V}=i\mathbf{qv}+\Delta\hat{I},$$

and in the first order of perturbation theory the mode χ_5^- is independent of the modes χ_1^-, χ_2^-, and φ_k, which results in splitting from the secular equation (11). This means that subject to the condition $qv_0 \sim \Delta\nu_k$, the mode χ_5^+ does not change, i.e., it does not exhibit dispersion.

We shall now give the explicit expressions for the eigenfunctions and eigenvalues of Eq. (11) in the first order of perturbation theory in the two limiting cases defined by $\Delta\nu_k \ll qv_0$ and $\Delta\nu_k \gg qv_0$.

In the former case when $\Delta\nu_k \ll qv_0$, we have

$$\begin{gathered}\chi_1=\chi_1{}^-, \quad \lambda_1=-iqu_-+\frac{1}{2}\left(1-\frac{u_+{}^2}{u_-{}^2}\right)\Delta\nu_k\frac{c_p{}^-}{c_v{}^-},\\ \chi_2=\chi_2{}^-, \quad \lambda_2=\lambda_1{}^*,\\ \varphi_k=\frac{1}{(c_p{}^+)^{1/2}}[\chi_5{}^- - \varphi_k{}^-(c_p{}^-)^{1/2}], \quad \lambda_k=\Delta\nu_k\left(1+\frac{1}{c_p{}^-}\right).\end{gathered} \qquad (12a)$$

In the latter case, when $\Delta\nu_k \gg qv_0$, the solution of the secular equation (11) is of the form

$$\begin{gathered}\chi_1=\chi_1{}^+, \quad \lambda_1=-iqu_++\frac{1}{2}\left(1-\frac{u_+{}^2}{u_-{}^2}\right)\frac{(qv_0)^2}{\Delta\nu_k},\\ \chi_2=\chi_2{}^+, \quad \lambda_2=\lambda_1{}^*,\\ \varphi_k=\frac{1}{(c_p{}^-)^{1/2}}\left[(c_p{}^-)^{1/2}\varphi_\kappa{}^- - \frac{E-\bar{E}^-}{\Delta E^-}\right], \quad \lambda_k=\Delta\nu_k\left(1+\frac{1}{c_v{}^-}\right).\end{gathered} \qquad (12b)$$

Here, E^- is the energy without allowance for the vibrational degrees of freedom, $\bar{E} = c_v^- T$, and $\Delta E^- = (c_v^-)^{1/2} T$.

As pointed out above, the problem of velocity dispersion and sound absorption in a gas with rotational degrees of freedom is discussed in Ref. 4. In addition, the system of equations (12) contains explicit expressions for the mode φ_k and the corresponding eigenvalue λ_k at various gas pressures, necessary for describing the modification of the triplet of the Rayleigh scattering of light in a gas.

4. MODIFICATION OF A TRIPLET OF THE RAYLEIGH SCATTERING OF LIGHT IN A GAS WITH INTERNAL DEGREES OF FREEDOM

The transport equation method is very convenient in a description of the structure of the spectrum of the Rayleigh scattering of light in a gas with internal degrees of freedom.[3] Fluctuations of the permittivity $\delta\varepsilon_{ij}(t,\mathbf{R})$ can then be reduced to fluctuations of the distribution function $\delta f(t,\mathbf{R},\Gamma)$:

$$\delta\varepsilon_{ij}(t,\mathbf{R})=4\pi\int\alpha_{ij}(\Gamma)\delta f(t,\mathbf{R},\Gamma)d\Gamma,$$

where $\alpha_{ij}(\Gamma)$ is the polarizability tensor of a single molecule. The above expression is a consequence of the well-known relationship for an ideal gas: $\varepsilon - 1 = 4\pi N\alpha$, where $N[\mathrm{cm}^{-3}]$ is the particle number density, which is defined as

$$N(t,\mathbf{R})=\int f(t,\mathbf{R},\Gamma)d\Gamma.$$

We can show that the problem of calculation of the light-scattering spectrum $J(\omega, \mathbf{q})$ reduces to the following transport equation:

$$\begin{gathered}i(\mathbf{qv}-\omega)\chi(\omega,\mathbf{q},\Gamma)+\hat{I}_0\chi(\omega,\mathbf{q},\Gamma)=B(\Gamma),\\ J(\omega,\mathbf{q})\propto\mathrm{Re}\int B(\Gamma)f_0(\Gamma)\chi(\omega,\mathbf{q},\Gamma)d\Gamma,\end{gathered} \qquad (13)$$

where

$$B(\Gamma)=\alpha_0(\mathbf{e}_1\mathbf{e}_2)-\frac{1}{2}\alpha_2\left[\left(\mathbf{e}_1\frac{\mathbf{M}}{M}\right)\left(e_2\frac{\mathbf{M}}{M}\right)-\frac{1}{3}(\mathbf{e}_1\mathbf{e}_2)\right].$$

Here, $\mathbf{q} = \mathbf{k}_2 = \mathbf{k}_1$ and $\omega = \omega_2 - \omega_1$ are the differences between the wave vectors and the frequencies of the scattered and incident light waves; $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors of the polarizations of the incident and scattered waves; α_0 and α_2 are the scalar and symmetric parts of the polarizability tensor of a molecule $\alpha_{ij}(\Gamma)$. The subsequent calculation of the spectrum is carried out in the basis of the eigenfunctions of the operator $\hat{I}_0$ [see Eqs. (2), (8), and (12)] using perturbation theory in terms of the parameter qv/ν. We are interested only in the scalar part of the polarized scattering of light $J_0(\omega, \mathbf{q}) \propto \alpha_0^2$, which is described by:[3]

$$\begin{aligned}J_0(\omega,\mathbf{q})&\\ \propto B_1{}^2&\left[\frac{\mathrm{Re}\,\lambda_1}{(\omega-\mathrm{Im}\,\lambda_1)^2+(\mathrm{Re}\,\lambda_1)^2}+\frac{\mathrm{Re}\,\lambda_2}{(\omega-\mathrm{Im}\,\lambda_2)^2+(\mathrm{Re}\,\lambda_2)^2}\right]\\ &+B_5{}^2\frac{\lambda_5}{\omega^2+\lambda_5{}^2}+B_k^2\frac{\lambda_k}{\omega^2+\lambda_\kappa{}^2}, \quad \lambda_1=\lambda_2{}^*.\end{aligned} \qquad (14)$$

Here,

$$B_i=\alpha_0\int f_0(\Gamma)\chi_i(\Gamma)d\Gamma$$

are the coefficients in the expansion of the scalar part of the function $B(\Gamma)$ in terms of the eigenfunctions of the operator $\hat{I}_0$. The expressions for the eigenfunctions χ_i and the eigenvalues λ_i in the hydrodynamic case are given by the system

(2) with $B_k = 0$. In the dispersion region $\lambda_i/\Delta\nu_k \sim 1$ there is a change in the eigenfunctions and eigenvalues which are then given by Eqs. (8) and (12).

We now consider how these changes are manifested in the structure of the spectrum. We begin with the range of low gas pressures, i.e., we assume $\Delta\nu_k \ll \lambda_5$ [expressions in Eq. (8a)], where the spectrum of Eq. (14) is a triplet with the following intensities:

$$I_B^- \equiv B_1^2 = \alpha_0^2 \frac{c_v^-}{2c_p^-}, \qquad I_0^- \equiv B_5^2 = \frac{\alpha_0^2}{c_p^-}, \qquad I_k \equiv B_k^2 = 0.$$

Here, I_B is the total intensity of a Brillouin scattering doublet and I_0 is the total intensity of the unshifted Rayleigh scattering line. Hence, we obtain the Landau–Placzek relationship:

$$\frac{J_{\text{doubl}}}{J_{\text{tot}}} = \frac{2B_1^2}{2B_1^2 + B_5^2} = \frac{c_v^-}{c_p^-}$$

for an ideal gas without allowance for the vibrational degrees of freedom. When we go over to the range of the gas densities characterized by $\lambda_5 < \Delta\nu < qv_0$, a new component I_k appears at the frequency $\omega = 0$ and its integrated intensity is $I_k = \alpha_0^2/c_p^-/c_p^+$, whereas the width is $\lambda_k \approx \Delta\nu_k$. The total intensity at the unshifted frequency, $I_0^+ + I_k$, does not change:

$$I_0^+ + I_k = \alpha_0^2 \left(\frac{1}{c_p^+} + \frac{1}{c_p^+ c_p^-} \right) = \frac{\alpha_0^2}{c_p^-} = I_0^-.$$

In this range of gas pressures the Brillouin components I_B remain unchanged. We recall that fluctuations of the gas density, to which the polarized scattering of light is related, are represented in the eigenfunctions χ_5 and φ_k by constant terms independent of the velocity and energy of the gas molecules. In the first case represented by Eq. (8a) the density fluctuations are related solely to the translational temperature (χ_5^- mode) and appear in the scattering spectrum as a narrow line of width λ_5^- at the unshifted frequency. At high gas densities [Eq. (8b)] the vibrational energy fluctuations give rise to fluctuations of the density and are manifested in the scattering spectrum. In this case the spectrum of Eq. (14) contains both modes, χ_5 and λ_k, and they have different widths (λ_5 and λ_k, where $\lambda_5 \ll \lambda_k$), but comparable integral intensities. The ratio of the integral intensities of the narrow to the wide profile is c_p^-. This low-frequency vibration or rotation is characterized by a fairly low frequency such that $E_k = \hbar\omega_k \sim T$ and we therefore have $c_k \sim 1$. In the intermediate case we have to use a more general expression for the specific heat[10]

$$c_k = \left(\frac{\hbar\omega}{T} \right)^2 \frac{\exp(\hbar\omega/T)}{[1 - \exp(\hbar\omega/T)]^2}$$

which gives rise to a ratio of the total intensities amounting to c_p^-/c_k.

As the pressure increases further, the new profile I_k expands and disappears after passing through the dispersion region of sound $\Delta\nu_k \sim qv_0$, i.e., when the condition $\Delta\nu_k \gg qv_0$ is satisfied, it follows from the expressions in Eq. (12b) that

$$I_k = 0, \ I_B^+ = \alpha_0^2 c_v^+/2c_p^+, \ I_0^+ = \alpha_0^2/c_p^+.$$

Once again the Landau–Placzek relationship is satisfied, but it now includes the vibrational degrees of freedom. This modification of the scattering spectrum as a function of the gas density is illustrated in Fig. 2.

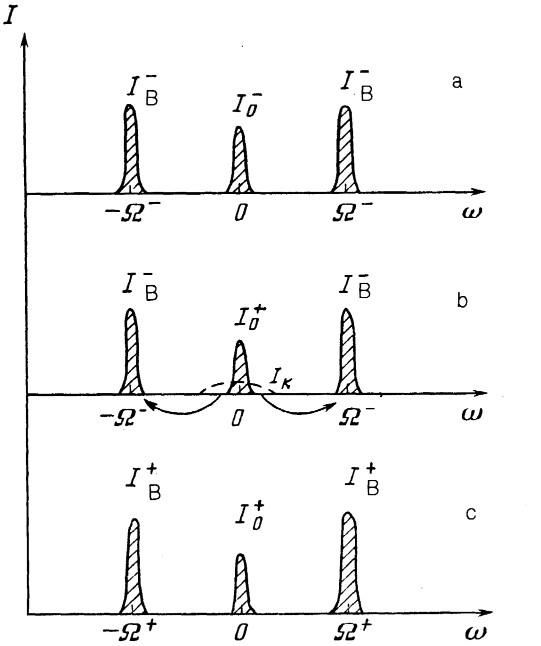

FIG. 2. Triplet of the polarized light scattering in a gas of diatomic molecules at different pressures: a) low gas pressures and densities $N \propto \Delta\nu_k \ll (v_0)^2/\nu$, when the vibrational degrees of freedom do not participate in the formation of the spectrum, $I_B^-/I_0^- = 5/4$; b) intermediate case, $(qv_0)^2\nu \ll \Delta\nu_k \ll qv_0$, the spectrum exhibits a new component I_k of integral intensity satisfying $I_0^+ + I_k = I_0^-$, where $I_k/I_0^+ = 2/7$, the width of this new component is $\Delta\nu_k$; c) high gas pressures and densities, $\Delta\nu_k \gg qv_0$, when vibrational degrees of freedom are activated, $I_B^+/I_0^+ = 7/4$. In all three cases the widths of the components of the triplet are assumed to be less than the width of the instrumental function of the spectroscopic instrument; $c_k = 1$, $c_v^- = 5/2$, $c_p^- = 7/2$, $c_v^+ = c_v^- + c_k$, $c_p^+ = c_p^- + c_k$.

It therefore follows that our method of calculation of the transport coefficients of gas makes it possible to describe modification of the polarized scattering triplet caused by activation of the internal degrees of freedom of molecules (see Fig. 2). It is clear from Fig. 2 that a reduction in the gas density results in a partial redistribution of the intensity of the central component to a new component of the spectrum (associated with the mode φ_k) of width $\Delta\nu_k$, which on further increase in the gas density "leaks away" to the shifted Brillouin components. In both limiting cases of high and low pressures, characterized by $\Delta\nu_k \gg qv_0$ and $\Delta\nu_k \ll qv_0$, the intensities in the triplet satisfy the Landau–Placzek relationship, but in the former case the specific heat includes the vibrational degrees of freedom, which is not true of the latter case.

An important result is the appearance of dispersion of the quantity $\varkappa/c_p$ at low frequencies $\sim (qv_0)^2/\nu$, which in contrast to the dispersion at acoustic frequencies $\sim qv_0$, makes it possible to obtain information on very slow processes of relaxation of the internal degrees of freedom from the spectrum of light scattered in a gas. The usual methods for the determination of the dispersion of the bulk viscosity from the scattering of light at acoustic frequencies $\Omega \sim qv_0$ make it possible to study the processes of relaxation with characteristic frequencies $\Delta\nu_k/\nu \sim qv_0/\nu$, and at low frequencies near the line center an investigation can be made even of slower processes:

$$\frac{\Delta\nu_k}{\nu} \approx \left(\frac{qv_0}{\nu}\right)^2 \frac{c_p^-}{c_k}.$$

When visible light is scattered, we find that $qv_0 \sim 10^9$ Hz for the scattering angle of 90°. At gas pressures of several tens of atmospheres we have $\nu \sim 10^{11}$ Hz. In this case the dispersion of sound can be used to study the relaxation processes characterized by $\Delta\nu_k/\nu \sim 10^{-2}$, whereas the dispersion at the line center observed under the same conditions can be used in investigations of relaxation processes with $\Delta\nu_k/\nu \sim 10^{-4}$. Such slow relaxation processes are, for example, those involved in the conversion of the vibrational energy into translational motion.

For example, in the case of the CO_2 molecule the process of vibrational relaxation of the bending vibrations ($\omega = 667$ cm^{-1}) is characterized by a probability $\Delta\nu_k/\nu = 2\times10^{-5}$ (Ref. 11). At room temperature ($T = 200$ cm^{-1}) the contribution of these vibrations to the specific heat is $c_k \approx 0.5$, which leads to the following ratio of the total intensities:

$$\frac{I_k}{I_0^+} = \frac{c_k}{c_p^-} = \frac{1}{9}.$$

Therefore, in order to observe such relaxation in the form of a new component in the spectrum, we must satisfy the condition

$$\frac{qv_0}{\nu} < \left. \frac{c_k}{c_p^-}\frac{\Delta\nu_k}{\nu}\right)^{1/2} \approx 10^{-3}.$$

If $\nu \sim 10^{11}$ Hz, then $qv_0 \sim 10^8$, which corresponds to the experimental scattering angle of $\theta \approx 10°$. The width of the instrumental function of the spectroscopic instrument $\delta\omega$ should not exceed $\delta\omega < \Delta\nu_k \approx 10^6$ Hz.

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[1] R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics*, Wiley, New York (1975).

[2] P. Resibois and M. F. de Leneer, *Classical Kinetic Theory of Fluids*, Wiley, New York (1977).

[3] T. L. Andreeva and A. V. Malyugin, Usp. Fiz. Nauk **150**, 525 (1986) [Sov. Phys. Usp. **29**, 1097 (1986)].

[4] L. A. Maksimov and Yu. V. Mikhaĭlova, Zh. Eksp. Teor. Fiz. **53**, 228 (1967) [Sov. Phys. JETP **26**, 153 (1968)].

[5] E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics*, Pergamon Press, Oxford (1981).

[6] H. van Houten, L. J. F. Hermans, and J. J. M. Beenakker, Physica A (Utrecht) **131**, 64 (1985).

[7] Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **51**, 1893 (1966); **60**, 1339 (1971) [Sov. Phys. JETP **24**, 1272 (1967); **33**, 725 (1971)].

[8] V. D. Borman, V. S. Laz'ko, and B. I. Nikolaev, Zh. Eksp. Teor. Fiz. **63**, 886 (1972); **66**, 1343 (1974) [Sov. Phys. JETP **36**, 466 (1973); **39**, 657 (1974)].

[9] L. I. Mandel'shtam and M. A. Leontovich, Zh. Eksp. Teor. Fiz. **7**, 438 (1937).

[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Vol. 1, 3rd ed.*, Pergamon Press, Oxford (1980).

[11] V. N. Kondrat'ev and E. E. Nikitin, *Kinetics and Mechanisms of Gas-Phase Reactions* [in Russian], Nauka, Moscow (1974), p. 194.

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