

On Light Scattering by Polyatomic Fluids

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“Scattering equations” are derived which relate the spectrum of the light scattered from a polyatomic fluid to the spectral functions of the fluctuating spherical (scalar) and anisotropic parts of the electric permeability tensor. The influence of a constant external (electric or magnetic) field is considered. For a gas of linear molecules, it is shown that the fluctuations leading to the depolarized Rayleigh light scattering are fluctuations of the mean (2nd rank) tensor polarization of the rotational angular momenta of the molecules. Furthermore, the fluctuations associated with the rotational Raman scattering are expressed by fluctuations of the mean values of (2nd rank) tensor operators which induce transitions between the rotational levels of a molecule.

The intensity and the frequency spectrum of the light scattered from a fluid are governed by the fluctuation of the electric permeability tensor^{1–4}. The relaxation coefficients (inverse relaxation times) and the eigenfrequencies of these fluctuations determine the line widths and the frequency shifts, respectively, of the scattered light². To relate the information contained in the spectrum to transport and relaxation properties of the fluid, and possibly to molecular interactions one has to proceed in three steps:

(1) A relation between the spectrum of the scattered light (for specified initial and final wave vectors and polarization vectors of the electric fields) and the spectral densities of the space-Fourier components of the electric permeability tensor has to be established (“scattering equations”).

(2) The fluctuations of the electric permeability tensor have to be expressed in terms of fluctuations of certain time and space dependent “macroscopic variables” which are distribution function averages of quantities depending on the observables specifying the states of the molecules (e. g. linear momenta, rotational angular momenta).

(3) The aforementioned macroscopic variables obey generalized hydrodynamical equations or “transport-relaxation equations”. Using ONSAGER’s

assumption⁵ that the regression of the spontaneous fluctuations is the same as that of “small” macroscopic deviations from the equilibrium state of the fluid, one can calculate the spectral functions from the transport-relaxation equations.

This paper is primarily concerned with points (1) and (2). The main emphasis lies on the fluctuations of the anisotropic (symmetric traceless) part of the electric permeability tensor (anisotropy fluctuations²). For completeness, some of the well known results for the fluctuations of the isotropic or spherical part of the electric permeability tensor (scalar fluctuations²) are also stated.

The scattering equations for the anisotropy fluctuations derived in this paper have already been used in an investigation of the effect of a constant magnetic field on the spectrum of the depolarized Rayleigh light⁶ (tensor polarization resonance).

These scattering equations are also used in a subsequent publication⁷ where the spectrum, in particular the line width of the depolarized Rayleigh light scattered from a gas of linear molecules is calculated from transport-relaxation equations obtained from the Waldmann-Snyder equation⁸.

In part I of this paper, a phenomenological approach to the derivation of scattering equations is presented which follows closely the ideas put for-

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¹ M. v. SMOLUCHOWSKI, Ann. Phys. Leipzig **25**, 205 [1908].
A. EINSTEIN, Ann. Phys. Leipzig **33**, 1275 [1910].

² L. D. LANDAU and E. M. LIFSHITZ, Electrodynamics of Continuous Media, Pergamon Press, London 1960.

³ I. L. FABELINSKII, Molecular Scattering of Light, Plenum Press, New York 1968.

⁴ D. MCINTYRE and J. V. SENGERS, Study of Fluids by Light Scattering, in Physics of Simple Liquids (ed. H. V. N. TEMPERLEY e. a.), North Holland Publ. Co., Amsterdam 1968.

⁵ L. ONSAGER, Phys. Rev. **37**, 405 [1931]; **38**, 2265 [1931].

⁶ S. HESS, Phys. Letters **29 A**, 108 [1969].

⁷ S. HESS, Z. Naturforsch. **24 a**, 1852 [1969] and to be published.

⁸ L. WALDMANN, Z. Naturforsch. **12 a**, 660 [1957]; **13 a**, 609 [1958]. — R. F. SNIDER, J. Chem. Phys. **32**, 1051 [1960]. — S. HESS, Z. Naturforsch. **22 a**, 1871 [1967].



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ward by EINSTEIN¹ and by LANDAU and LIFSCHITZ². Firstly, it is indicated how one can obtain an inhomogeneous wave equation for the electric field of the scattered light (§ 1). The inhomogeneity term involves the electric field of the incident light and the fluctuating, i. e. time and space dependent part of the electric permeability tensor. Then the solution of the aforementioned wave equation and the corresponding intensity of the scattered light are given (§ 2). For stationary fluctuations, the scattering equations are discussed in detail for the light scattered due to scalar and anisotropic fluctuations (§§ 3, 4). Furthermore, the general modifications of the scattering equations introduced by the influence of a constant external (magnetic or electric) field on the anisotropy fluctuations are studied (§ 4). It seems worthwhile to point out that the angle dependence of the intensity of the scattered light can be written in a rather simple way if the unit vectors parallel to the electric field vectors of the incident light and of the detected scattered light are used.

Part I of this paper, as far as the scattering equations in the absence of a constant external field are concerned, should be compared with several derivations of scattering equations⁹ which have recently been given in the vein of VAN HOVE's neutron scattering theory¹⁰.

Part II of this paper, dealing with the aforementioned point (2), is confined to gases, in particular to gases of linear molecules. First, it is noticed that the difference between the electric permeability tensors of a gas and of the vacuum is proportional to the molecular polarizability tensor (operator) averaged over a one-particle distribution function of the gas (§ 5). Then, after some remarks on the one-particle distribution function (operator) for a gas of linear molecules (§ 6), the scalar fluctuations and the anisotropy fluctuations are discussed separately (§§ 7, 8).

The scalar fluctuations are found to be caused by fluctuations of the number density (as is well known) and of the rotational temperature. The latter fluctuations are associated with the centrifugal stretching of the rotating molecules. Furthermore, it is shown that the anisotropy fluctuations governing the

depolarized Rayleigh scattering are fluctuations of the mean (2nd rank) tensor polarization of the rotational angular momenta of the molecules. The corresponding fluctuations leading to the rotational Raman scattering are fluctuations of the mean values of certain (2nd rank) tensor operators which are nondiagonal in the rotational quantum numbers. Hence the calculation of the spectrum of the scattered light is reduced to a calculation of the spectrum of the fluctuations of the number density, the rotational temperature, the mean 2nd rank tensor polarization and certain mean 2nd rank tensor operators.

Appendix I is devoted to some remarks on time-independent fluctuation theory. In appendix II, the definition of Cartesian tensor operators (which are akin to the well-known spherical tensor operators) and some of their general properties are given.

I. Phenomenological Scattering Theory for Polyatomic Fluids

§ 1. Wave Equation

Displacement, electric field and wave vectors of the scattered light will be denoted by \mathbf{D} , \mathbf{E} , and \mathbf{k} , respectively. The corresponding quantities for the incident linearly polarized monochromatic light (frequency ω') are denoted by the corresponding primed variables. The polarization of the incident and detected scattered light are specified by unit vectors \mathbf{e}' and \mathbf{e} . Space and time variables are denoted by \mathbf{x} and t , respectively.

At optical frequencies, the magnetic induction is equal to the magnetic field \mathbf{H} . Thus, the field vectors of the scattered light obey the Maxwell equations²

$$\text{rot } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t}, \quad \text{rot } \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}, \quad (1.1)$$

which give upon elimination of \mathbf{H} , the result

$$\text{rot rot } \mathbf{E} + \frac{1}{c^2} \frac{\partial^2 \mathbf{D}}{\partial t^2} = 0. \quad (1.2)$$

To obtain a closed equation for either \mathbf{E} or \mathbf{D} , an additional relation between these field vectors is required.

Restriction to "low" intensities of the incident light and to scattering from "transparent" fluids (which show no selective absorption in the optical frequency range), and the assumption that the interparticle separation is small compared with the wave-

⁹ L. J. KOMAROV and I. Z. FISHER, Soviet Phys.—JETP 16, 1358 [1963]. — R. PECORA, J. Chem. Phys. 40, 1604 [1964]. — R. PECORA and W. A. STEELE, J. Chem. Phys. 42, 1872 [1965]. — M. TANAKA, Progr. Theor. Phys. 40, 975 [1968].

¹⁰ L. VAN HOVE, Phys. Rev. 95, 249 [1954].

length of the light, results in

$$D_\mu + D'_\mu = \varepsilon_{\mu\nu} (E_\nu + E'_\nu), \quad (1.3)$$

where $\varepsilon_{\mu\nu} = \varepsilon_{\mu\nu}(t, \mathbf{x})$ is the electric permeability tensor. Greek subscripts refer to Cartesian components of vectors and tensors, and the summation convention is used.

The tensor $\varepsilon_{\mu\nu}$ can be divided into a constant (isotropic) part $\varepsilon \delta_{\mu\nu}$ and a time and space dependent (fluctuating) part which, in turn contains isotropic and anisotropic parts:

$$\varepsilon_{\mu\nu}(t, \mathbf{x}) = \varepsilon \delta_{\mu\nu} + \bar{\varepsilon}(t, \mathbf{x}) \delta_{\mu\nu} + \overline{\varepsilon_{\mu\nu}}(t, \mathbf{x}). \quad (1.4)$$

The sign $\overline{}$ denotes the irreducible (symmetric traceless) part of a tensor. In Eq. (1.4) the constant anisotropic part of $\varepsilon_{\mu\nu}$ that arises in the presence of constant electric or magnetic fields due to a thermal alignment of the molecules has been disregarded.

By inserting

$$\mathbf{D}' = \varepsilon \mathbf{E}' \quad (1.5)$$

for the displacement vector of the incident light and using (1.4) one can rewrite Eq. (1.3) as follows

$$E_\mu = \varepsilon^{-1} D_\mu - \varepsilon^{-1} (\bar{\varepsilon} \delta_{\mu\nu} + \overline{\varepsilon_{\mu\nu}}) (E_\nu + E'_\nu). \quad (1.6)$$

Assuming $\mathbf{E} \ll \mathbf{E}'$, one can neglect E_ν on the r.h.s of Eq. (1.6) and hence in the "single scattering approximation", Eq. (1.6) reduces to

$$E_\mu = \varepsilon^{-1} D_\mu - \varepsilon^{-1} (\bar{\varepsilon} \delta_{\mu\nu} + \overline{\varepsilon_{\mu\nu}}) E'_\nu. \quad (1.7)$$

Substituting (1.7) into (1.2) and using $\text{div } \mathbf{D} = 0$, one finds the following inhomogeneous wave equation for the \mathbf{D} -field of the scattered light:

$$\Delta D_\mu - \frac{\varepsilon}{c^2} \frac{\partial^2 D_\mu}{\partial t^2} = K_{\mu\nu} (\bar{\varepsilon} \delta_{\nu\lambda} + \overline{\varepsilon_{\nu\lambda}}) E'_\lambda, \quad (1.8)$$

where

$$\Delta = \frac{\partial^2}{\partial x_\alpha \partial x_\alpha}, \quad K_{\mu\nu} = \Delta \delta_{\mu\nu} - \frac{\partial^2}{\partial x_\mu \partial x_\nu}. \quad (1.9)$$

Writing the electric field of the incident linearly polarized monochromatic light as

$$E'_\mu = E' e'_\mu \exp\{i(\mathbf{k}' \cdot \mathbf{x} - \omega' t)\} \text{ for } 0 < t < \mathcal{T} \\ \text{and } E'_\mu = 0 \text{ for } t < 0; t > \mathcal{T} \quad (1.10)$$

and denoting the time-Fourier transform of $\mathbf{D}(t, \mathbf{x})$ by $\mathbf{D}(\omega, \mathbf{x})$, one obtains from (1.8)

$$(\Delta + k^2) D_\mu(\omega, \mathbf{x}) = E' \int_0^{\mathcal{T}} dt e^{i(\omega - \omega')t} K_{\mu\nu} \cdot [\bar{\varepsilon}(t, \mathbf{x}) \delta_{\nu\lambda} + \varepsilon_{\nu\lambda}(t, \mathbf{x})] e'_\lambda \exp\{i\mathbf{k}' \cdot \mathbf{x}\} \quad (1.11)$$

$$\text{where } k^2 = \varepsilon \omega^2 / c^2. \quad (1.12)$$

The Fourier transform $f(\omega)$ of a time dependent function $f(t)$ is defined by

$$f(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} f(t). \quad (1.13)$$

In Eqs. (1.10, 11), \mathcal{T} is the duration of observation of the scattered light assumed to be large compared with all relaxation times and inverse frequencies. Hence one can take the limit $\mathcal{T} \rightarrow \infty$.

The solution of Eq. (1.11) and the corresponding intensity of the scattered light is discussed in the following section.

§ 2. Electric Field and Intensity of the Scattered Light

The solution of Eq. (1.11) is straightforward and at a point $\mathbf{x} = r \hat{\mathbf{k}}$ ($\hat{\mathbf{k}}$ unit vector parallel to \mathbf{k}) far from the scattering volume ($\mathbf{x} = 0$ is a point within the scattering volume) given by

$$D_\mu(\omega, \mathbf{x}) = (e^{ikr}/r) E' (k^2 \delta_{\mu\nu} - k_\mu k_\nu) \\ \times \frac{1}{4\pi} \int_0^{\mathcal{T}} dt e^{i(\omega - \omega')t} [\bar{\varepsilon}(t, \mathbf{q}) e'_\nu + \overline{\varepsilon_{\nu\lambda}}(t, \mathbf{q}) e'_\lambda], \quad (2.1)$$

with

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'. \quad (2.2)$$

In Eq. (2.1), $\bar{\varepsilon}(t, \mathbf{q})$ and $\overline{\varepsilon_{\nu\lambda}}(t, \mathbf{q})$ are space Fourier transforms of $\bar{\varepsilon}(t, \mathbf{x})$ and of $\varepsilon_{\nu\lambda}(t, \mathbf{x})$, respectively. The space Fourier transform $g(\mathbf{q})$ of a function $g(\mathbf{x})$ is defined by

$$g(\mathbf{q}) = \int d^3x \exp\{-i\mathbf{q} \cdot \mathbf{x}\} g(\mathbf{x}). \quad (2.3)$$

The integration, in Eq. (2.3), is extended over the scattering volume V , and

$$g(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{q}} \exp\{i\mathbf{q} \cdot \mathbf{x}\} g(\mathbf{q}). \quad (2.4)$$

With $\mathbf{E} = \varepsilon^{-1} \mathbf{D}$, Eq. (2.1) yields the electric field of the light that is scattered due to a time- and space-dependent permeability tensor. If this time and space dependence is caused by thermal fluctuations, the average electric field is zero. The intensity of the scattered light, being proportional to the average of the square of the electric field, however, is nonzero.

The intensity per frequency interval of the light with a polarization specified by the unit vector \mathbf{e} that is scattered into a solid angle element d^2k in the

direction determined by $\hat{\mathbf{k}}$ is

$$J d^2\hat{k} = \frac{c}{4\pi} \frac{1}{2\pi\mathcal{T}} |\overline{\mathbf{e} \cdot \mathbf{E}(\omega, \mathbf{x})}|^2 r^2 d^2\hat{k}. \quad (2.5)$$

The bar in Eq. (2.5) refers to an average over the probability distribution for the fluctuations¹¹.

Due to (2.1), one has

$$\mathbf{e} \cdot \mathbf{E}(\omega, \mathbf{x}) = (e^{ikr}/r) (\omega^2/c^2) E' F(\omega - \omega', \mathbf{q}; \mathbf{e}, \mathbf{e}'), \quad (2.6)$$

where

$$F(\omega, \mathbf{q}; \mathbf{e}, \mathbf{e}') = \frac{1}{4\pi} \int_{-\mathcal{T}}^{\mathcal{T}} dt e^{i\omega t} [\tilde{\varepsilon}(t, \mathbf{q}) \mathbf{e} \cdot \mathbf{e}' + e_{\mu} \overline{\varepsilon_{\mu\nu}}(t, \mathbf{q}) e'_{\nu}]. \quad (2.7)$$

Instead of describing the light scattering by the spectral intensity J it may as well be characterized by the "scattering function" I which is defined by

$$J = \frac{c}{4\pi} \frac{\omega^4}{c^4} E'^2 I(\omega - \omega', \mathbf{q}; \mathbf{e}, \mathbf{e}'). \quad (2.8)$$

With (2.5, 6), this gives

$$I = I(\omega - \omega', \mathbf{q}; \mathbf{e}, \mathbf{e}') = \frac{1}{2\pi\mathcal{T}} |\overline{F(\omega - \omega', \mathbf{q}; \mathbf{e}, \mathbf{e}')}|^2. \quad (2.9)$$

The scalar (or isotropic) fluctuations and the anisotropy fluctuations are uncorrelated and thus I is the sum of the contributions $I^{(sc)}$ and $I^{(an)}$ from both types of fluctuations. In the next sections these contributions are discussed separately.

§ 3. Light Scattering Caused by Scalar Fluctuations

According to Eqs. (2.7) and (2.9), the scattering function $I^{(sc)}$ associated with the scalar fluctuations is

$$I^{(sc)} = \frac{1}{(4\pi)} \frac{1}{2\pi\mathcal{T}} \int_0^{\mathcal{T}} dt \int_0^{\mathcal{T}} dt' e^{i(\omega - \omega')(t - t')} \overline{\tilde{\varepsilon}(t, \mathbf{q}) \tilde{\varepsilon}^*(t', \mathbf{q})} (\mathbf{e} \cdot \mathbf{e}')^2. \quad (3.1)$$

If the probability distribution for the fluctuations is stationary (invariant under time translations), the average occurring in (3.1) depends only on the time difference $\tau = t - t'$, i. e.

$$\overline{\tilde{\varepsilon}(t, \mathbf{q}) \tilde{\varepsilon}^*(t', \mathbf{q})} = \overline{\tilde{\varepsilon}(\tau, \mathbf{q}) \tilde{\varepsilon}^*(0, \mathbf{q})} = \overline{\tilde{\varepsilon}(0, \mathbf{q}) \tilde{\varepsilon}^*(-\tau, \mathbf{q})}. \quad (3.2)$$

Thus, using the integration variables τ and $\frac{1}{2}(t + t')$ instead of t and t' , performing the integration over $\frac{1}{2}(t + t')$ and then taking the limit $\mathcal{T} \rightarrow \infty$, one finds that

$$(4\pi)^2 I^{(sc)} = \frac{1}{2\pi} \int_0^{\infty} d\tau [e^{i(\omega - \omega')\tau} \overline{\tilde{\varepsilon}(\tau, \mathbf{q}) \tilde{\varepsilon}^*(0, \mathbf{q})} + e^{-i(\omega - \omega')\tau} \overline{\tilde{\varepsilon}(0, \mathbf{q}) \tilde{\varepsilon}^*(-\tau, \mathbf{q})}] (\mathbf{e} \cdot \mathbf{e}')^2. \quad (3.3)$$

Defining $A^{(sc)}(t | \mathbf{q})$ by the relation

$$\tilde{\varepsilon}(t, \mathbf{q}) = A^{(sc)}(t | \mathbf{q}) \tilde{\varepsilon}(0, \mathbf{q}); \quad A^{(sc)}(0 | \mathbf{q}) = 1, \quad (3.4)$$

and the "spectral function" $S^{(sc)}(\omega | \mathbf{q})$ by

$$S^{(sc)}(\omega | \mathbf{q}) = \frac{1}{\pi} \text{Re} \int_0^{\infty} dt e^{i\omega t} A^{(sc)}(t | \mathbf{q}), \quad (3.5)$$

one obtains from Eq. (3.3) the scattering equation

$$I^{(sc)} = (\mathbf{e} \cdot \mathbf{e}')^2 S^{(sc)}(\omega - \omega' | \mathbf{q}) \frac{1}{(4\pi)^2} |\overline{\tilde{\varepsilon}(\mathbf{q})}|^2, \quad (3.6)$$

where $\tilde{\varepsilon}(\mathbf{q})$ is written for $\tilde{\varepsilon}(0, \mathbf{q})$. Note that $A^{(sc)}(t | \mathbf{q})$ and $S^{(sc)}(\omega | \mathbf{q})$, in contrast to $\tilde{\varepsilon}(t, \mathbf{q})$, are not Fourier transforms with respect to space.

The factor $(\mathbf{e} \cdot \mathbf{e}')^2$ in Eq. (3.6) reflects the fact that scalar fluctuations do not affect the polarization of the light. The light scattered due to scalar fluctuations (polarized Rayleigh scattering, Brillouin scattering) contains no depolarized component since $I^{(sc)} = 0$ for $\mathbf{e} \perp \mathbf{e}'$. It is clear that the unit vectors \mathbf{e} and \mathbf{e}' , being perpendicular to the wave vectors \mathbf{k} and \mathbf{k}' , depend on the directions of these wave vectors though this is not indicated explicitly in the notation used here. For an incident beam of "natural" light instead of linearly polarized light $\mathbf{e}'_{\mu} \mathbf{e}'_{\nu}$ has to be replaced by $\delta_{\mu\nu} - k'_{\mu} k'_{\nu} / k'^2$ in Eq. (3.6).

If the probability distribution for the fluctuations is spatially homogeneous (within the scattering volume), then $|\tilde{\varepsilon}(\mathbf{q})|^2$ is proportional to the scattering Volume V . For a gas at equilibrium, a calculation of this quantity is given in Appendix I.

§ 4. Light Scattering Caused by Anisotropy Fluctuations

For stationary anisotropy fluctuations, the formula corresponding to (3.3) is

¹¹ L. D. LANDAU and E. M. LIFSHITZ, Statistical Physics, Pergamon Press, London 1959.

$$\begin{aligned}
& (4\pi)^2 I^{(\text{an})} \\
&= \frac{1}{2\pi} \int_0^\infty e^{i(\omega-\omega')\tau} e_\mu e'_\nu \overline{\varepsilon_{\mu\nu}(\tau, \mathbf{q})} e_\lambda e'_\kappa \overline{\varepsilon_{\lambda\kappa}^*(0, \mathbf{q})} \\
&+ \frac{1}{2\pi} \int_0^\infty e^{-i(\omega-\omega')\tau} e_\mu e'_\nu \overline{\varepsilon_{\mu\nu}(0, \mathbf{q})} e_\lambda e'_\kappa \overline{\varepsilon_{\lambda\kappa}^*(-\tau, \mathbf{q})}. \quad (4.1)
\end{aligned}$$

In analogy with (3.4), one may introduce a function relating $\overline{\varepsilon_{\mu\nu}}$ at time t with $\overline{\varepsilon_{\mu\nu}}$ at time 0. In the presence of a constant electric or magnetic field, this function will not be a scalar but a 4th rank tensor, i. e.

$$\overline{\varepsilon_{\mu\nu}}(t, \mathbf{q}) = A_{\mu\nu, \mu'\nu'}^{(\text{an})}(t | \mathbf{q}) \varepsilon_{\mu'\nu'}(0, \mathbf{q}), \quad (4.2)$$

with

$$A_{\mu\nu, \mu'\nu'}(0 | \mathbf{q}) = \Delta_{\mu\nu, \mu'\nu'}, \quad (4.3)$$

where

$$\Delta_{\mu\nu, \mu'\nu'} = \frac{1}{2} (\delta_{\mu\mu'} \delta_{\nu\nu'} + \delta_{\mu\nu} \delta_{\nu\mu'}) - \frac{1}{3} \delta_{\mu\nu} \delta_{\mu'\nu'} \quad (4.4)$$

is an isotropic 4th rank tensor. — The spectral tensor associated with the anisotropy fluctuations is

$$S_{\mu\nu, \mu'\nu'}^{(\text{an})}(\omega | \mathbf{q}) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i\omega t} A_{\mu\nu, \mu'\nu'}^{(\text{an})}(t | \mathbf{q}). \quad (4.5)$$

The general symmetry properties of the tensors $A_{\mu\nu, \mu'\nu'}^{(\text{an})}$ and $S_{\mu\nu, \mu'\nu'}^{(\text{an})}$ are the same as those of the shear viscosity tensor¹²⁻¹⁴.

Consistent with the previous assumption that the thermal alignment of the molecules is small the dependence of the probability distribution for fluctuations on external fields can also be neglected. Then, writing $\overline{\varepsilon_{\mu\nu}}(\mathbf{q})$ for $\overline{\varepsilon_{\mu\nu}}(0, \mathbf{q})$

$$\overline{\varepsilon_{\mu\nu}}(\mathbf{q}) \varepsilon_{\mu'\nu'}^*(\mathbf{q}) = \frac{1}{5} \overline{\varepsilon_{\lambda\kappa}}(\mathbf{q}) \overline{\varepsilon_{\lambda\kappa}^*}(\mathbf{q}) \Delta_{\mu\nu, \mu'\nu'}, \quad (4.6)$$

is obtained, so that

$$\begin{aligned}
I^{(\text{an})} &= e_\mu e'_\nu S_{\mu\nu, \mu'\nu'}^{(\text{an})}(\omega - \omega' | \mathbf{q}) e_{\mu'} e'_{\nu'} \\
&\cdot \frac{1}{(4\pi)^2} \frac{1}{5} \overline{\varepsilon_{\lambda\kappa}}(\mathbf{q}) \overline{\varepsilon_{\lambda\kappa}^*}(\mathbf{q}). \quad (4.7)
\end{aligned}$$

The influence of an external field on the way the anisotropy fluctuations change with time is related to the fact that $S_{\mu\nu, \mu'\nu'}^{(\text{an})}(\omega | \mathbf{q})$ is not proportional to

the isotropic tensor $\Delta_{\mu\nu, \mu'\nu'}$. This influence may be appreciable even at field strengths where the aforementioned thermal alignment is negligible; for an example see Ref. 6.

In the absence of external fields and if the coupling between $\overline{\varepsilon_{\mu\nu}}$ and the friction pressure tensor^{14a} is disregarded, $A_{\mu\nu, \mu'\nu'}^{(\text{an})}$ and $S_{\mu\nu, \mu'\nu'}^{(\text{an})}$ are isotropic, i. e.

$$A_{\mu\nu, \mu'\nu'}^{(\text{an})}(t | \mathbf{q}) = A^{(\text{an})}(t | \mathbf{q}) \Delta_{\mu\nu, \mu'\nu'} \quad (4.8)$$

and

$$S_{\mu\nu, \mu'\nu'}^{(\text{an})}(\omega | \mathbf{q}) = S^{(\text{an})}(\omega | \mathbf{q}) \Delta_{\mu\nu, \mu'\nu'}, \quad (4.9)$$

where $S^{(\text{an})}$ is related to $A^{(\text{an})}$ in the same way as $S^{(\text{sc})}$ is linked with $A^{(\text{sc})}$ by Eq. (3.5).

Thus, if Eqs. (4.8, 9) are fulfilled, the scattering equation for the light scattering caused by anisotropy fluctuations is

$$\begin{aligned}
I^{(\text{an})} &= \left[\frac{1}{2} + \frac{1}{6} (\mathbf{e} \cdot \mathbf{e}')^2 \right] S^{(\text{an})}(\omega - \omega' | \mathbf{q}) \\
&\cdot \frac{1}{(4\pi)^2} \frac{1}{5} \overline{\varepsilon_{\lambda\kappa}}(\mathbf{q}) \overline{\varepsilon_{\lambda\kappa}^*}(\mathbf{q}). \quad (4.10)
\end{aligned}$$

In contrast to $I^{(\text{sc})}$, the scattering function $I^{(\text{an})}$ does not vanish if \mathbf{e} is perpendicular to \mathbf{e}' . Hence the light scattered due to anisotropy fluctuations (depolarized Rayleigh scattering, rotational Raman scattering) contains a depolarized component.

II. Electric Permeability and Scattering Equations for Polyatomic Gases

§ 5. Electric Permeability and Average Molecular Polarizability of a Gas

The optical properties of a molecule can be characterized by the electric polarizability tensor $\alpha_{\mu\nu}$. The discussion here is restricted to molecules which have a polarizability that is approximately frequency-independent in the optical range.

Since the electric field that acts on a specific molecule in a gas is only slightly modified by the surrounding molecules, the electrical polarization \mathbf{P} of a gas of nonpolar molecules can be assumed to be given by

$$P_\mu = n \langle \alpha_{\mu\nu} \rangle E_\nu, \quad (5.1)$$

where \mathbf{E} is the vacuum electric field. In Eq. (5.1), n is the number density of the gas and the bracket $\langle \rangle$ re-

¹² W. VOIGT, *Lehrbuch der Kristallphysik*, Teubner, Leipzig 1910.

¹³ M. v. LAUE, *Ann. Phys. Leipzig* **23**, 1 [1935].

¹⁴ G. J. HOOYMANN, P. MAZUR, and S. R. DE GROOT, *Physica* **21**, 355 [1955]; see also: S. R. DE GROOT and P. MAZUR, *Non-equilibrium Thermodynamics*, North Holland Publishing Co., Amsterdam 1962.

^{14a} V. VOLTERRA, *Phys. Rev.* **180**, 156 [1969].

fers to an average over a one-particle distribution function to be specified later. With $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, Eq. (5.1) leads to the well-known relation

$$\varepsilon_{\mu\nu} = \delta_{\mu\nu} + 4\pi n \langle \alpha_{\mu\nu} \rangle. \quad (5.2)$$

Equation (5.2) can only be applied if the number density n fulfills two conditions: firstly, the interparticle separation has to be small compared with the wavelength λ of the light, i. e.

$$n\lambda^3 \gg 1, \quad (5.3)$$

and, secondly, n has to obey the inequality

$$\alpha n \ll 1, \quad (5.4)$$

where

$$\alpha = \frac{1}{3} \alpha_{00}. \quad (5.5)$$

The second inequality guarantees the validity of Eq. (5.1).

A feeling for the limitations imposed on n by (5.3) and (5.4) can be obtained from the following order of magnitude considerations: for $\lambda \approx 5 \cdot 10^{-5}$ cm and $n \approx 3 \cdot 10^{16}$ cm $^{-3}$, $n\lambda^3 \approx 3 \cdot 10^3$; on the other hand, α being of the order of 10^{-24} cm 3 , $\alpha n \approx 3 \cdot 10^{-3}$, for $n \approx 3 \cdot 10^{21}$ cm $^{-3}$. These numbers represent reasonable upper and lower bounds of 1 Torr and 100 atm on the pressures at room temperature for which the theory developed here can be considered applicable.

With Eqs. (5.2) and (5.5), the constant part of the electric permeability (cf. 1.4) is given by

$$\varepsilon = 1 + 4\pi n_0 \langle \alpha \rangle_0. \quad (5.6)$$

In Eq. (5.6), n_0 is the (constant) equilibrium number density and the bracket $\langle \rangle_0$ refers to an average over an (absolute) equilibrium distribution function. A thermal alignment of $\overline{\alpha_{\mu\nu}}$ in an external field, i. e. a term $\langle \overline{\alpha_{\mu\nu}} \rangle_0$ is neglected.

For the fluctuating isotropic and anisotropic parts of $\varepsilon_{\mu\nu}$ one finds (in the "linear" approximation),

$$\tilde{\varepsilon} = 4\pi n_0 \langle \alpha \rangle_0 \left[\frac{n - n_0}{n_0} + \frac{\langle \alpha \rangle - \langle \alpha \rangle_0}{\langle \alpha \rangle_0} \right], \quad (5.7)$$

$$\overline{\varepsilon_{\mu\nu}} = 4\pi n_0 \langle \overline{\alpha_{\mu\nu}} \rangle. \quad (5.8)$$

Hence the "scalar fluctuations" are due to fluctuations of the number density and of the mean isotropic part of the molecular polarizability. On the other hand, the anisotropy fluctuations are fluctuations of the mean anisotropic part of $\alpha_{\mu\nu}$.

For particles with spherical symmetry, e. g. monoatomics, regular tetrahedral (CH $_4$), and regular octahedral (SF $_6$) molecules the polarizability is isotropic, i. e., $\overline{\alpha_{\mu\nu}} = 0$.

For linear molecules or symmetric top molecules the polarizability depends on the angle between the electric field and the molecular axis or the figure axis with direction specified by the unit vector \mathbf{u} . Denoting the polarizability for the electric field parallel to or perpendicular to \mathbf{u} by $\alpha_{||}$ and α_{\perp} , respectively, one has

$$\alpha = \frac{1}{3} (\alpha_{||} + 2\alpha_{\perp}) \quad (5.9)$$

and

$$\overline{\alpha_{\mu\nu}} = (\alpha_{||} - \alpha_{\perp}) \overline{u_{\mu} u_{\nu}}. \quad (5.10)$$

clearly, the anisotropic polarizability $\overline{\alpha_{\mu\nu}}$ vanishes if α_{\perp} equals $\alpha_{||}$.

§ 6. Distribution Function for a Gas of Linear Molecules

In this section the discussion is restricted to a gas of linear molecules. The explicit meaning of the averages $\langle \rangle$ and $\langle \rangle_0$ over one-particle nonequilibrium and equilibrium distribution functions (operators) will be stated and some general features of the distribution functions will be discussed. First, however, a number of preliminary remarks are necessary.

It is assumed that the translational motion of the molecules can be treated classically (i. e. position and linear momentum of a particle are specified by the classical variables \mathbf{x} and \mathbf{p}). The rotational motion of the molecules, treated quantum mechanically, is characterized by the rotational angular momentum operator \mathbf{J} (in units of \hbar) whose Cartesian components obey the commutation relations

$$J_{\mu} J_{\nu} - J_{\nu} J_{\mu} = i \varepsilon_{\mu\nu\lambda} J_{\lambda}, \quad (6.1)$$

where $\varepsilon_{\mu\nu\lambda}$ is the 3rd rank isotropic tensor with $\varepsilon_{123} = 1$. For a linear molecule (rotator), \mathbf{J} is perpendicular to the molecular axis, i. e.

$$\mathbf{J} \cdot \mathbf{u} = 0. \quad (6.2)$$

The normalized internal wave functions of a molecule in the j -th rotational state are denoted by $|jM\rangle$ where M is the magnetic quantum number with respect to an arbitrary axis of quantization. Projection operators

$$P_j = \sum_M |jM\rangle \langle jM|; \quad j = 0, 1, \dots \quad (6.3)$$

which have the properties

$$\sum_j P_j = 1; \quad P_i P_j = \delta_{ij} P_j, \quad J^2 P_j = P_j J^2 = j(j+1) P_j, \quad (6.4)$$

$$\text{tr } P_j = 2j + 1. \quad (6.5)$$

will also prove useful. In (6.5), "tr" denotes the trace over the magnetic quantum numbers.

For any operator, Φ with the matrix elements

$$\langle j M | \Phi | j' M' \rangle = \Phi_{MM'}^{jj'}$$

we define " $(j j')$ -operators" by

$$\Phi^{jj'} = P_j \Phi P_{j'} = \sum_{M, M'} |j M\rangle \Phi_{MM'}^{jj'} \langle j' M'|. \quad (6.6)$$

The part of an operator which is diagonal in j can be written as a function of the Cartesian components of the operator \mathbf{J} :

$$\sum_j \Phi^{jj} = \sum_j P_j \Phi P_j = \Phi(\mathbf{J}). \quad (6.7)$$

Now a discussion of the one-particle distribution function characterizing the (nonequilibrium) state of the gas can be given. The distribution "function" f is a distribution operator with matrix elements depending on the position and the (linear) momentum of a molecule as well as on the time t . Splitting f into a part which is diagonal in j and into nondiagonal parts, one has

$$f(t, \mathbf{x}, \mathbf{p}) = f(t, \mathbf{x}, \mathbf{p}, \mathbf{J}) + \sum_{j \neq j'} \Phi^{jj'}(t, \mathbf{x}, \mathbf{p}). \quad (6.8)$$

Similarly, the local instantaneous mean value $\langle \Phi \rangle$ of an operator $\Phi(\mathbf{p})$ can be written as

$$\langle \Phi \rangle = \langle \Phi(\mathbf{p}, \mathbf{J}) \rangle + \sum_{j \neq j'} \langle \Phi^{jj'}(\mathbf{p}) \rangle, \quad (6.9)$$

where

$$\langle \Phi(\mathbf{p}, \mathbf{J}) \rangle = \frac{1}{n} \text{Tr} \int d^3 p \Phi(\mathbf{p}, \mathbf{J}) f(t, \mathbf{x}, \mathbf{p}, \mathbf{J}), \quad (6.10)$$

$$\langle \Phi^{jj'}(\mathbf{p}) \rangle = \frac{1}{n} \text{tr} \int d^3 p \Phi^{jj'}(\mathbf{p}) f^{jj'}(t, \mathbf{x}, \mathbf{p}), \quad (6.11)$$

and

$$n(t, \mathbf{x}) = \text{Tr} \int d^3 p f(t, \mathbf{x}, \mathbf{p}, \mathbf{J}) \quad (6.12)$$

is the number density. In Eqs. (6.10, 12) " $\text{Tr} \dots$ " stands for $\sum_j \text{tr } P_j \dots P_j$. The average $\langle \rangle_0$ is defined in the same way as (6.9, 10) but with f replaced by the equilibrium distribution function

$$f_0(\mathbf{p}, \mathbf{J}) = n_0 (2\pi m k T_0)^{-3/2} Q^{-1} \exp \left\{ -\frac{p^2}{2 m k T_0} - \frac{\hbar^2}{2 \Theta k T_0} J^2 \right\}, \quad (6.13)$$

which is diagonal in the rotational quantum numbers j . In Eq. (6.13), n_0 and T_0 are the equilibrium number density and temperature, respectively; k is Boltzmann's constant and

$$Q = \text{Tr} \exp \left\{ -(\hbar^2/2 \Theta k T_0) J^2 \right\} \quad (6.14)$$

is the internal partition function. The mass and the moment of inertia of a molecule have been denoted by m and Θ , respectively.

Before the average of $\alpha_{\mu\nu}$ occurring in (5.1, 2) and (5.6–8), over the one-particle distribution function can be evaluated (at least formally), it is necessary to express $\alpha_{\mu\nu}$ as a sum of (j, j') -operators defined by (6.6). This point will be discussed separately in the next 2 sections for the isotropic and the anisotropic parts of $\alpha_{\mu\nu}$.

§ 7. Isotropic Electric Permeability, Scalar Scattering

The isotropic or spherical part of the molecular polarizability is diagonal both in rotational and in magnetic quantum numbers. Centrifugal stretching will lead to a simple dependence on J^2 so that $\alpha(J)$ will be of the form¹⁵

$$\alpha(J^2) = \alpha_0 [1 + \xi J^2], \quad (7.1)$$

where α_0 is independent of the rotational levels of the molecule. Calculations of α have been made for H_2 , HD, and D_2 molecules^{16, 17}. The difference in the polarizability between H_2 molecules in the 0th and 1st rotational states has been measured¹⁸. From the data given in Ref. ¹⁷ one can indeed infer that $\alpha(J^2)$ is of the form (7.1); the value of ξ is approximately 10^{-3} for H_2 . Thus the polarizability of hydrogen exhibits a weak dependence on the magnitude of the rotational angular momentum.

¹⁵ A. BABLOYANTZ and A. BELLEMANS, Mol. Phys. **3**, 313 [1960]. — H. F. P. KNAAP and J. J. M. BEENAKKER, Physica **27**, 523 [1961]. — A. D. BUCKINGHAM, Discussions Faraday Soc. **40**, 171 [1965].

¹⁶ E. ISHIGURO, T. ARAI, M. KOTANI, and M. MIZUSHIMA, Proc. Phys. Soc. London A **65**, 178 [1952].

¹⁷ W. KOLOS and L. WOLNIEWICZ, J. Chem. Phys. **46**, 1426 [1967].

¹⁸ L. J. F. HERMANS, J. J. DE GROOT, H. F. P. KNAAP, and J. J. M. BEENAKKER, Physica **31**, 1537 [1965].

Using (7.1) one obtains

$$\langle \alpha_0 \rangle = \alpha_0 [1 + \xi \langle J^2 \rangle_0], \quad (7.2)$$

and

$$\langle \alpha \rangle - \langle \alpha \rangle_0 = \alpha_0 \xi [\langle J^2 \rangle - \langle J^2 \rangle_0]. \quad (7.3)$$

Since the rotational energy of a molecule

$$E_{\text{rot}} = (\hbar^2/2 \Theta) J^2$$

is proportional to J^2 , the fluctuations of the spherical part of the electric polarizability are, according to (7.3), proportional to fluctuations of the rotational energy or of the rotational temperature T_{rot} . The rotational (non-equilibrium) temperature is defined by

$$(\hbar^2/2 \Theta) [\langle J^2 \rangle - \langle J^2 \rangle_0] = c_{\text{rot}}(T_{\text{rot}} - T_0), \quad (7.4)$$

where

$$c_{\text{rot}} = \frac{\hbar^2}{2 \Theta} \frac{d \langle J^2 \rangle_0}{dT_0} = k \left(\frac{\hbar^2}{2 \Theta k T_0} \right) [\langle J^4 \rangle_0 - \langle J^2 \rangle_0^2] \quad (7.5)$$

is the (equilibrium) rotational specific heat per molecule. Thus (7.3) can be rewritten as

$$\langle \alpha \rangle - \langle \alpha \rangle_0 = \alpha_0 \xi (2 \Theta / \hbar^2) c_{\text{rot}} (T_{\text{rot}} - T_0). \quad (7.6)$$

The intensity of the light scattered due to scalar fluctuations is a sum of the contributions from fluctuations of the number density and of the rotational temperature since these fluctuations are uncorrelated.

Introduction of the abbreviations

$$a_1 = (n - n_0)/n_0 \quad (7.7)$$

and

$$a_2 = \langle \Phi^{(2)}(\mathbf{J}) \rangle = \sqrt{c_{\text{rot}}/k} (T_{\text{rot}} - T_0)/T_0, \quad (7.8)$$

where

$$\Phi^{(2)}(\mathbf{J}) = \sqrt{k/c_{\text{rot}}} (\hbar^2/2 \Theta k T_0) (J^2 - \langle J^2 \rangle_0), \quad (7.9)$$

and of the symbols S_1 , S_2 and I_1 , I_2 , respectively for the spectral functions and scattering functions corresponding to a_1 and a_2 leads to

$$I^{(\text{sc})} = I_1 + I_2, \quad (7.10)$$

with

$$I_1 = (\mathbf{e} \cdot \mathbf{e}')^2 S_1(\omega - \omega' | \mathbf{q}) (n_0 \langle \alpha \rangle_0)^2 \overline{a_1(\mathbf{q})}^2, \quad (7.11)$$

and

$$I_2 = (\mathbf{e} \cdot \mathbf{e}')^2 S_2(\omega - \omega' | \mathbf{q}) (n_0 \alpha_0 \xi)^2 \cdot (c_{\text{rot}}/k) (2 \Theta k T_0 / \hbar^2)^2 \overline{a_2(\mathbf{q})}^2. \quad (7.12)$$

The proportionality constant occurring in (7.9) has been chosen such that

$$\langle \Phi^{(2)} \Phi^{(2)} \rangle_0 = 1. \quad (7.13)$$

This implies, for a gas at equilibrium (see Appendix I), that

$$\overline{a_2(\mathbf{q})}^2 = \overline{a_1(\mathbf{q})}^2 = n V, \quad (7.14)$$

where V is the scattering volume. The factor $(c_{\text{rot}}/k) (2 \Theta k T_0 / \hbar^2)^2$ occurring in (7.12) is equal to $\langle J^4 \rangle_0 - \langle J^2 \rangle_0^2$.

With (7.14), the ratio of the intensities (integrated over all frequencies) of the light scattered due to fluctuations of the rotational temperature and the number density is given by

$$(c_{\text{rot}}/k) (\xi \cdot 2 \Theta k T_0 / \hbar^2)^2. \quad (7.15)$$

The quantity ξ is, apart from a numerical factor of the order of 1, given by $\hbar^2 (\Theta \omega_{\text{vib}})^{-2}$, where ω_{vib} is a vibration frequency of a molecule. Thus the ratio (7.15) is approximately equal to

$$(c_{\text{rot}}/k) (2 k T_0 / \Theta \omega_{\text{vib}}^2)^2. \quad (7.16)$$

For linear molecules such as H_2 , N_2 , O_2 , CO_2 the quantity $\frac{1}{2} \Theta \omega_{\text{vib}}^2$ corresponds to temperature of the order of $3 \cdot 10^3$ °K to $3 \cdot 10^4$ °K. Hence, at room temperature, the intensity of the light scattered due to fluctuations of $(T_{\text{rot}} - T_0)$ can be disregarded.

§ 8. Anisotropic Electric Permeability. Scattering Due to Anisotropy Fluctuations

This section deals with the anisotropic part of the molecular polarizability as given by (5.10). For simplicity, the scalar factor $\alpha_{||} - \alpha_{\perp}$ which, in general, depends on the magnitude of the rotational angular momentum is replaced by $\langle \alpha_{||} - \alpha_{\perp} \rangle_0$. The operator $\overline{u_{\mu} u_{\nu}}$ contains a part diagonal in j proportional to $\overline{J_{\mu} J_{\nu}}$, i. e.,

$$\overline{u_{\mu} u_{\nu}}(\mathbf{J}) = \sum_j P_j \overline{u_{\mu} u_{\nu}} P_j \propto \overline{J_{\mu} J_{\nu}}, \quad (8.1)$$

as well as parts that are nondiagonal with respect to the rotational quantum numbers. The proportionality constant required in (8.1) can be found by using $\mathbf{J} \cdot \mathbf{u} = 0$ and

$$\overline{J_{\mu} J_{\nu}} \overline{J_{\mu} J_{\nu}} = J^2 (J^2 - \frac{3}{4}). \quad (8.2)$$

Thus, the relation^{19, 20}

$$\overline{u_{\mu} u_{\nu}}(\mathbf{J}) = -\frac{1}{2} [J^2 - \frac{3}{4}]^{-1} \overline{J_{\mu} J_{\nu}}. \quad (8.3)$$

¹⁹ S. HESS and W. E. KÖHLER, Z. Naturforsch. **23a**, 1903 [1968].

²⁰ F. M. CHEN and R. F. SNIDER, J. Chem. Phys. **48**, 3185 [1968].

is obtained. For $j \geq 2$, $[J^2 - \frac{3}{4}]^{-1}$ may be replaced by $[J^2(J^2 - \frac{3}{4})]^{-1/2}$. Then $\langle \mathbf{u}_\mu \mathbf{u}_\nu(\mathbf{J}) \rangle$ becomes proportional to the mean 2nd rank tensor polarization (quadrupolarization)

$$a_{\mu\nu} = \langle \Phi_{\mu\nu}(\mathbf{J}) \rangle, \quad (8.4)$$

where

$$\Phi_{\mu\nu} = \sqrt{15/2} [J^2(J^2 - \frac{3}{4})]^{-1/2} \overline{J_\mu J_\nu}. \quad (8.5)$$

The constant occurring in Eq. (8.5) has been chosen such that

$$\langle \Phi_{\mu\nu} \Phi_{\mu'\nu'} \rangle_0 = \Delta_{\mu\nu, \mu'\nu'}. \quad (8.6)$$

Thus if the molecules are predominantly in rotational states with $j \geq 2$, one has approximately

$$\langle \mathbf{u}_\mu \mathbf{u}_\nu(\mathbf{J}) \rangle = -\frac{1}{2} \sqrt{2/15} a_{\mu\nu}. \quad (8.7)$$

Hence the fluctuations leading to the depolarized Rayleigh scattering are caused by fluctuations of the tensor polarization (8.4).

Before turning to a discussion on those parts of the operator $\mathbf{u}_\mu \mathbf{u}_\nu$ which are nondiagonal in j firstly notice that for arbitrary j, j' (see Appendix II),

$$\begin{aligned} \overline{(\mathbf{u}_\mu \mathbf{u}_\nu)^{jj'}} &= P_j \overline{\mathbf{u}_\mu \mathbf{u}_\nu} P_{j'} \\ &= \sqrt{2/15} \sqrt{2j+1} (j0, 20 | j'0) T_{\mu\nu}^{jj'}, \end{aligned} \quad (8.8)$$

where the Clebsch-Gordan coefficient²¹ $(j0, 20 | j'0)$ vanishes unless

$$j' = j, j \pm 2. \quad (8.9)$$

In Eq. (8.8), the operators $T_{\mu\nu}^{jj'}$ are 2nd rank Cartesian tensor operators related to the well-known spherical tensor operators^{19, 21} $T_{2m}^{jj'}$ by

$$T_{\mu\nu}^{jj'} \overline{b_\mu b_\nu} = \sqrt{2/15} \sqrt{4\pi} \sum_m T_{2m}^{jj'} Y_{2m}(\mathbf{b}). \quad (8.10)$$

Here \mathbf{b} is an arbitrary unit vector and $Y_{lm}(\mathbf{b})$ is a spherical harmonic depending on the polar angles of \mathbf{b} with respect to the axis of quantization.

The Cartesian tensor operators have the following properties:

$$(T_{\mu\nu}^{jj'})^\dagger = (-1)^{j-j'} T_{\mu\nu}^{jj'}, \quad (8.11)$$

$$\text{tr} \{ (T_{\mu\nu}^{jj'})^\dagger T_{\mu'\nu'}^{jj'} \} = \Delta_{\mu\nu, \mu'\nu'}. \quad (8.12)$$

The definition of Cartesian tensor operators of rank $l=1, 2, 3, \dots$ and some of their general properties are given in Appendix II.

Notice that the "diagonal" operators $T_{\mu\nu}^{jj}$ are proportional to $\Phi_{\mu\nu}^{jj}$, where Φ is given by (8.5), i. e.

$$\sqrt{2j+1} T_{\mu\nu}^{jj} = \Phi_{\mu\nu}^{jj}. \quad (8.13)$$

With $(j0, 20 | j0) = -\left(\frac{j(j+1) - \frac{3}{4}}{j(j+1)}\right)^{1/2}$ (8.7) is recovered from (8.8).

For the mean values of the "nondiagonal" operators $T_{\mu\nu}^{jj'}$ we introduce the abbreviations

$$a_{\mu\nu}^{(jj')} = \langle T_{\mu\nu}^{jj'} \rangle. \quad (8.14)$$

The fluctuations the tensors (8.14), for $j' = j \pm 2$, lead to the occurrence of rotational Raman scattering.

With (5.8, 10), (8.7, 8) and (8.14) the result finally obtained is

$$\begin{aligned} \overline{\epsilon_{\mu\nu}} &= 4\pi n_0 \langle \alpha_{||} - \alpha_{\perp} \rangle_0 \sqrt{2/15} \\ &\cdot \left[-\frac{1}{2} a_{\mu\nu} + \sum_{j=0} c_j (a_{\mu\nu}^{(j, j+2)} + a_{\mu\nu}^{(j+2, j)}) \right], \end{aligned} \quad (8.15)$$

where the abbreviation

$$\begin{aligned} c_j &= \sqrt{2j+1} (j0, 20 | j+2, 0) \\ &= \sqrt{2j+5} (j+20, 20 | j0) \end{aligned} \quad (8.16)$$

has been used.

Since the fluctuations of the tensor polarization $a_{\mu\nu}$ and of all $a_{\mu\nu}^{(j, j+2)}$, and $a_{\mu\nu}^{(j+2, j)}$ are uncorrelated for a gas at equilibrium, the scattering function $I^{(\text{an})}$ is a sum of the various contributions

$$I^{(\text{an})} = I^{(0)} + \sum_j [I^{(j, j+2)} + I^{(j+2, j)}]. \quad (8.17)$$

The scattering function $I^{(0)}$ which characterizes the depolarized Rayleigh scattering is given by

$$\begin{aligned} I^{(0)} &= e_\mu e'_\nu S_{\mu\nu, \mu'\nu'}^{(0)}(\omega - \omega' | \mathbf{q}) e_{\mu'} e_{\nu'} \\ &\cdot \frac{1}{30} (n_0 \langle \alpha_{||} - \alpha_{\perp} \rangle_0)^2 \frac{1}{5} a_{\lambda\kappa}(\mathbf{q}) a_{\lambda\kappa}^*(\mathbf{q}). \end{aligned} \quad (8.18)$$

Here $S_{\mu\nu, \mu'\nu'}^{(0)}$ is the spectral function pertaining to $a_{\mu\nu}(t, \mathbf{q})$; for its general definition see (4.2) and (4.5).

The scattering functions $I^{(j, j+2)}$ and $I^{(j+2, j)}$ for the rotational Raman lines are given by

$$I^{(j, j+2)} = e_\mu e'_\nu S_{\mu\nu, \mu'\nu'}^{(j, j+2)}(\omega - \omega' | \mathbf{q}) e_{\mu'} e_{\nu'} \quad (8.19)$$

$\cdot \frac{2}{15} (c_j n_0 \langle \alpha_{||} - \alpha_{\perp} \rangle_0)^2 \frac{1}{5} a_{\lambda\kappa}^{(j, j+2)}(\mathbf{q}) a_{\lambda\kappa}^{(j+2, j)*}(-\mathbf{q})$, and $I^{(j+2, j)}$ may be obtained from Eq. (8.19) by interchanging j and $j+2$ in the superscripts. The spectral function associated with $a_{\mu\nu}^{(jj')}(t, \mathbf{q})$ has been denoted by $S_{\mu\nu, \mu'\nu'}^{(jj')}$.

Hence, by (8.17–19), the calculation of the spectrum of the depolarized Rayleigh light and of

²¹ A. R. EDMONDS, Angular Momentum in Quantum Mechanics, Princeton University Press, Princeton, N.J. 1957.

the rotational Raman lines is reduced to a calculation of the spectral functions $S_{\mu\nu,\mu'\nu'}^{(0)}$ and $S_{\mu\nu,\mu'\nu'}^{(j,j')}$ ($j' = j \pm 2$) which are associated with the fluctuations of the mean (2nd rank) tensor polarization (8.4) and of the tensors (8.14).

Concluding Remarks

The spectrum of the light scattered due to scalar fluctuations in a gas is expressed through (7.11) and (7.12) in terms of the spectral functions pertinent to the space Fourier transforms of the fluctuating number density and the fluctuating rotational temperature. Similarly, the spectrum of the light scattered due to anisotropy fluctuations is related through (8.18) and (8.19), to the spectral functions for the fluctuating mean 2nd rank tensor polarization (depolarized Rayleigh scattering) and for the fluctuations of mean values of 2nd rank tensor operators inducing transitions $\Delta j = \pm 2$ between the rotational levels of the molecules (rotational Raman scattering).

Using Onsager's assumption, the relevant spectral functions can be calculated from generalized hydrodynamical or transport-relaxation equations. In general, such equations can be obtained by using the standard techniques of nonequilibrium thermodynamics. For gases, the transport-relaxation equations can also be derived from a kinetic equation, i. e., a (generalized) Boltzmann equation. In this case, the transport coefficients and relaxation times involved can be expressed in terms of collision bracket integrals obtained from the linearized collision term of the (generalized) Boltzmann equation.

The spectrum of the light scattered due to density fluctuations in fluids was first investigated theoretically by BRILLOUIN²², MANDELSTAM³, and by LANDAU and PLACZEK²³. For more recent treatments see Refs.²⁻⁴ and the articles by MOUNTAIN²⁴, by RYTOV²⁴, and by FELDERHOF²⁵. A „Boltzmann equation approach” to light scattering from monatomic gases has been used by NELKIN and YIP²⁶, by GROSS²⁷ and by FOCH²⁸. The spectral function for density fluctuations in polyatomic gases has been calculated by SUGAWARA and YIP²⁹ who used transport-relaxation equations obtained from the WANG CHANG-UHLENBECK equation³⁰.

The kinetic equation relevant for transport properties of polyatomic gases is the WALDMAN-SNIDER equation⁸. It has widely been used to investigate the influence of magnetic and electric fields on the heat conductivity and the viscosity of polyatomic gases^{31, 32} (SENFTLEBEN-BEENAKKER effect^{33, 34}) as well as to study nuclear spin relaxation³⁵ and spin diffusion³⁶ in gases. The Waldmann-Snider equation, being a kinetic equation for the part of the one-particle distribution function which is diagonal in the rotational quantum numbers j , can be used to derive the transport-relaxation equations which are needed for the evaluation of the spectral functions pertaining to the fluctuations of the density, the rotational temperature and of the mean tensor polarization. The latter, determining the spectrum of the depolarized Rayleigh light, is calculated in a subsequent paper⁷. Notice, however, that a generalization of the Waldmann-Snider equation for those parts of the distribution function which are non-diagonal in the rotational quantum numbers is required if one wants to study the spectral functions

²² L. BRILLOUIN, C. R. Acad. Sci. Paris **158**, 1331 [1914]; Z. Phys. (Paris) **17**, 88 [1922].

²³ L. D. LANDAU and G. PLACZEK, Phys. Z. Sowjetunion **5**, 172 [1934].

²⁴ R. D. MOUNTAIN, Rev. Mod. Phys. **38**, 205 [1966]. — M. S. RYTOV, Soviet Phys.—JETP **27**, 147 [1968].

²⁵ B. N. FELDERHOF, J. Chem. Phys. **44**, 602 [1966].

²⁶ M. NELKIN and S. YIP, Phys. Fluids **9**, 380 [1966].

²⁷ E. P. GROSS, in Lectures in Theoretical Physics 9c (ed. W. E. BRITTIN et al.), Gordon and Breach, New York 1967.

²⁸ J. FOCH, Phys. Fluids **11**, 2336 [1968].

²⁹ A. SUGAWARA and S. YIP, Phys. Fluids **10**, 1911 [1967].

³⁰ C. S. WANG CHANG and G. E. UHLENBECK, Eng. Res. Inst. Univ. Michigan Report CM 681 [1951]. — C. S. WANG CHANG, G. E. UHLENBECK, and J. DE BOER, in Studies in Statistical Mechanics II (ed. J. DE BOER and G. E. UHLENBECK), North Holland Publishing Co., Amsterdam 1964.

³¹ L. WALDMANN and H. D. KUPATT, Z. Naturforsch. **18a**, 86 [1963]. — S. HESS and L. WALDMANN, Z. Naturforsch. **21a**, 1529 [1966]; **23a**, 1893 [1968]. — F. R. MCCOURT

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³² L. WALDMANN, in Fundamental Problems in Statistical Mechanics II (ed. E. G. D. COHEN), North Holland Publishing Co., Amsterdam 1968.

³³ H. SENFTLEBEN, Phys. Z. **31**, 822, 961 [1930]. — J. J. M. BEENAKKER, G. SCOLES, H. F. P. KNAAP, and R. M. JONKMAN, Phys. Letters **2**, 5 [1962].

³⁴ J. J. M. BEENAKKER, in Festkörperprobleme VIII (ed. O. MADLUNG), Vieweg, Braunschweig 1968.

³⁵ F. M. CHEN and R. F. SNIDER, J. Chem. Phys. **46**, 3937 [1967]. — S. HESS, Thesis, Erlangen 1967.

³⁶ S. HESS, Z. Naturforsch. **23a**, 898 [1968]; Physica **42**, 633 [1969].

associated with the rotational Raman scattering. Such a generalized Waldmann-Snider equation, valid under the condition that the frequency differences between the rotational Raman lines are large compared with their widths (sufficient level spacing), has recently been obtained by TIP³⁷ and by the author³⁸.

Appendix I. Time Independent Fluctuations

A calculation of the squares of the time independent space Fourier coefficients of the fluctuating quantities occurring in Eqs. (7.11, 12) and (8.18) will be given in this appendix for a gas at a thermal equilibrium (number density n_0 , temperature T_0).

Let φ_i ($i = 1, 2, \dots$) be a set of fluctuating quantities with equilibrium values $\varphi_{i0} = 0$ and probability averages $\bar{\varphi}_i = 0$. The general definition of the probability average of a function $g(\varphi) = g(\varphi_1, \varphi_2, \dots)$ is¹¹

$$\bar{g} = \int d\varphi g(\varphi) w(\varphi), \quad (\text{I.1})$$

where $d\varphi = d\varphi_1 d\varphi_2 \dots$ and $w(\varphi) = w(\varphi_1, \varphi_2, \dots)$ is the probability distribution function with

$$\int d\varphi w(\varphi) = 1. \quad (\text{I.2})$$

The general ideas for obtaining the required probability distribution for fluctuating quantities are due to EINSTEIN³⁹. The first application to light scattering caused by density fluctuations were those of V. SMOLUCHOWSKY¹ and EINSTEIN¹. Anisotropy fluctuations have been considered by GANS⁴⁰.

The probability distribution $w(\varphi)$ is related to the nonequilibrium entropy $S(\varphi)$ by^{11, 39}

$$w(\varphi) \propto e^{(1/k) S(\varphi)} \quad (\text{I.3})$$

where k is Boltzmann's constant. For $\varphi = 0$ (equilibrium) the entropy reaches its maximum S_0 . Expanding around this maximum and keeping the lowest order terms only, gives

$$(1/k) S(\varphi) \approx (1/k) S_0 - \frac{1}{2} \sum_{i,l} \beta_{il} \varphi_i \varphi_l. \quad (\text{I.4})$$

Use of Eq. (I.4) leads to a Gaussian probability distribution which yields¹¹

$$\overline{\varphi_i \varphi_l} = (\beta^{-1})_{il} \quad (\text{I.5})$$

where β^{-1} is the inverse of the matrix β .

Hence in order to find the probability average of the square of the Fourier components of the quanti-

ties occurring in Eqs. (7.11, 12) and (8.18) in a "Gaussian approximation", it is sufficient to know the entropy as a function of these quantities in a form analogous to Eq. (I.4).

To obtain the required nonequilibrium entropy as a function of macroscopic variables, we follow an idea of WALDMANN⁴¹. Firstly, the nonequilibrium distribution function f is expanded around its equilibrium value f_0 (in a way to be specified immediately) and then the (Boltzmann) entropy

$$(1/k) (S - S_0) = - \int d^3x \text{Tr} \int d^3p f \ln(f_0^{-1} f) \quad (\text{I.6})$$

is evaluated up to terms quadratic in the quantities characterizing the deviation from the equilibrium state.

For the distribution function f we write

$$f = f_0 (1 + a_1 + \sum_{n,l} a_{\mu_1 \dots \mu_l}^{(n)} \Phi_{\mu_1 \dots \mu_l}^{(n)}), \quad (\text{I.7})$$

where the $\Phi_{\mu_1 \dots \mu_l}^{(n)}$ constitute a system of orthonormalized expansion tensors of rank $l = 0, 1, 2, \dots$ which depend on \mathbf{p} and \mathbf{J} . The expansion tensors have the properties

$$\langle \Phi_{\dots}^{(n)} \rangle_0 = 0; \langle \Phi_{\mu_1 \dots \mu_l}^{(n)} \Phi_{\nu_1 \dots \nu_l}^{(n')} \rangle_0 = \Delta_{\mu_1 \dots \mu_l, \nu_1 \dots \nu_l}^{(l)} \delta^{(nn')}, \quad (\text{I.8})$$

where $\Delta_{\dots}^{(l)}$ is an isotropic tensor of rank $2l$ which projects, when applied on any l^{th} rank tensor, on the irreducible (symmetric, traceless) part of this tensor⁴². The first three of these tensors are $\Delta^{(0)} = 1$, $\Delta_{\mu\nu}^{(1)} = \delta_{\mu\nu}$, and $\Delta_{\mu\nu, \mu'\nu'}^{(2)} = \Delta_{\mu\nu, \mu'\nu'}$ as defined by (4.4). In general, one has

$$\Delta_{\mu_1 \dots \mu_l, \mu_1 \dots \mu_l}^{(l)} = 2l + 1. \quad (\text{I.9})$$

The expansion coefficient $a_{\mu_1 \dots \mu_l}^{(n)}$ are the space dependent nonequilibrium averages of the expansion tensors, in particular one has

$$a_1 = (n - n_0)/n_0; \quad a_{\mu_1 \dots \mu_l}^{(n)} = \langle \Phi_{\mu_1 \dots \mu_l}^{(n)} \rangle. \quad (\text{I.10})$$

With (I.7 - 10) and by neglecting terms of higher than 2nd order in the expansion coefficients, one obtains from⁴¹ (I.6):

$$(1/k) S = (1/k) S_0 - \frac{1}{2} n_0 \int d^3x [a_1^2(x) + \sum_{n,l} a_{\mu_1 \dots \mu_l}^{(n)}(\mathbf{x}) a_{\mu_1 \dots \mu_l}^{(n)}(\mathbf{x})]. \quad (\text{I.10}')$$

Using space Fourier transforms (cf. 2.3, 4) one finds

$$(1/k) S = (1/k) S_0 - \frac{1}{2} (n_0/V) \cdot \sum_{\mathbf{q}} [|a_1(\mathbf{q})|^2 + \sum_{n,l} a_{\mu_1 \dots \mu_l}^{(n)}(\mathbf{q}) a_{\mu_1 \dots \mu_l}^{(n)}(-\mathbf{q})]. \quad (\text{I.11})$$

³⁷ A. TIP, private communication.

³⁸ S. HESS, to be published.

³⁹ A. EINSTEIN, Ann. Phys. Leipzig **19**, 371 [1905].

⁴⁰ R. GANS, Z. Phys. **17**, 353 [1923].

⁴¹ L. WALDMANN, Z. Naturforsch. **15a**, 19 [1960].

⁴² S. HESS, Z. Naturforsch. **23a**, 1095 [1968].

Notice that, due to the orthogonality of the expansion tensors only quadratic but no bilinear terms occur in Eqs. (I.10, 11). This implies that the fluctuations of all the expansion coefficients a_1 , $a_{\mu_1 \dots \mu_l}^{(n)}$ are uncorrelated.

Hence, using Eqs. (I.4, 5) and (I.11), we finally obtain

$$\overline{|a_1(\mathbf{q})|^2} = n_0^{-1} V, \quad (\text{I.12})$$

and

$$\overline{a_{\mu_1 \dots \mu_l}^{(n)}(\mathbf{q}) a_{\nu_1 \dots \nu_l}^{(n')}(-\mathbf{q})} = n_0^{-1} V \Delta_{\mu_1 \dots \mu_l, \nu_1 \dots \nu_l}^{(l)} \delta^{(nn')} \delta^{(ll')}. \quad (\text{I.13})$$

Eq. (7.14) follows from (I.12, 13). Furthermore, due to Eq. (I.13) one has $\frac{1}{5} \overline{a_{\lambda\kappa}(\mathbf{q}) a_{\lambda\kappa}(-\mathbf{q})} = n_0^{-1} V$ (cf. 8.18).

Appendix II. Cartesian Tensor Operators

Spherical components of a l^{th} rank tensor operator are defined by²¹

$$T_{lm}^{jj'} = \sum_{M, M'} (-1)^{j-M} \langle j' M', j-M | l m \rangle | j M \rangle \langle j' M' |, \quad (\text{II.1})$$

where $\langle j' M', j-M | l m \rangle$ is a Clebsch-Gordan coefficient and $| j M \rangle$ is a normalized rigid rotator wave function pertaining to the rotational and magnetic quantum numbers j and M . The spherical components of the tensor operators have the following properties²¹

$$(T_{lm}^{jj'})^\dagger = (-1)^{j-j'+m} T_{l-m}^{jj'}, \quad (\text{II.2})$$

$$\text{tr} \{ (T_{lm}^{jj'})^\dagger T_{l'm'}^{jj'} \} = \delta_{ll'} \delta_{mm'}. \quad (\text{II.3})$$

The operator $T_{lm}^{jj'}$ is nonzero only if $|j-j'| \leq j+j'$.

Cartesian tensor operators $T_{\mu_1 \dots \mu_l}^{jj'}$ of rank l can be defined by the relation

$$\begin{aligned} \sqrt{4\pi} \sum T_{lm}^{jj'} Y_{lm}(\mathbf{b}) \\ = \sqrt{(2l+1)!!/l!} T_{\mu_1 \dots \mu_l}^{jj'} \overline{b_{\mu_1} \dots b_{\mu_l}}, \end{aligned} \quad (\text{II.4})$$

where \mathbf{b} is an arbitrary unit vector, $Y_{lm}(\mathbf{b})$ is a spherical harmonic depending on the polar angles of \mathbf{b} with respect to the axis of quantization, and $\overline{b_{\mu_1} \dots b_{\mu_l}}$ is an irreducible tensor of rank l (constructed from the Cartesian components of \mathbf{b}) with the normalization determined by

$$\overline{b_{\mu_1} \dots b_{\mu_l} b_{\mu_1} \dots b_{\mu_l}} = l! / (2l+1)!! \quad (\text{II.5})$$

The Cartesian tensor operators defined by (II.4) have the properties

$$(T_{\mu_1 \dots \mu_l}^{jj'})^\dagger = (-1)^{j-j'} T_{\mu_1 \dots \mu_l}^{jj'}, \quad (\text{II.6})$$

and

$$\text{tr} \{ (T_{\mu_1 \dots \mu_l}^{jj'})^\dagger T_{\nu_1 \dots \nu_l}^{jj'} \} = \Delta_{\mu_1 \dots \mu_l, \nu_1 \dots \nu_l}^{(l)} \delta_{ll'}. \quad (\text{II.7})$$

With the definition (II.4), Eqs. (II.6, 7) are a consequence of Eqs. (II.2, 3) which can be seen by using

$$Y_{lm}^* = (-1)^m Y_{l-m} \quad \text{and} \quad \sum_m Y_{lm}^* Y_{lm} = (2l+1)/4\pi.$$

Cartesian tensor operators for $j=0$, $j'=1$ have been used previously by KÖHLER and FICK⁴⁴.

Let \mathbf{u} be a unit vector (operator) parallel to the axis of the rotator, i. e. $\mathbf{J} \cdot \mathbf{u} = 0$, where \mathbf{J} is the angular momentum operator. The scalar product of two l^{th} rank Cartesian tensors constructed from the components of \mathbf{u} and an arbitrary unit vector \mathbf{b} is proportional to the Legendre polynomial $L_l(\mathbf{u} \cdot \mathbf{b})$ [normalization: $L_l(0) = 1$]:

$$\overline{u_{\mu_1} \dots u_{\mu_l} b_{\mu_1} \dots b_{\mu_l}} = \frac{l!}{(2l-1)!!} L_l(\mathbf{u} \cdot \mathbf{b}). \quad (\text{II.8})$$

Now

$$L_l^{jj'}(\mathbf{u} \cdot \mathbf{b}) = \sum_{M, M'} | j M \rangle \langle j M | L_l(\mathbf{u} \cdot \mathbf{b}) | j' M' \rangle \langle j' M' | \quad (\text{II.9})$$

can be expressed in terms of spherical tensor operators by^{19, 21}

$$\begin{aligned} L_l^{jj'}(\mathbf{u} \cdot \mathbf{b}) = \sqrt{4\pi} (2l+1)^{-1} \sqrt{2j+1} \langle j 0, l 0 | j' 0 \rangle \\ \cdot \sum_m Y_{lm}(\mathbf{b}) T_{lm}^{jj'}. \end{aligned} \quad (\text{II.10})$$

Using the definition (II.4) of the Cartesian tensor operators and Eqs. (II.9, 10) one finds

$$\begin{aligned} \overline{(u_{\mu_1} \dots u_{\mu_l})^{jj'}} = \sqrt{\frac{l!}{(2l+1)!!}} \\ \cdot \sqrt{2j+1} \langle j 0, l 0 | j' 0 \rangle T_{\mu_1 \dots \mu_l}^{jj'}. \end{aligned} \quad (\text{II.11})$$

For $l=2$ one obtains (8.7) from (II.11).

Using

$$J_\lambda = \frac{1}{i} \varepsilon_{\lambda\varrho\tau} u_\varrho \frac{\partial}{\partial u_\tau},$$

one can show that⁴²

$$[J_\lambda, \overline{u_{\mu_1} \dots u_{\mu_l}}] = -i l \square_{\mu_1 \dots \mu_l, \lambda, \nu_1 \dots \nu_l}^{(l)} \overline{u_{\nu_1} \dots u_{\nu_l}}, \quad (\text{II.12})$$

⁴³ S. DEVONS and L. J. B. GOLDFARB, in *Handbuch der Physik* (ed. S. FLÜGGE), Vol. 42, 362, Springer, Berlin 1957.

⁴⁴ W. E. KÖHLER and D. FICK, *Z. Phys.* **215**, 408 [1968].

where $\square_{\dots\lambda\dots}^{(l)}$ is an isotropic tensor of rank $2l+1$ defined by⁴²

$$\square_{\mu_1\dots\mu_l,\lambda,\mu_1'\dots\mu_l'}^{(l)} = \Delta_{\mu_1\dots\mu_l,\nu_1\dots\nu_{l-1}\nu_l}^{(l)} \varepsilon_{\nu_1\lambda\nu_l} \Delta_{\nu_1'\nu_2'\dots\nu_{l-1}'\mu_1'\dots\mu_l'}^{(l)} \\ = \frac{l+1}{l} \frac{2l+3}{2l+1} \Delta_{\mu_1\dots\mu_l,\mu_1'\dots\mu_l'}^{(l+1)} \varepsilon_{\mu_1\mu_1'\lambda} \quad (\text{II.13})$$

The normalization of this tensor is given by:

$$\varepsilon_{\mu_1\lambda\mu_1'} \square_{\mu_1\dots\mu_l-1\mu_l,\lambda,\mu_1\dots\mu_l-1\mu_l'}^{(l)} = \frac{l+1}{l} (2l+1). \quad (\text{II.14})$$

Thus, due to (II.11 and II.12) one has the following commutation relations for the Cartesian operators:

$$[J_\lambda, T_{\mu_1\dots\mu_l}^{jj'}] = -il \square_{\mu_1\dots\mu_l,\lambda,\nu_1\dots\nu_l}^{(l)} T_{\nu_1\dots\nu_l}^{jj'}. \quad (\text{II.15})$$

For $j'=j$ the l^{th} rank tensor operator is proportional to the l^{th} rank irreducible tensor constructed from the Cartesian components of \mathbf{J} (cf. Ref. 19):

$$\sqrt{2j+1} T_{\mu_1\dots\mu_l}^{jj'} = \sqrt{(2l+1)!/l!} \\ \cdot P_j(J_0 J_1 \dots J_{l-1})^{-1} \overline{J_{\mu_1\dots\mu_l}}, \quad (\text{II.16})$$

where

$$P_j = \sum_M |jM\rangle \langle jM|, \quad P_j J^2 = j(j+1) P_j, \quad \text{and} \\ J_k^2 = J^2 - \frac{1}{2} k(\frac{1}{2} k + 1). \quad (\text{II.17})$$

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On the Pressure Dependence of the Transport Properties of Dilute Polyatomic Gases

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It is shown that the transport coefficients of dilute polyatomic gases in the ordinary Navier-Stokes regime contain an extra pressure dependence when the internal state Hamiltonian does not commute with the nonequilibrium distribution function-density matrix for the gas. As a specific example, the pressure dependence of the shear viscosity of a gas of paramagnetic $^2\Sigma$ molecules is considered. Furthermore, the pressure dependence of the Senftleben and Senftleben-Beenakker effects is discussed and examples are given of the different types of molecules for which pressure dependence in the field-free as well as in the field-dependent transport coefficients may be expected.

The transport properties of polyatomic gases can be calculated from the linearized Waldmann-Snider equation

$$(\mathbf{p}/m) \cdot \nabla \ln f^{(0)} = J_0 \varphi - (i/\hbar) [\mathcal{H}^{(\text{int})}, \varphi], \quad (1)$$

where $f^{(0)}$ is the local equilibrium distribution function-density matrix given by

$$f^{(0)} = n Q^{-1} (2\pi m k T)^{-3/2} \exp\{-W^2 - \mathcal{H}^{(\text{int})}/kT\}$$

with Q the internal state partition function and \mathbf{W} the reduced peculiar velocity $\mathbf{W} = (m/2kT)^{1/2} \mathbf{V}$. Furthermore, J_0 is the (dissipative) collision super-operator representing the effect of binary collisions

and defined by

$$J_0 \varphi \equiv (2\pi)^4 \hbar^2 \text{tr}_1 \int d\mathbf{p}_1 f_1^{(0)} \\ \cdot \{ \int t_{g'}^g(\varphi' + \varphi_1') \delta(E) t_{g'}^{g'} d\mathbf{p}' \\ - (i/2\pi) [t_g^g(\varphi + \varphi_1) - (\varphi + \varphi_1) t_g^{g'}] \},$$

where the quantities t_g^g and $t_g^{g'}$ represent the (binary collision) transition operator and its adjoint (these are matrix elements in linear momentum space but still operators in the internal state space), a prime denotes a functional dependence on \mathbf{p}' and \mathbf{p}_1' , the

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