

NIELINIOWA OPTYKA MOLEKULARNA

chapter 5

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1 V. OPTICAL REFRACTION AND MOLECULAR SCATTERING OF LIGHT

1. DISPERSION OF MOLECULAR REFRACTION

Consider a system of molar volume V_m isotropic in the absence of external fields. Many of its optical properties are described by the molecular refraction R_m (known also as the Lorentz–Lorenz function)

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m \quad (1)$$

According to Maxwell's equations (Chapter IV Eq.(54)) both electric permittivity $\epsilon(\omega)$ and magnetic permittivity $\mu(\omega)$ contribute

to the refraction index at a selected frequency ω . However, in dielectric optically inactive systems in the first approximation it is sufficient to consider only the contribution to $n(\omega)$ due to the electric vector $\mathbf{E}(\mathbf{r}, t)$ of the light wave thus neglecting the contributions due to $\mathbf{H}(\mathbf{r}, t)$. We assume that our molar volume is immersed in a vacuum ($\epsilon_0 = 1$) where the electric field of the light wave considered reads $\mathbf{E}_0(\mathbf{r}, t)$. Then, according to Eq.(91) of section IV, for a selected frequency we have

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \mathbf{E}_0(\mathbf{r}, t) = \frac{4\pi}{3} \mathbf{P}(\mathbf{r}, t) \quad (2)$$

By Eqs (1) and (2) and taking into account definition (93) of Chapter IV we write:

$$R_m \mathbf{E}_0(\mathbf{r}, t) = \frac{4\pi}{3} V_m \mathbf{P}(\mathbf{r}, t) = \frac{4\pi}{3} \left\langle \sum_{p=1}^{N_A} \mathbf{d}^{(p)}(\mathbf{r}, t) \right\rangle_{\mathbf{E}_0} \quad (3)$$

Assuming that V_m consists of N_A identical noninteracting atoms or molecules we obtain

$$R_m \mathbf{E}_0(\mathbf{r}, t) = \frac{4\pi}{3} N_A \langle \mathbf{d}(\mathbf{r}, t) \rangle_{\mathbf{E}_0} \quad (4)$$

For a system with no Yvon-Kirkwood intrinsic molecular field, in the first approximation, for the induced dipole moment we have

$$\mathbf{d}(\mathbf{r}, t) = a(\omega) \mathbf{E}_0(\mathbf{r}, t) \quad (5)$$

where

$$a(\omega) = \frac{1}{3} (a_{11}^{\omega} + a_{22}^{\omega} + a_{33}^{\omega}) \quad (6)$$

stands for the mean molecular polarizability at frequency ω .

Inserting the induced moment (5) into (4) we arrive at the well known Lorentz-Lorenz equation (1880)

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m = \frac{4\pi}{3} N_A a(\omega) \quad (7)$$

telling us that molecular refraction is a constant independent of the molecule structure and thermodynamic state. Relation (7) is exact only in the first approximation. In general R_m depends on temperature T , density ρ as well as the pressure of the real gas.

1.1 The Lorentz electron theory

Maxwell's phenomenological relation is valid when we take $\epsilon(\omega)$ and $\mu(\omega)$ for the same frequency in the form of the refractive index

$$n(\omega)^2 = \epsilon(\omega) \mu(\omega) \quad (8)$$

For gases and simple fluids, relation (8) is valid in a broad range of frequencies. For polar systems, however, $\epsilon(\omega)$ strongly depends on

the frequency of the electromagnetic wave. Then, in the case of dispersion and/or absorption relation (8) is not valid. The macroscopic phenomenological Maxwell's theory was not able to explain the phenomena of absorption and dispersion. They were explained by the electron theory of Lorentz (1909) and the dipole-relaxation theory of Debye (1929) (Eq.(30) of Chapter IV).

The main idea of the Lorentz theory is based on a calculation of the mutual force between the elementary atomic or molecular oscillator (formed by an electron tied to a nuclei by quasi-elastic force) and the rapidly oscillating electric field $\mathbf{E}(\mathbf{r}, t)$. Due to this interaction harmonic oscillators are excited to stimulated oscillations at the frequency ω . For each electron of mass m tied in an atom or a molecule we write the equation of motion

$$m \frac{d^2 \mathbf{r}}{dt^2} = \mathbf{f}_1 + \mathbf{f}_2 + \mathbf{f}_3 \quad (9)$$

The quasi-elastic force \mathbf{f}_1 is proportional to \mathbf{r} and directed to the point of equilibrium

$$\mathbf{f}_1 = -m \omega_0^2 \mathbf{r} \quad (10)$$

where ω_0 stands for the electron-free oscillation frequency.

The force of the second kind, i.e. that of the electromagnetic field

$$\mathbf{f}_2 = e \mathbf{E}(\mathbf{r}, t) \quad (11)$$

leads to a stimulated electron vibration.

The force of the third kind, the damping force \mathbf{f}_3 in the first approximation reads

$$\mathbf{f}_3 = -m\gamma \frac{d\mathbf{r}}{dt} \quad (12)$$

where γ is a damping constant.

Then the equation of motion

$$m \left(\frac{d^2 \mathbf{r}}{dt^2} + \gamma \frac{d \mathbf{r}}{dt} + \omega_0^2 \mathbf{r} \right) = e \mathbf{E}(r) e^{-i\omega t} \quad (13)$$

gives the following solution

$$\mathbf{r}(t) = \frac{e \mathbf{E}(r) e^{-i\omega t}}{m (\omega_0^2 - \omega^2 - i\gamma\omega)} \quad (14)$$

When we write the induced dipole moment in the form

$$\mathbf{d}(t) = e \mathbf{r}(t) \quad (15)$$

then from (5) and (14) for the scalar electron polarizability we have

$$a(\omega) = \frac{e^2}{m(\omega_0^2 - \omega^2 - i\gamma\omega)} \quad (16)$$

This relation gives the frequency dependence of the polarizability, which can be written as:

$$a(\omega) = \frac{a(0)}{1 - \left(\frac{\omega}{\omega_0}\right)^2 - i\gamma\frac{\omega}{\omega_0^2}} \quad (17)$$

where

$$a(0) = \frac{e^2}{m\omega_0^2} \quad (18)$$

stands for the zero frequency polarizability or static polarizability (the polarizability due to a static electric field).

In general however, the electron polarizability is complex and can be written as

$$a(\omega) = a'(\omega) + i a''(\omega) \quad (19)$$

where

$$a'(\omega) = \frac{e^2 (\omega_0^2 - \omega^2)}{m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]} \quad (20)$$

gives its real part connected with the electron dispersion and

$$a''(\omega) = \frac{e^2 \gamma \omega}{m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]} \quad (21)$$

gives its imaginary part due to the electron absorption.

1.2 Positive electron dispersion

Our calculations can easily be extended to the case of a multi-electron atom or molecule. Let's assume that the s th electron has

charge e_s , mass m_s damping constant γ_s . Then for the electron polarizability we have

$$a(\omega) = \sum_s \frac{e_s^2}{m_s (\omega_s^2 - \omega^2 - i \gamma_s \omega)} \quad (22)$$

The atom or molecule has several resonance frequencies ω_s connected to the respective s-th oscillator strengths

$$f_s = \left(\frac{e_s}{e} \right)^2 \frac{m}{m_s} \quad (23)$$

and the sum of all f_s equals the total number of electrons of the system (atom, molecule).

$$\sum_s f_s = Z \quad (24)$$

This rule of additivity of the oscillator strengths is obvious since each electron brings an independent contribution. The oscillator strengths (23) describe intensities of absorption or radiation lines (bands) of a system. Inserting Eq.(23) to (22) we obtain the electron polarizability in the form

$$\tilde{a}(\omega) = \frac{e^2}{m} \sum_s \frac{f_s}{\omega_s^2 - \omega^2 - i \gamma_s \omega} \quad (25)$$

For a gaseous system $n \approx 1$, then according to (7), the complex refraction index can be written as:

$$\tilde{n}(\omega) = n'(\omega) + i n''(\omega) = 1 + 2\pi\rho\tilde{a}(\omega) \quad (26)$$

where the real and imaginary parts are given respectively by

$$n'(\omega) = 1 + 2\pi\rho \frac{e^2}{m} \sum_s \frac{f_s (\omega_s^2 - \omega^2)}{(\omega_s^2 - \omega^2)^2 + \gamma_s^2 \omega^2} \quad (27)$$

$$n''(\omega) = 2\pi\rho \frac{e^2}{m} \sum_s \frac{f_s \gamma_s \omega}{(\omega_s^2 - \omega^2)^2 + \gamma_s^2 \omega^2} \quad (28)$$

Since $f_s > 0$, then the above equations describe the positive

dispersion. When $\frac{dn(\omega)}{d\omega} > 0$ (the positive slope of the dispersion curve) we have the normal dispersion, however, when $\frac{dn(\omega)}{d\omega} < 0$ (the negative step of the dispersion curve) then we have the anomalous dispersion.

Far from the absorption region ($\omega > \omega_s$) we neglect the term $\gamma_s^2 \omega^2$ in comparison with $(\omega_s^2 - \omega^2)$ and then it suffices to consider the real part of the refractive index (27) only

$$n'(\omega) = 1 + 2\pi\rho \frac{e^2}{m} \sum_s \frac{f_s}{\omega_s^2 - \omega^2} \quad (29)$$

Table V.1 presents values of $n(\lambda)$ for several liquids.

TABLE V.1

When the frequency of light ω is very close to the intrinsic

frequencies of the oscillators ω_s ($\omega_s \approx \omega$) then the resonance component $(\omega_s^2 - \omega^2)^2$ is small in comparison to $\gamma_s^2 \omega^2$ and the refractive index is composed of the imaginary part only given by the absorption coefficient

$$n''(\omega) = 2\pi\rho \frac{e^2}{m} \sum_s \frac{f_s}{\gamma_s \omega} \quad (30)$$

When we measure the refractive index in the transparent region of a system (very far from the absorption band) then for the molecular refraction we obtain

$$R_m = \frac{n^2 - 1}{n^2 + 2} V_m = \frac{4\pi}{3} N_A \frac{e^2}{m} \sum_s \frac{f_s}{\omega_s^2 - \omega^2} \quad (31)$$

However, when in our experiment the absorption process dominates then, Eqs (28) or (30) considering the absorption bands appearance should be used.

1.3 Quantum theory of electron polarizability

In the classical theory of electron polarizability we consider an atom or a molecule as a set of harmonic oscillators composed of optical electrons of the charge e_s and intrinsic frequencies ω_s assuming, however, that oscillator strengths are given by experiment. Nevertheless, the experiment gives a surprising result that the oscillator strength are given by non-integer numbers and frequently are lower than unity ($f_s < 1$). The classical equation (22) is valid in the quantum approach as well, however, its physical

interpretation is now different. In particular the quantum theory permits us to calculate the oscillator strength f_s in full agreement with the experiment and moreover it predicts the negative dispersion impossible in the classical theory.

Here we shall give a brief presentation of the semiclassical theory of dispersion (after the work of Kramers and Heisenberg, 1925).

Consider the quantum system (an atom or a molecule) under the influence of an electromagnetic wave with λ considerably greater than the system's linear dimensions. In the perturbation Hamiltonian we restrict to the electric dipole interaction

$$W(t) = -\mathbf{d} \cdot \mathbf{E}(\mathbf{r}, t) = -\frac{1}{2} \mathbf{d} \cdot \mathbf{E}^+(\mathbf{r}) e^{i\omega t} - \frac{1}{2} \mathbf{d} \cdot \mathbf{E}^-(\mathbf{r}) e^{-i\omega t} \quad (32)$$

Let our quantum system be in one of its quantum states E_m^0 in the

absence of an electromagnetic wave. We denote the relevant wave function by $\psi_{0m}(\mathbf{r}, t)$. In the presence of the optical field $\mathbf{E}(\mathbf{r}, t)$ the quantum system is in an excited state described by the wave function obeying the Schroedinger equation. When the intensity of the light wave is not too high, then in the expansion (101) of Chapter IV we can restrict to the linear approximation and the perturbed wave function is of the form

$$\psi_m(\mathbf{r}, t) = \sum_k \left\{ \delta_{km} + c_{km}^{(1)}(t) + \dots \right\} \psi_k(\mathbf{r}, 0) \exp(-i \omega_k t) \quad (33)$$

where the transition coefficients $c_{km}^{(1)}(t)$ for a harmonic perturbation are given by Eq.(105) of Chapter IV.

Knowing the wave function (33) we calculate the m - th state mean quantum-mechanical value of the dipole moment operator due to

an electro-magnetic perturbation of the form of equation (103) given in Chapter IV:

$$\mathbf{d}(t) = \int \psi_m^*(\mathbf{r}, t) \mathbf{d} \psi_m(\mathbf{r}, t) d\tau = \mathbf{d}^{(0)} + \mathbf{d}^{(1)}(t) + \dots \quad (34)$$

where

$$\mathbf{d}^{(0)} = \langle m | \mathbf{d} | m \rangle \quad (35)$$

stands for the time independent dipole moment in the absence of perturbation. The diagonal elements of this moment

$\mathbf{d}_{mm}^{(0)} = \langle m | \mathbf{d} | m \rangle$ vanish for all states of well defined parity.

In the first approximation, the perturbed dipole moment of the

$m - th$ state is given by

$$\mathbf{d}(t) = \sum_k \left\{ \langle m | \mathbf{d} | k \rangle c_{km}^{(1)}(t) \exp(i \omega_{mk} t) + \langle k | \mathbf{d} | m \rangle c_{km}^{(1)}(t)^* \right\} \quad (36)$$

or by Eq.(105a) of Chapter IV in the form

$$\mathbf{d}^{(1)}(t) = \frac{1}{2} \left\{ \mathbf{d}^{(1)}(\omega) \exp(i \omega t) + \mathbf{d}^{(1)}(-\omega) \exp(-i \omega t) \right\} \quad (37)$$

Then in the first approximation the induced dipole moment consists of the two parts oscillating at a frequency ω and the respective amplitudes are of the form

$$\mathbf{d}^{(1)}(\pm \omega) = -\frac{1}{\hbar} \sum_k \left\{ \langle m | \mathbf{d} | k \rangle \frac{\langle k | W^\pm | m \rangle}{\omega_{km} \pm \omega} + \frac{\langle m | W^\mp | k \rangle}{\omega_{km} \mp \omega} \right\} \quad (38)$$

Comparing the perturbation (104) of Chapter IV and Eq.(32) we

obtain the amplitude of the perturbation as

$$W^{\pm} = -\mathbf{d} \cdot \mathbf{E}^{\pm}(\mathbf{r}) \quad (39)$$

then we transform Eq.(38) to

$$\mathbf{d}^{(1)}(\pm\omega) = \mathbf{a}(\pm\omega) \cdot \mathbf{E}^{\pm}(\mathbf{r}) \quad (40)$$

where we define the polarizability tensor of the molecule

$$\mathbf{a}(\pm\omega) = \frac{1}{\hbar} \sum_k \left\{ \langle m|\mathbf{d}|k\rangle \frac{\langle k|\mathbf{d}|m\rangle}{\omega_{km} \pm \omega} + \frac{\langle m|\mathbf{d}|k\rangle}{\omega_{km} \mp \omega} \langle k|\mathbf{d}|m\rangle \right. \quad (41)$$

Since

$$\frac{1}{\omega_{km} \pm \omega} + \frac{1}{\omega_{km} \mp \omega} = \frac{2\omega_{km}}{\omega_{km}^2 - \omega^2} \quad (42)$$

then $\mathbf{a}(+\omega) = \mathbf{a}(-\omega)$ and Eq.(41) transforms to

$$\mathbf{a}(\omega) = \frac{2}{\hbar} \sum_k \langle m | \mathbf{d} | k \rangle \langle k | \mathbf{d} | m \rangle \frac{\omega_{km}}{\omega_{km}^2 - \omega^2} \quad (43)$$

This quantum-mechanical form of the isotropic molecular polarizability reads analogously to its classical counterpart (22), if we define the matrix elements of the isotropic oscillator strength as

$$f_{gh} = \frac{2m\omega_{kg}}{3\hbar e^2} |\langle g | \mathbf{d} | k \rangle|^2 \quad (44)$$

In this way, in the absence of absorption, we have two expressions for the molecular polarizability

1. one resulting from the classical theory of electrons

$$\mathbf{a}(\omega)_{CL} = \frac{e^2}{m} \sum_s \frac{f_s}{\omega_s^2 - \omega^2} \quad (45)$$

2. the second one implied by the quantum–mechanics

$$\mathbf{a}(\omega)_{QM} = \frac{e^2}{m} \sum_k \frac{f_{gk}}{\omega_{kg}^2 - \omega^2} \quad (46)$$

We conclude that the oscillator strengths in the quantum theory have quite a different meaning than their correspondents in the classical approach. In the quantum theory f_{gk} are computed numerically by Eq.(44) provided that we have the wave functions of an atom or a molecule. According to experiments, the f_{gk} are fractional numbers with their sum equal unity

$$\sum_k f_{gk} = 1 \quad (47)$$

1.4 Positive and negative dispersion

The briefly reviewed quantum–mechanical theory of the molecular

polarizability, enables for a gas of the density ρ with the use of Eq.(46) to write the following dispersion formula of the refractive index

$$n(\omega) = 1 + 2\pi\rho \frac{e^2}{m} \sum_k \frac{f_{gk}}{\omega_{kg}^2 - \omega^2} \quad (48)$$

We show first that for the quantum harmonic oscillator model, Eq.(48) transforms into the classical equation (29). In this case the Schrödinger equation reads

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x) \psi \quad (49)$$

where, in the quadratic approximation the potential energy of a perturbed oscillator is

$$U(x) = \frac{1}{2} m \omega_0^2 x^2 - e x E(r) \quad (50)$$

and its eigenvalue reads

$$E_k = \left(k + \frac{1}{2}\right) \hbar \omega \quad k = 0, 1, 2 \dots \quad (51)$$

For the ground state energy $g = 0$ we have

$$E_0 = \frac{1}{2} \hbar \omega \quad (52)$$

According to the harmonic oscillator selection rule $\Delta k = \pm 1$ for the respective matrix elements we obtain

$$\langle g|x|g-1 \rangle = x_0 \left(\frac{g}{2}\right)^{\frac{1}{2}} \quad \langle g|x|g+1 \rangle = x_0 \left(\frac{g+1}{2}\right)^{\frac{1}{2}}$$

where

$$x_0 = \left(\frac{\hbar}{m \omega_0}\right)^{\frac{1}{2}} \quad (53)$$

Taking into account these results and Eq.(53–54) we have

$$\omega_{g+1,g} = \omega_0, \quad \omega_{g-1,g} = -\omega_0 \quad f_{g,g+1} = g+1, \quad f_{g-1,g} = -g \quad (54)$$

Calculating f_{gk} we assume that for an isotropic harmonic oscillator we have

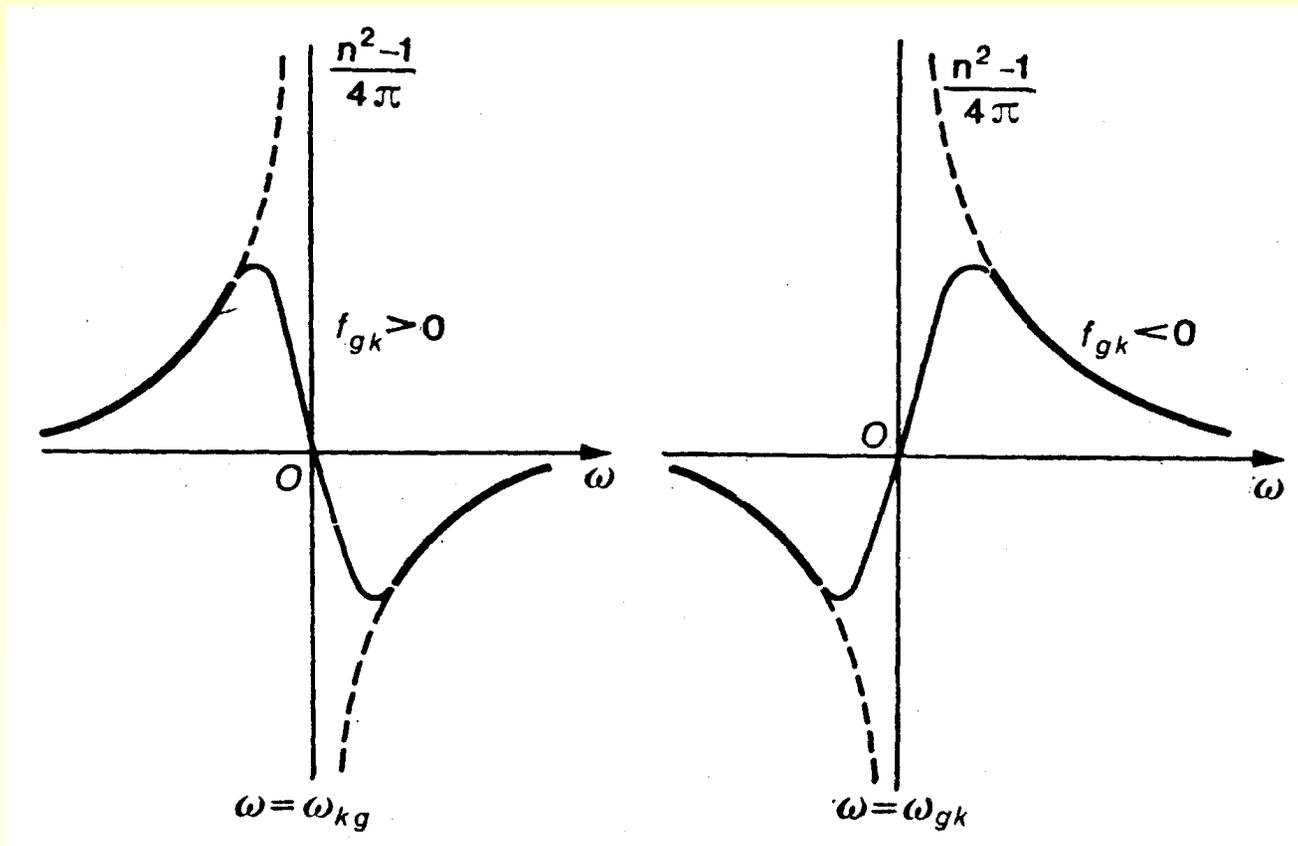
$$|\langle g|\mathbf{d}|k\rangle|^2 = 3e^2 |\langle g|x|k\rangle|^2 \quad (55)$$

When inserting these results to Eq.(48) we obtain the classical equation (29). The results show that the process of light interaction with matter (dispersion, absorption) can be described in classical terms by the model of isotropic harmonic oscillator. We have to remember, however, that in the classical theory we have frequencies of electron free oscillations ω_s whereas in the quantum theory $\omega_{kg} = (E_k - E_g)/\hbar$ have the meaning of energy transitions in the process of absorption or emission. The quantum

theory allows us to calculate oscillator strengths (44) by using wave functions of a system and relate f_{gk} with properties of atoms or molecules. Such calculations are, however, only feasible for simple quantum systems of spherical symmetry (atoms) and are highly complicated for multi-electron asymmetric ones (e.g. molecules). For complicated molecular systems the wave-functions are calculated by approximated methods. Therefore, we often use the classical theory which allows us to analyze the experimental data by the empirical oscillator strengths f_s .

When atoms or molecules are in their ground state ($m=g$), then $f_{gk} > 0$ and according to Eq.(48) the refraction index increases with increasing frequency. This is the case of the positive dispersion discussed recently. The oscillator strength f_{gk} can be negative as well; if $\omega_{kg} < 0$ then $E_k < E_g$. This situation arises for

systems with inverted population, i.e. (when the number of atoms in an excited state is higher than in the ground state). This is the case of the negative dispersion having its explanation in the quantum theory and being totally unexpected by the classical theory. Then according to Eq.(48) the refractive index decreases with increasing frequency (Fig. V.1). The first accurate investigation of the positive dispersion in sodium vapor are due to Lorie (1909) and Rozdiestwienski (1912). The quantum dispersion equations (41)-(48) are valid only in the range of wavelengths λ far from the absorption bands. In the range of absorption lines or bands in which anomalous dispersion appears, the lifetimes of excited levels of the quantum system should be taken into account. In this case instead of the polarizability tensor (20) we obtain



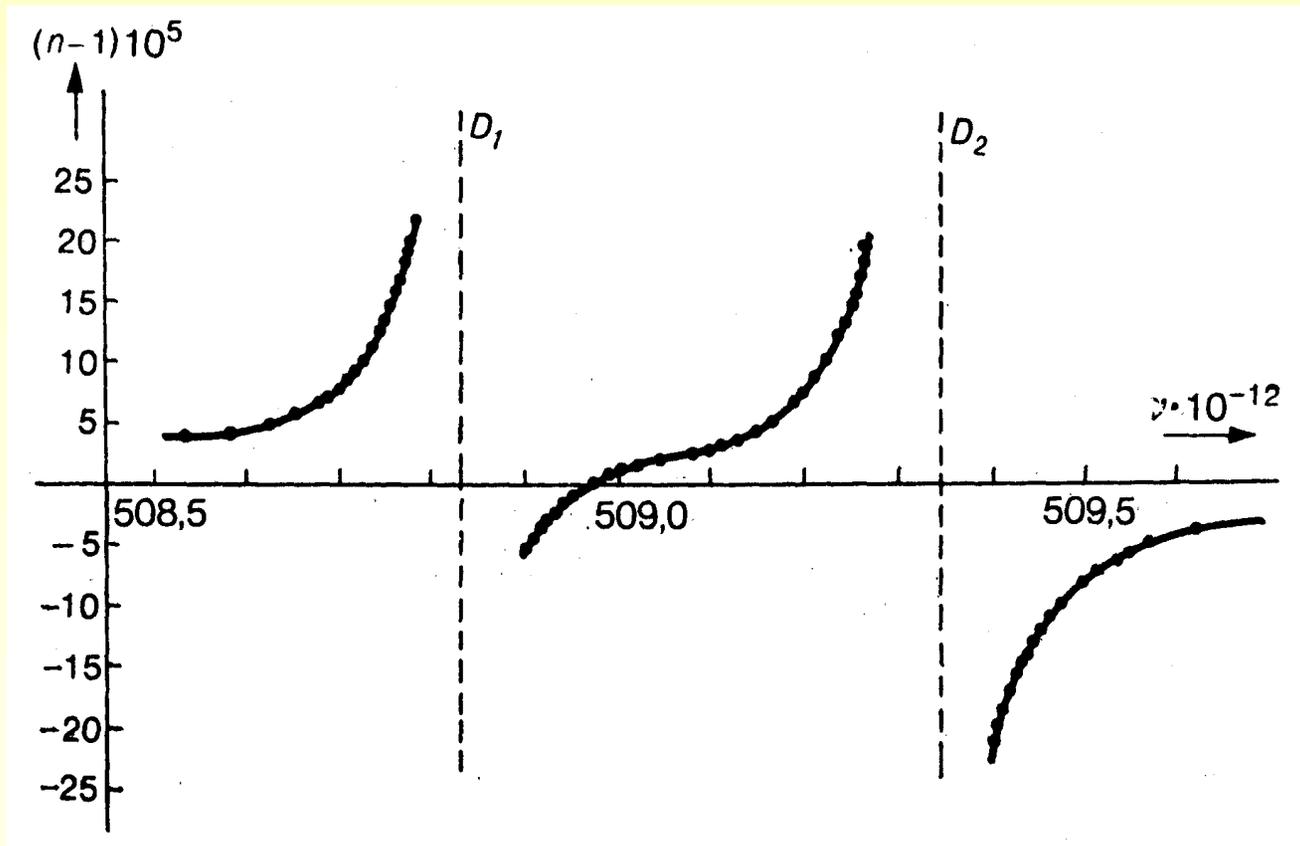
Rysunek 1: The frequency dependence of the refractive index (a) the positive dispersion $f_n > 0$ (b) the negative dispersion $f_n < 0$.

$$\mathbf{a}(\pm \omega) = \frac{1}{\hbar} \sum_k \left\{ \frac{\langle m | \mathbf{d} | k \rangle \langle k | \mathbf{d} | m \rangle}{\omega_{km} \pm \omega \pm i\Gamma_{km}} + \frac{\langle m | \mathbf{d} | k \rangle \langle k | \mathbf{d} | m \rangle}{\omega_{km} \mp \omega \mp i\Gamma_{km}} \right\} \quad (56)$$

Taking the isotropic average of equation (41) for the refractive index we have

$$n(\omega) - 1 = \frac{2\pi}{3\hbar} \rho \sum_{km} \rho_m |\langle m | \mathbf{d} | k \rangle|^2 \left\{ \frac{\omega_{km} + \omega - i\Gamma_{km}}{(\omega_{km} + \omega)^2 + \Gamma_{km}^2} + \frac{\omega_{km} - \omega + i\Gamma_{km}}{(\omega_{km} - \omega)^2 + \Gamma_{km}^2} \right\} \quad (57)$$

where ρ_m stands for the density matrix.



Rysunek 2: The Rozdienstwienskij's dispersion curves for the refractive index in sodium vapors close to absorption lines (bands) D_1 and D_2 .

1.5 Phase shift and dipolar dispersion

The time of equilibration of a given process or phenomenon induced by time dependent external fields depends on the microscopic structure of matter. The frequency dispersion (or the time dispersion) is defined by the ratio of the frequency of a stimulation field ω to the free oscillation frequency of the matter ω_M (ω/ω_M). The fastest sets the electric polarization of the electron nature whose relaxation time is of order r_a/v_c , where v_c is the velocity of an electron in an atom of the linear dimensions r_a . The electric polarization is the first to reach an equilibrium value. The linear size of the hydrogen atom is of the order $r_a \approx 1 \text{ \AA} = 10^{-8} \text{ cm}$, whereas its electron's velocity $v_c \approx 10^8 \text{ cm/s}$, so the electron relaxation time amounts to $\tau_c \approx 10^{-16} \text{ s}$. In the optical range the frequency of light is so high ($\omega = 10^{15} \text{ Hz}$) that only the external electrons are stimulated. The electron relaxation time is proportional to the inversion of the attenuation constant $\tau_c = \gamma^{-1}$.

The orientation relaxation time of a molecule in the electric field is of the order of $10^{-10} - 10^{-12}$ s so the frequency dispersion appears for centimeter waves.

According to the classical theory, in an isotropic system the electric polarization induced by the electric field

$$\mathbf{P}(\mathbf{r}, t) = \rho a(\omega) \mathbf{E}(\mathbf{r}, t) \quad (58)$$

can be written as

$$\mathbf{P}(\mathbf{r}) \exp[-i(\omega t + \delta)] = \rho \sum_s \frac{e_s^2 m_s^{-1}}{(\omega_s^2 - \omega^2 - i\gamma_s \omega)} \mathbf{E}(\mathbf{r}) \exp(-i\omega t) \quad (59)$$

From this equation we can see that in the presence of the electron attenuation, the polarization vector \mathbf{P} is shifted in phase by δ in comparison with the electric field vector \mathbf{E} . The angle δ of the

phase shift is given by

$$\operatorname{tg}\delta = \frac{a'(\omega)}{a''(\omega)} \approx \frac{\gamma\omega}{\omega_0^2 - \omega^2} \quad (60)$$

In the absence of resonance, for light frequencies ω located below ω_0 ($\omega \ll \omega_0$) $\operatorname{tg}\delta \rightarrow +0$ and then $\delta = 0$ indicating that the polarization vector \mathbf{P} is in phase with the electric field vector \mathbf{E} (the vectors \mathbf{P} and \mathbf{E} are parallel). In the case of a resonance $\omega = \omega_0$, $\operatorname{tg}\delta \rightarrow \infty$, so the polarization vector is delayed in phase by $\delta = \pi/2$ relative to the electric field. For high frequencies $\omega \gg \omega_0$, the $\operatorname{tg}\delta$ goes to zero from the negative side and then the polarization is delayed in phase relative to the field by $\delta = \pi$, so the vectors \mathbf{P} and \mathbf{E} are antiparallel.

In dipolar dielectrics besides the electron and atomic polarization

the polarization due to the field induced reorientation of dipoles takes place. Obviously in time dependent external field the reorientation of molecules depends on the field frequency. In static fields and in slowly varying fields permanent dipoles of molecules reorient according to statistical theory of Langevin (1905) and Debye (1912) (see Kuro 1912 as well). With increasing frequency, the reorientation of dipoles vanishes at some moment since the inert dipoles are not able to follow changes of the electric field.

Debye (1929) was the first to formulate the theory of dipolar relaxation processes considering dilute solution of dipolar system in a viscous solvent. Generally, this problem has been considered in Chapter IV when we derive the Debye equation for the polarization

vector

$$\mathbf{P}_d(\omega) = \rho \frac{d^2}{3 k_B T} \frac{\mathbf{E}(r) \exp(-i\omega t)}{1 - i\omega\tau_D} \quad (61)$$

In a constant electric field, ($\omega = 0$) then we obtain the Langevin-Debye equation for dipolar polarization

$$\mathbf{P}_d(0) = \frac{\rho d^2}{3 k_B T} \mathbf{E}(r) \quad (62)$$

In the field of very high frequency when $\omega\tau_D \rightarrow \infty$ the dipolar polarization is not able to set up

$$\mathbf{P}_d(\infty) \rightarrow 0 \quad (63)$$

According to the Debye formula (Chap.IV, Eq.(19))

$$\tau_D = \frac{4\pi r_0^3 \eta}{k_B T} = \frac{3V \eta}{k_B T} \quad (64)$$

the dipolar relaxation time is proportional to the molecular volume $V=4\pi r_0^3/3$ and the macroscopic viscosity of the solution η as well as to the inverse of temperature $1/T$. The values of the relaxation times for the most important molecules and macromolecules are given in table V.2.

Similarly as for the electron polarization, also for the dipolar polarization we observe a phase shift between the polarization vector \mathbf{P}_d and the electric field \mathbf{E} , given by

$$\text{tg} \delta_d = \omega \tau_D \quad (65)$$

Coming back to Eq.(2) for the electric polarization we write

$$\mathbf{P}_m = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} V_m = \mathbf{P}_m^e + \mathbf{P}_m^a + \mathbf{P}_m^d \quad (66)$$

where

$$\mathbf{P}_m^e = \frac{4\pi}{3} N_A a_e(\omega) \quad (67)$$

stands for the electron polarization, which for the optical frequency equals to the molecular optical refraction R_m . The electron polarization $a_e(\omega)$ is given by the classical equation (22) or by the quantum formula, Eq.(41).

TABLE V.2

TABLE V.3

Generally, it is difficult to calculate the atomic (or ionic) polarization \mathbf{P}_m^a , moreover in many cases it amounts to no more than 10 percent of the electron polarization \mathbf{P}_m^e . The time of

setting of the atomic polarization is almost equal to the time of oscillations of the infrared radiation, $\tau_a \approx 10^{-13}$ s

In ionic crystals the ionic elastic polarization appears. The time of setting of this polarization is about $10^{-12} - 10^{-13}$ s. The molecular dipolar polarization is given by

$$\mathbf{P}_m^d = \frac{4\pi}{3} N_A a_d(\omega) \quad (68)$$

whereas according to Debye (1929) the dynamic dipolar polarization reads

$$a_d(\omega) = \frac{d^2}{3 k_B T} \frac{1}{1 - i\omega\tau_D} \quad (69)$$

The we observe that the individual polarization processes set up in completely different time scales so exhibit different inertia in the time dependent external field.

Table V.3 gives individual components of the molecular polarization for several liquids.

2. MOLECULAR REFRACTION OF DENSE SYSTEMS

Thorough experimental studies have shown that the Lorentz-Lorenz equation (7) applies only for gases and other fluids when there are no significant short-range interactions between atoms or molecules (dimension of the Lorentz sphere). For other systems the molecular refraction R_m varies with pressure, density and temperature.

Experiments show that in many systems with increasing pressure, R_m increases the faster the lower the temperature. After reaching its maximum, R_m decreases and the decrease is more rapid than the initial increase.

Deviations from the Lorentz-Lorenz equation are explained by changes in atom or molecular polarizabilities and fluctuations of molecular fields.

2.1 Local field models

Bötcher (1952) applied the local Onsager field for the molecular refraction calculations. He used

$$R_m = \frac{4\pi}{3} N_A g(n) a \quad (70)$$

where

$$g(n) = \frac{9n^2}{(n^2 + 2)[(2n^2 + 1) - 2(n^2 - 1)ar^{-3}]} \quad (71)$$

This equation explains the temperature as well as the density dependence of R_m through the refraction index $n(\rho, T)$. The

problems in applying the Butcher's model are based on the respective choice of the radius of Onsager cavity. Several authors investigated the influence of the Lorentz field anisotropy (Raman 1927) and the Onsager field anisotropy (Frenkel 1946) on the molecular refraction. The Lorentz field for the ellipsoidal cavity

$$F_{ei} = \{1 + (n^2 - 1) L_i\} E_i \quad (72)$$

can be written as

$$F_{ei} = \frac{n^2 + 2}{3} E_i + F_i^{aniso} \quad (73)$$

Now, besides the isotropic part of the local field, a new contribution appears

$$F_i^{aniso} = (n^2 - 1) \left(L_i - \frac{1}{3} \right) E_i \quad (74)$$

giving the local Lorentz field anisotropy, and therefore the Lorentz field deviation from its spherical cavity form. Obviously for the spherical cavity the shape parameter reads $L_i = 1/3$ and the anisotropy vanishes. Assuming that the molecule has the same polarizability along the three main axes $a_{11}, a_{22}, a_{33} = a$ we write for the induced dipole moment components ($i=1,2,3$)

$$d_i(\mathbf{E}) = a_i F_{ei} = a_i^* E_i \quad (75)$$

where

$$a_i^* = \{1 + (n^2 - 1)L_i\} a_i \quad (76)$$

are components of the effective polarizability through the polarizability of a free molecule a_i . In particular for the spherical

cavity the effective polarizability, Eq.(76) reduces to

$$a_i^* = \frac{n^2 + 2}{3} a_i \quad (77)$$

Bringing in the effective polarizability in the molecular refraction equation we obtain

$$R_m = \frac{4\pi}{3} N_A \left(\frac{a_1^* + a_2^* + a_3^*}{n^2 + 2} \right) \quad (78)$$

When we apply the Onsager-Scholte model already discussed in Chap.IV to the optical case then for the effective polarizability we have (Kielich, Pieczynska 1970)

$$a_i^* = \frac{n^2 a_i}{[n^2 + (1 - n^2)L_i](1 - f_i a_i)} \quad (79)$$

where the parameter of the reaction field is of the form

$$f_i = \frac{3(n^2 - 1)(1 - L_i)L_i}{[n^2 + (1 - n^2)L_i]r_1r_2r_3} \quad (80)$$

TABLE V.4

In the case of the spherical Onsager cavity, the effective polarizability reduces to

$$a_i^* = \frac{3n^2r^3a_i}{(2n^2 + 1)r^3 - 2(n^2 - 1)a_i} \quad (81)$$

When we insert this polarizability into Eq.(78) for the molecular refraction and we neglect the molecular polarizability anisotropy setting $a_1 = a_2 = a_3 = a$ we obtain the Bötcher equation (70).

When we use

$$a_i^* = \frac{(n^2 - 1)r_1r_2r_3}{3[1 + (n^2 - 1)L_i]} \quad (82)$$

the effective polarizabilities of Eq.(82) transform into the polarizabilities (76) of the Lorentz model. In Table V.4 we give the values of the optical polarizabilities, semi-axis as well as the cavity shape parameters. Table V.5 gives the calculated (eq.78) and experimental molecular refraction data.

2.2 Statistical translational fluctuations.

Kirkwood (1936) and Yvon (1936) developed the fundamentals of the statistical molecular theory of refraction of atomic fluids. They have shown that in fluids and atomic liquids the induced dipole moment varies in subsequent phases of their thermal motion and consequently the fluctuations of induced dipole moments contribute to the Lorentz field. Let us recall that we obtain the

Lorentz field in its isotropic form

$$\mathbf{F} = \frac{n^2 + 2}{3} \mathbf{E} \quad (83)$$

assuming that contributions resulting from the molecules of the infinitesimal dielectric cavity vanish.

If in a system molecular fields are present than, instead of Eq.(3), the moment induced in an atom or isotropically polarized molecule is

$$\mathbf{d}^{(p)}(\mathbf{r}, t) = a \{ \mathbf{E}_0(\mathbf{r}, t) \mathbf{F}_p(\mathbf{r}, t) \} \quad (84)$$

where the molecular field is given by the Kirkwood–Yvon expansion (see (87a) of Chapter IV)

$$\mathbf{F}_p(\mathbf{r}, t) = -a \sum_{q=1}^N \mathbf{T}_{pq} \cdot \mathbf{E}_0 + a^2 \sum_{q=1}^N \sum_{r=1}^N \mathbf{T}_{pq} \cdot \mathbf{T}_{qr} \cdot \mathbf{E}_0 - \dots (85)$$

By Eqs (84) and (85) for the dipole moment induced in the molecule p immersed in a system with fluctuations of molecular fields we obtain

$$\begin{aligned}
\mathbf{d}^{(p)}(\mathbf{r}, t) &= a \mathbf{E}_0 - a^2 \sum_{q=1}^N \mathbf{T}_{pq} \cdot \mathbf{E}_0 \\
&+ a^2 \sum_{q=1}^N \sum_{r=1}^N \mathbf{T}_{pq} \cdot \mathbf{T}_{qr} \cdot \mathbf{E}_0 - \dots \quad (86)
\end{aligned}$$

The first term defines the dipole moment induced in a p -th molecule by the external field \mathbf{E}_0 only. The second term results from dipole moments induced by \mathbf{E}_0 in the molecules surrounding??? the molecule p . The next terms describe contributions to the induced moments due to subsequent molecular spheres.

Inserting the moment expressed in the form (86) into equation (7) for the molecular refraction we have

where \mathbf{e} stands for the unit vector in the direction of \mathbf{E}_0 .

In the case of gases and liquids we can perform the isotropic averaging resulting in

$$\begin{aligned}\langle \mathbf{e} \cdot \mathbf{T}_{pq} \cdot \mathbf{e} \rangle &= 0 \\ \langle \mathbf{e} \cdot \mathbf{T}_{pq} \cdot \mathbf{T}_{qr} \mathbf{e} \rangle &= \frac{1}{3} \mathbf{T}_{pq} : \mathbf{T}_{qr}\end{aligned}\quad (87)$$

enabling us to write the molecular refraction in the form

$$R_m - R_m^{(1)} = \Delta R_m \quad (88)$$

where

$$R_m^{(1)} = \frac{4\pi}{3} N_A a \quad (89)$$

is the molecular refraction of the ideal gas (without any molecular

correlations), whereas

$$\Delta R_m = \frac{4\pi}{9} a^3 \left\langle \sum_{p=1}^{N_A} \sum_{q=1}^{N_A} \sum_{r=1}^{N_A} \mathbf{T}_{pq} : \mathbf{T}_{qr} \right\rangle + \dots \quad (90)$$

defines a change of the molecular refraction due to molecular fields. Let us now discuss the contribution (90) in detail. In particular when $p = q = r$, ΔR_m vanishes since the tensor of molecular interactions $\mathbf{T}_{pq} = 0$ for $p = q$. Then, in the absence of molecular interactions, ΔR_m vanishes.

In the binary approximation the contribution, Eq.(90) is nonzero

only when $p=r$ so

$$R_m^{(2)} = \frac{4\pi}{9} a^3 \left\langle \sum_{p=1}^{N_A} \sum_{q=1}^{N_A} \mathbf{T}_{pq} : \mathbf{T}_{pq} \right\rangle = \frac{4\pi}{9} a^3 N_A (N_A - 1) \langle \mathbf{T}_{pq} : \mathbf{T}_{pq} \rangle$$

In the ternary approximation for $p \neq q \neq r$ we have

$$R_m^{(3)} = \frac{4\pi}{9} a^3 \left\langle \sum_{p=1}^{N_A} \sum_{q \neq p}^{N_A} \sum_{r \neq q \neq p}^{N_A} \mathbf{T}_{pq} : \mathbf{T}_{qr} \right\rangle = \frac{4\pi}{9} a^3 N_A (N_A - 1)(N_A - 2) \langle \mathbf{T}_{pq} : \mathbf{T}_{qr} \rangle \quad (92)$$

Taking into account the definition of the interaction tensor between dipoles p and q

$$\mathbf{T}_{pq} = -r_{pq}^{-5} (3 \mathbf{r}_{pq} \mathbf{r}_{pq} - r_{pq}^2 \mathbf{U}), \quad p \neq q \quad (93)$$

generally we obtain

$$\mathbf{T}_{pq} : \mathbf{T}_{qr} = 3r_{pq}^{-5} r_{qr}^{-5} \left\{ 3 \left(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr} \right)^2 - r_{pq}^2 r_{qr}^2 \right\} \quad (94)$$

or in particular for $p = r$

$$\mathbf{T}_{pq} : \mathbf{T}_{pq} = 6 r_{pq}^{-6} \quad (95)$$

Taking into account Eqs (94) and (95) and using the definitions of the molecular correlation functions already discussed in Chapter II

$$\begin{aligned} \rho^2 g^{(2)}(\mathbf{r}_p, \mathbf{r}_q) &= N(N-1) P^{(2)}(\mathbf{r}_p, \mathbf{r}_q) \\ \rho^3 g^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) &= N(N-1)(N-2) P^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) \end{aligned} \quad (96)$$

finally we obtain (Kielich 1962)

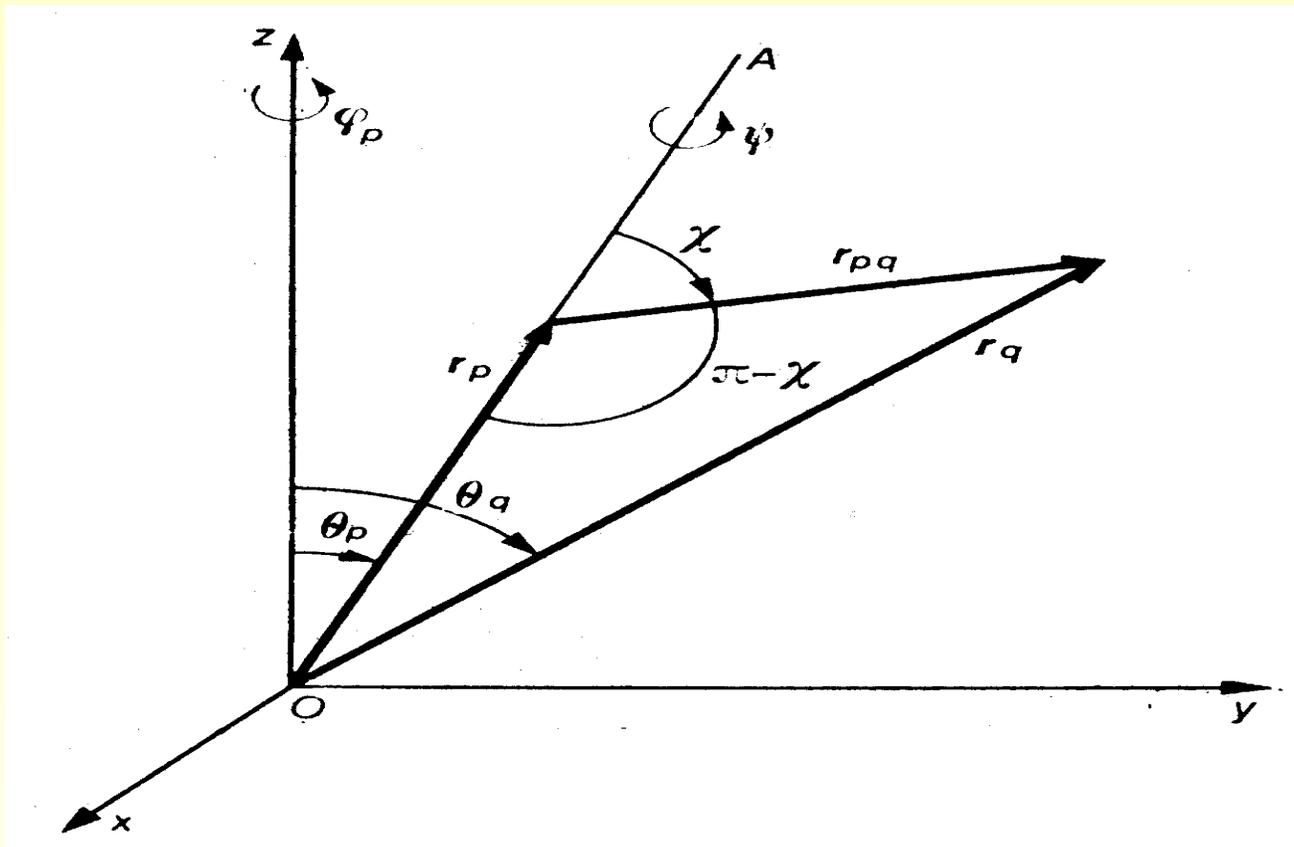
$$\Delta R_m^{(2)} = 2a^2 R_m^{(1)} \langle r_{pq}^{-6} \rangle + \dots \quad (97)$$

$$\Delta R_m^{(3)} = 2a^2 R_m^{(1)} \langle r_{pq}^{-3} r_{qr}^{-3} \rangle + \dots \quad (98)$$

Here we introduced the radial binary and ternary correlation parameters

$$\langle r_{pq}^{-6} \rangle = \frac{\rho}{V} \int \int r_{pq}^{-6} g^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (99)$$

$$\begin{aligned} \langle r_{pq}^{-3} r_{qr}^{-3} \rangle &= \frac{\rho^2}{2V} \int \int \int r_{pq}^{-5} r_{qr}^{-5} \left\{ 3 (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^2 - r_{pq}^2 r_{qr}^2 \right\} \\ &\quad g^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r \end{aligned} \quad (100)$$



Rysunek 3: The sketch to determine the infinitesimal volume $d\mathbf{r}_{pq}$.

where $g^{(2)}(\mathbf{r}_p, \mathbf{r}_q)$ is the double correlation function between the molecules p and q having their positions at \mathbf{r}_p and at \mathbf{r}_q . The $g^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)$ stands for the triple correlation function between

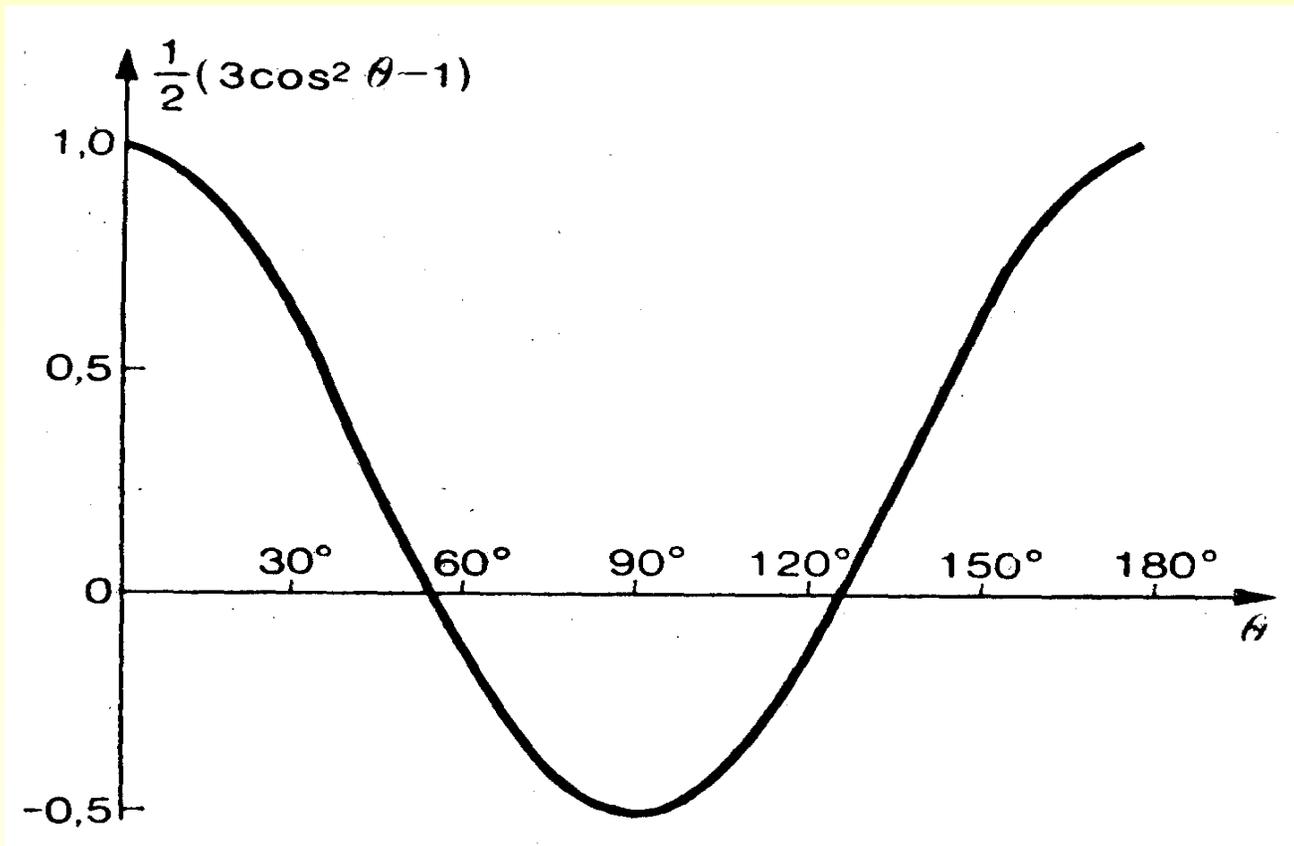
three molecules p, q, r and having their positions at $\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r$.

The volume element of q-th molecule $d\mathbf{r} = r_q^2 dr_q \sin\theta_q d\theta_q d\phi_q$ for fixed position of the molecule p with the help of fig.V.3 can be transformed to DOKONCZYC

Then the binary radial correlation parameter (99) reads

$$\langle r_{pq}^{-6} \rangle = 4\pi\rho \int_0^\infty r_{pq}^{-4} g(r_{pq}) dr_{pq} \quad (101)$$

since the correlation function $g(r_{pq})$ depends only on the relative distance between molecules p and q and $d\mathbf{r}_p = V$,



Rysunek 4: The angle $\theta = \theta_{pq}$ dependence of the Legendre P_2 function

The correlation parameter is calculated numerically provided that we know the form of the correlation function $g(r_{pq})$. In the case of

a low density gas we can use the approximate result

$$g(r_{pq}) = \exp[-\beta u(r_{pq})] [1 + O(\rho)] \quad (102)$$

If, for simplicity, we use the interaction energy $u(r_{pq})$ of the Lennard-Jones form, then we obtain

$$\langle r_{pq}^{-n} \rangle = 4\pi\rho \int r_{pq}^{2-n} g(r_{pq}) dr_{pq} = \frac{\pi\rho\sigma^{3-n}}{3y^4} H_n(y) \quad (103)$$

where the Pople's functions $H_n(y)$ are given by Eq.(5) of Chapter IV. For liquids we can use the Kirkwood (1936) model of hard spheres of the radius $d/2$ and volume $v = \pi d^3/6$. Since in this case the radial distribution function is of the form case

$$(104)$$

and then for $n \geq 4$ we have (Kielich 1968)

$$\langle r_{pq}^{-n} \rangle = \frac{4\pi\rho}{n-3} \left(\frac{\pi}{6v} \right)^{\frac{n-3}{3}} \quad (105)$$

Then the binary correlation contribution to the molecular refraction reads

$$\Delta R_m^{(2)} = \frac{4\pi^2}{9v} a^2 \rho R_m^{(1)} \quad (106)$$

This equation is suitable for numerical estimations, since the value of the $u = \rho v$ is from the range 0.6 — 0.74 (Stuart 1967).

As follows from Eqs.(88-98) the relative change of the molecular refraction amounts to

$$\frac{R_m - R_m^{(1)}}{R_m^{(1)}} = 2a^2 (\langle r_{pq}^{-6} \rangle + \langle r_{pq}^{-3} r_{qr}^{-3} \rangle) + \dots \quad (107)$$

Then within the Kirkwood model (106) we have

$$\frac{R_m - R_m^{(1)}}{R_m^{(1)}} = \frac{4\pi}{9u} a^2 \rho^2 + \dots \quad (108)$$

So the difference between the molecular refraction of liquid R_m and gas $R_m^{(1)}$ states is proportional to the square of the number density of molecules ρ .

Generally, the numerical calculations of the ternary correlation parameter (100) are difficult. However, in certain situations they are possible with some model assumptions (Helwarth 1970, Gray 1974, Wozniak 1975). This parameter is particularly interesting since its value can be positive as well as negative depending on the model of interactions of three molecules. Using the Legendre

polynomial of the second order

$$P_2 \left(\frac{\mathbf{r}_{pq} \cdot \mathbf{r}_{qr}}{r_{pq} r_{qr}} \right) = \frac{1}{2} \left\{ 3 \left(\frac{\mathbf{r}_{pq} \cdot \mathbf{r}_{qr}}{r_{pq} r_{qr}} \right)^2 - 1 \right\} = \frac{1}{2} (3 \cos^2 \theta_{pqr} - 1) \quad (109)$$

we write the parameter (100) in the form

Taking into account the properties of P_2 (see Fig.V.4) we observe that this parameter is positive for the angles θ_{pqr} between the vectors \mathbf{r}_{pq} and \mathbf{r}_{qr} ranging from 0 to 180 except the range 54 to 125 degrees when the parameter is negative. The ternary correlations can thus increase or decrease the relative changes of the molecular refraction depending on the type of mutual interactions of three atoms or molecules.

2.3 Mixtures of gases and liquids.

Consider the case when in the macroscopic sphere of the volume V there are atoms or molecules of different kinds, in particular $N_1 = x_1 N$ molecules of the first kind, $N_2 = x_2 N$ molecules of the second kind, $N_s = x_s N$ molecules of the s -th kind, moreover $x_i = N_i/N$ is the molar fraction of the i -th species of the system in which the total number of molecules amounts to $N = \sum_{i=1}^s N_i$. The sum of all molar fractions equals to unity:

$$\sum_{i=1}^s x_i = 1 \quad (110)$$

For a multi-component system the polarization vector reads

$$\mathbf{P}(\mathbf{r}, t) = \sum_{i=1}^s \sum_{p=1}^{N_i} \mathbf{d}^{(pi)}(\mathbf{r}, t) \quad (111)$$

where $\mathbf{d}^{pi}(r, t)$ stands for the electric dipole moment induced in the $i - th$ molecule. Inserting the polarization (111) into Eq.(2) instead of Eq.(3) we obtain the following general formula for the molecular refraction

$$R_m \mathbf{E}_0(\mathbf{r}, t) = \frac{4\pi}{3} \sum_{i=1}^s \left\langle \sum_{p=1}^{N_i} \mathbf{d}^{(pi)}(\mathbf{r}, t) \right\rangle \quad (112)$$

When there are molecular fields in our system, Eq.(5) applies. Then, in this approximation by Eq.(112) we obtain

$$R_m = \frac{4\pi}{3} N_A \sum_{i=1}^s x_i a^{(i)} = \sum_{i=1}^s x_i R_m^{(i)} \quad (113)$$

This result gives us the molecular refraction additivity rule for multi-component systems. The molecular refractions of individual

components are

$$R_m^{(i)} = \frac{4\pi}{3} N_A a^{(i)} \quad (114)$$

where $a^{(i)}$ denotes the scalar polarizability of i – th component of the mixture.

The molecular refraction R_m is strictly additive only in mixtures of perfect gases when no molecular correlations take place. In mixtures of real gases and in liquids due to correlations of molecules of the same kind and/or correlation of molecules of different kinds, the molecular refraction R_m is no longer additive and writes as the following power series of the molecular fractions

$$R_m = \sum_i x_i R_m^{(i)} + \sum_{ij} x_{ij} R_m^{(ij)} + \sum_{ijk} x_i x_j x_k R_m^{(ijk)} + \quad (115)$$

The first term of this series applies to the perfect gas mixture. The

next terms are responsible for deviations from additivity, Eq.(113), due to intermolecular interactions or statistical fluctuations. In the binary correlation approximation we have:

$$R_m^{(ij)} = \frac{4\pi}{3} N_A a^{(i)} a^{(j)} [a^{(i)} + a^{(j)}] \langle r_{pq}^{-6} \rangle_{ij} \quad (116)$$

where the parameter of binary correlations $\langle r_{pq}^{-6} \rangle_{ij}$ is given by Eq.(99).

The ternary correlations give

$$R_m^{(ijk)} = \frac{8\pi}{3} N_A a^{(i)} a^{(j)} a^{(k)} \langle r_{pq}^{-3} r_{qr}^{-3} \rangle_{ijk} \quad (117)$$

where the parameter of ternary correlations is given by Eq.(100).

In our calculations we silently assume that the molecules considered are optically isotropic. In the absence of molecular correlations the anisotropy does not change Eq.(114). It is

sufficient to write there for the mean value of molecular polarizability of the $i - th$ kind:

$$a^{(i)} = \frac{1}{3}(a_1^{(i)} + a_2^{(i)} + a_3^{(i)}) \quad (118)$$

The effect of anisotropy is manifested in the presence of binary correlations when instead of Eq.(116) the following formula should be used (Kielich 1962, 1965)

$$R_m^{(ij)} = \frac{4\pi}{9} N_A \left\{ a^{(i)} (\mathbf{a}^{(j)} : \mathbf{a}^{(j)}) + (\mathbf{a}^{(i)} : \mathbf{a}^{(i)}) a^{(j)} \right\} \langle r_{pq}^{-6} \rangle_{ij} \quad (119)$$

In the particular case of the axially symmetric molecules (with the symmetry axis \mathbf{s} directed along the main axis 3 of the molecule)

the polarizability tensor is of the form:

$$\mathbf{a} = a\mathbf{U} + a\kappa(3\mathbf{ss} - \mathbf{U}) \quad (120)$$

then

$$\mathbf{a} : \mathbf{a} = 3a^2(1 + 2\kappa^2) \quad (121)$$

and Eq.(119) reads

$$R_m^{(ij)} = \frac{4\pi}{9} N_A a^{(i)} a^{(j)} \left\{ a^{(i)} (1 + 2\kappa_j^2) + a^{(j)} (1 + 2\kappa_i^2) \right\} \langle r_{pq}^{-6} \rangle_{ij} \quad (122)$$

When we neglect the anisotropy letting ($\kappa = 0$), we get Eq.(116).

3. TYPES OF LIGHT SCATTERING

3.1 Rayleigh scattering

It has been over one hundred years since the pioneer works of Tyndall (1868) and Lord Rayleigh (1871) on light scattering caused by optical inhomogeneities of material media. Opaque and colloidal media are very intense light scatterers, but the process of light scattering known as the Tyndall phenomenon will not be discussed. We will concentrate on the light scattering phenomena in the optically transparent and homogeneous (in the macroscopic sense) media taking place as a result of different statistical fluctuations (in density, concentration, anisotropy, etc.). The media homogeneous in the macroscopic sense are gases, molecular and atomic liquids or their mixtures. This phenomenon is called the molecular light scattering and its theoretical background has been provided by Lord Rayleigh (1899), Smoluchowski (1908) and

Einstein (1910). Lord Rayleigh, trying to find out why the sky was blue, established that the intensity of radiation I^R scattered by individual atoms or molecules (non-absorbing ones) is inversely proportional to the wavelength of the incident light in the fourth power λ , and directly proportional to its intensity I

$$I^R \approx \frac{1}{\lambda^4} I \quad (123)$$

It is the elastic scattering known also as the Rayleigh scattering in which the wavelengths of the incident and scattered radiation are the same. In the quantum approach, the Rayleigh scattering involves absorption of a photon of the incident light by an atom or molecule and simultaneous emission of another photon of the same energy but not necessarily of the same direction. Smoluchowski has shown that on the microscopic scale the media cannot be

absolutely homogeneous, as the accidental thermal motions induce the appearance of spontaneous density fluctuations in elementary volumes (of the linear size smaller than the wavelength) (Kocinski 1972).

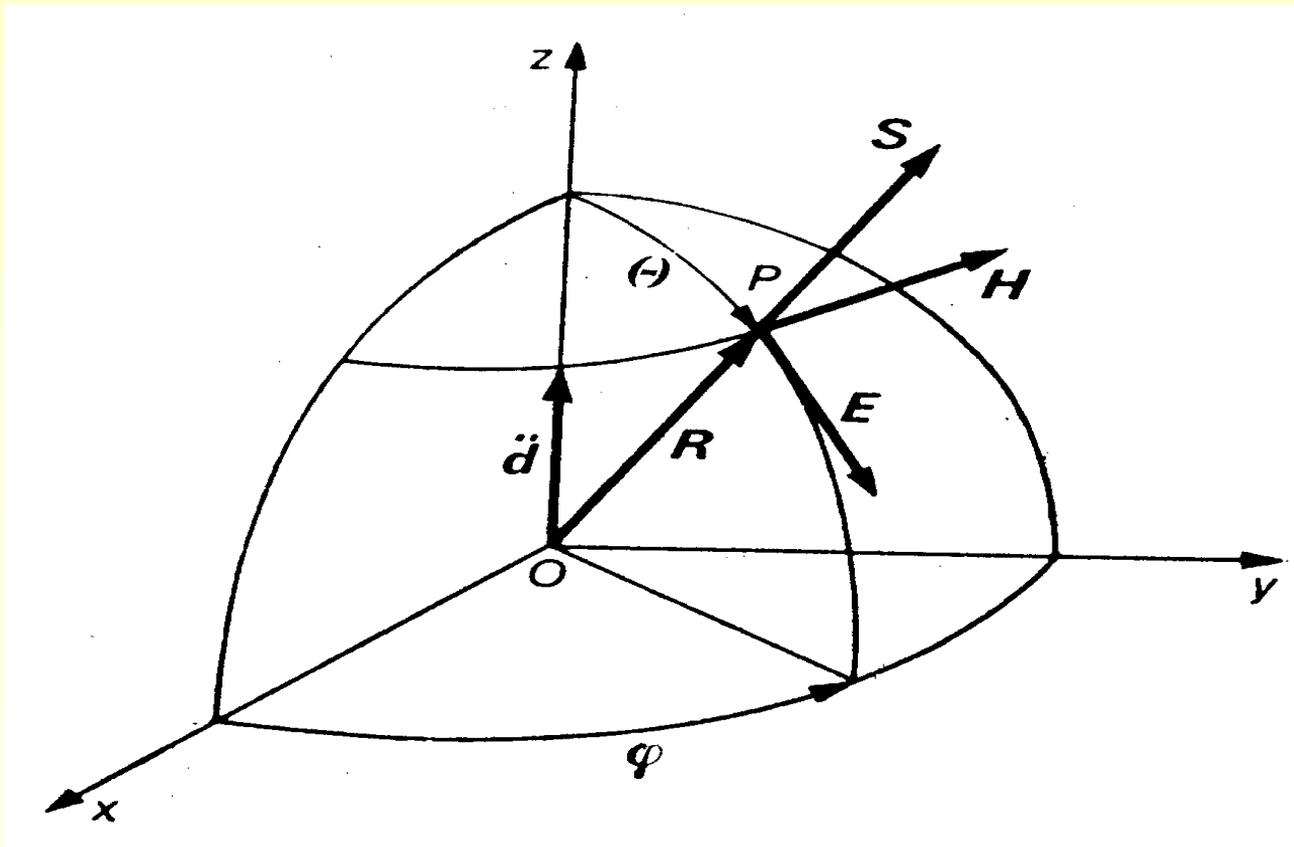
As follows from the Lorentz-Lorenz (5) relation, the thermal fluctuations of density induce local changes in the light refraction index, so are responsible for optical inhomogeneity. In this way Smoluchowski proved that the true origin of molecular light scattering (and thus the blue colour of the sky) are the density fluctuations, which considerably increase near the critical state of a given substance, causing the phenomenon of critical opalescence. Einstein (1910) developed the ideas of Rayleigh and Smoluchowski and presented a thermodynamic theory of light scattering in liquids and solutions, taking into regard not only fluctuations of density but also fluctuations of solution concentrations. Important

contributions to the theory of elastic light scattering have also been the works of Born (1917), Cabannes (1920) and Gans (1923), who studied the light scattering caused by anisotropy of molecular polarisability. The information on the linear optical polarizability of individual molecules and anisotropy of their polarizability is provided from the studies of depolarization of scattered light in gas states (Wolkensztejn 1951, Stuart 1967, Fabelinskij 1968) and from the study of the depolarized component in dilute solutions (Bothorel 1969). Light scattering in liquids and solutions provide also the information on close-range ordering both radial and orientational (Kielich 1960, 1967).

3.2. Raman scattering

In a general case, apart from the elastic light scattering with no change in the wavelength, the phenomenon of inelastic light scattering takes place in which the scattered radiation has its

wavelength changed in a way characteristic of a given scattering substance. This kind of scattering was discovered by Raman and Krishnan (1928) and in crystals - by Landsberg and Mandelsztam (1928). The changes in the wavelength of the radiation scattered by liquids are of the order of magnitude of the oscillation or rotational vibrations



Rysunek 5: Directions of vectors \mathbf{E} and \mathbf{H} at the wave distance for the Hertz dipole.

of the molecules of the liquids.

The process of Raman (or combinatory) scattering can be described as follows: under the effect of the incident photon of a

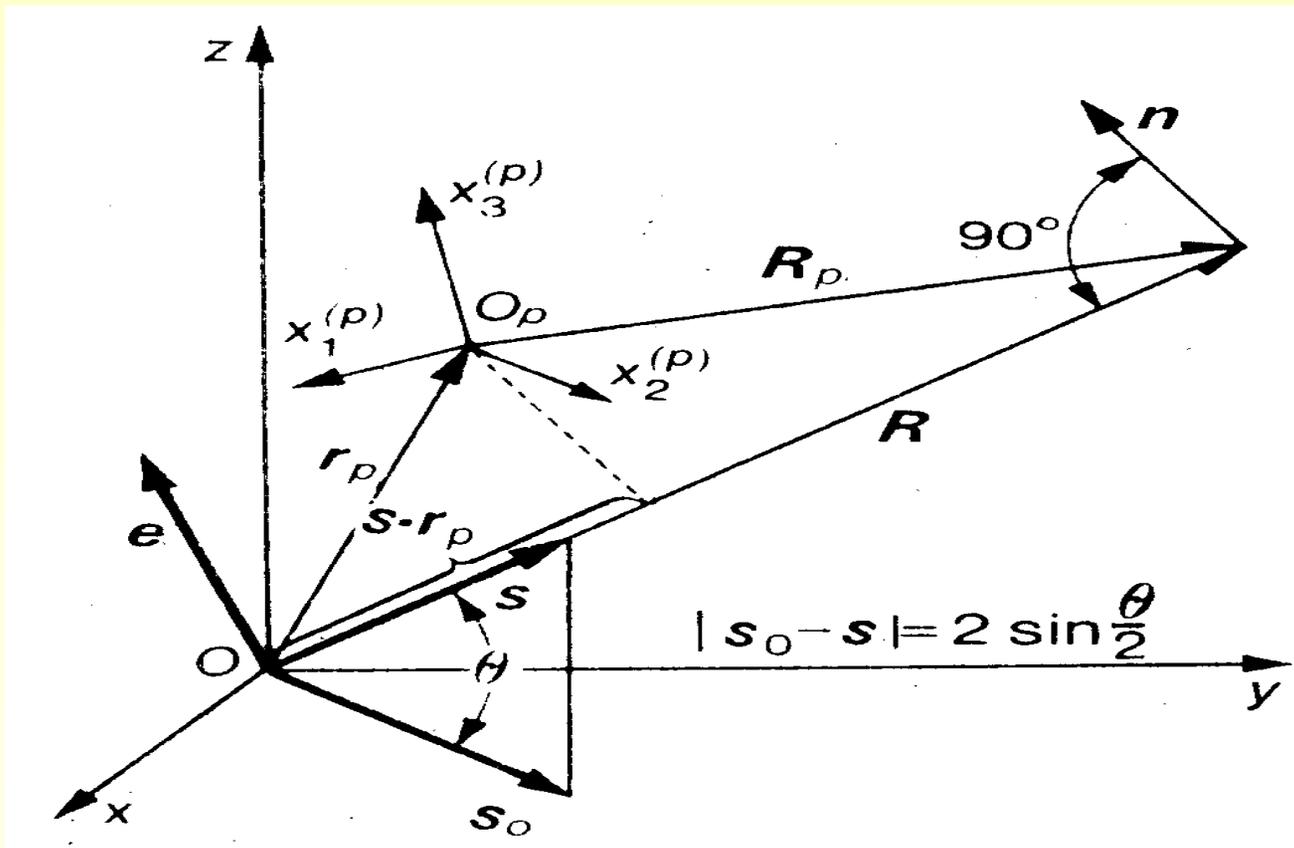
frequency ω , the molecule undergoes a transition from the initial state into any discrete quantum state, scattering a photon of an altered frequency ω' . The quantum description of the process of Raman scattering was proposed already by Smekala (1923). The fundamentals of the quantum-mechanical theory of light scattering were proposed by Kramers and Heisenberg (1925) and Dirac (1927). Let $\omega_m = (E_m - E_n)/\hbar$ stand for the frequency of transition between the energy levels E_m and E_n . According to the quantum theory of light scattering we can observe either the scattered light of the frequency $\omega_s = \omega - \omega_{mn}$ (the Stokes line) smaller than that of the incident light, or of the frequency $\omega_{as} = \omega + \omega_{mn}$ (the anti-Stokes line). The appearance of the Stokes lines is more probable than that of the anti-Stokes lines because at the ambient temperature there are many more molecules in the ground than in the excited state. In the spectrum

of light scattered in molecular substances we observe a strong Rayleigh band accompanied at one side by an about 1000 times weaker Stokes band and on the other side by still weaker anti-Stokes band (for low frequencies of oscillations). Placzek (1934) explained the mechanism of Raman light scattering by a simple theory of molecular polarization changes. In the infrared spectrum only these vibrations are active during which the dipolar moment of the molecule changes. The condition of the appearance of Raman lines in the spectrum of the scattered light is the change of polarizability during the molecule nuclei vibrations. As a result of different selection rules in the IR and Raman spectra, some vibrations by Eq.(21b) inactive in infrared range can be active in the Raman scattering and vice versa. Therefore, the information on molecular structure (internuclear distances, force constants) in particular in the multiatomic molecules (Bhagavantam 1942,

Brandmüller 1962, Suszczinski 1969) are provided by infrared spectroscopy in combination with Raman scattering.

3.3 Electromagnetic fields

Let us consider a molecular system composed of electric charges e_s having their positions \mathbf{r}_s at the moment of time $t' = t - R/c$, where R stands for the distance of our point of observation from the center of the molecular system. The Hertz vector for this system is defined by



Rysunek 6: The mutual orientation of the laboratory reference frame x, y, z in respect to the moving reference frame x_1, y_1, z_1 connected with the scattering light molecule p . Vectors s_0 and s give us the directions of the incident and scattered light.

$$\mathbf{Z} = \sum_s e_s \mathbf{r}_s(t') \quad (124)$$

In the wave zone the electromagnetic field is given by the vectors

$$\mathbf{E}_R = \frac{1}{R^3 c^2} \left\{ \mathbf{R} \times \left(\mathbf{R} \times \frac{d^2 \mathbf{Z}}{dt^2} \right) \right\} \quad (125)$$

$$\mathbf{H}_R = - \frac{1}{R^2 c^2} \left(\mathbf{R} \times \frac{d^2 \mathbf{Z}}{dt^2} \right) \quad (126)$$

taken at \mathbf{R} in a moment of time $t - R/c$.

The vectors (125) and (126) give perpendicular radiation since both vectors are mutually perpendicular as well as perpendicular to \mathbf{R} .

Taking into account the vector relation

$$\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = (\mathbf{A} \cdot \mathbf{C}) \mathbf{B} - (\mathbf{A} \cdot \mathbf{B}) \mathbf{C} \quad (127)$$

according to (125) and (126) for Poynting vector we obtain

$$\mathbf{S} = \frac{c}{4\pi} \mathbf{E}_R \times \mathbf{H}_R = \frac{\mathbf{R}}{4\pi R^5 c^3} \left\{ R^2 \left(\frac{d^2 \mathbf{Z}}{dt^2} \cdot \frac{d^2 \mathbf{Z}}{dt^2} \right) - \left(\mathbf{R} \cdot \frac{d^2 \mathbf{Z}}{dt^2} \right)^2 \right.$$

Let us consider a sphere of the radius \mathbf{R} in the center of which

there is a molecular system endowed with the Hertz vector. The directed surface element of the sphere amounts to $d\boldsymbol{\sigma} = \mathbf{s} R^2 d\Omega$, where $d\Omega = \sin\theta d\theta d\phi$ stands for the solid angle and \mathbf{s} denotes the unit vector in the direction of observation $\mathbf{R} = \mathbf{s} R$. The flux of energy transmitted through $d\boldsymbol{\sigma} = \mathbf{s} R^2 d\Omega$ per unit of time amounts to

$$dS = \mathbf{S} \cdot d\boldsymbol{\sigma} = \mathbf{S} \cdot \mathbf{s} R^2 d\Omega \quad (129)$$

and according to (128) in the explicit form

$$\frac{dS}{d\Omega} = \frac{1}{4\pi c^3} \left\{ \left(\frac{d^2\mathbf{Z}}{dt^2} \cdot \frac{d^2\mathbf{Z}}{dt^2} \right) - \left(\mathbf{s} \cdot \frac{d^2\mathbf{Z}}{dt^2} \right)^2 \right\} \quad (130)$$

According to the classical electrodynamics, electric dipoles induced in molecules emit secondary electrodynamic radiation dispersed in all directions. This electric dipolar radiation is of the same frequency as the incident light. It results as the scattering called the classic or Rayleigh scattering. In fact in each molecule immersed in the light wave a complicated distribution of electric charge is produced. This distribution is of the same frequency as that of the incident light wave ω . When the wavelength of the incident light is long in comparison with the linear dimension of the molecules, mainly dipole moments are induced. However, when the

size of the molecules is comparable with the incident radiation wavelength then, besides dipoles, quadrupoles and higher order multipoles are involved. Consequently, such systems produce the electric and magnetic multipolar scattering. The theory of this scattering for atomic spectra was discussed first by RUBINOWICZ (1930). Moreover quadrupole, octopole etc. radiation is very important when the dipolar process is not allowed.

In general the Hertz vector (124) is composed of the electric and magnetic parts

$$\mathbf{z} = \sum_{n=1} \left(\mathbf{z}_e^{(n)} + \mathbf{z}_m^{(n-1)} \right) \quad (131)$$

whose respective multipolar contributions are of the form

(KIELICH 1965)

$$\mathbf{Z}_e^{(n)} = \frac{2^n n!}{(Rc)^{n-1} (2n)!} \mathbf{R}^{n-1} [n-1] \frac{d^{n-1} \mathbf{m}_e^{(n)}}{dt^{n-1}} \quad (132)$$

$$\mathbf{Z}_m^{(n-1)} = - \frac{2^{n-1} (n-1)!}{R^{n-1} c^{n-2} (2n-2)!} \mathbf{R}^{n-2} [n-2] \left(\mathbf{R} \times \frac{d^{n-2} \mathbf{m}_m^{(n-1)}}{dt^{n-2}} \right)$$

The above dipole moments $\mathbf{m}_e^{(n)}$ are described by Eq.(??), whereas the magnetic moments $\mathbf{m}_m^{(n)}$ are given by Eq.(??) of Chapter IV.

The expansion (132) defines the 2^n -pole electric radiation whereas

Eq.(133) gives the $2^{(n-1)}$ - pole magnetic radiation. In the first approximation ($n=1$), vector (132) reduces to

$$\mathbf{Z}_e^{(1)} = \mathbf{d}(t) \quad (134)$$

and then we deal with the dipolar radiation. In the second approximation ($n=2$) the vector (132) contains contributions of quadrupolar origin

$$\mathbf{Z}_e^{(2)} = \frac{1}{3 c R} \left(\mathbf{R} \cdot \frac{d\mathbf{q}}{dt} \right) = \frac{1}{3 c} \left(\mathbf{s} \cdot \frac{d\mathbf{q}}{dt} \right) \quad (135)$$

whereas vector (133) contributes to magnetic dipolar radiation

$$\mathbf{Z}_m^{(1)} = \frac{1}{R} \mathbf{m} \times \mathbf{R} = \mathbf{m} \times \mathbf{s} \quad (136)$$

Electric dipole radiation When considering the Hertz dipole in the first approximation, the electric and magnetic fields read

$$\mathbf{E}_R = \frac{1}{R^3 c^2} \left\{ \mathbf{R} \times (\mathbf{R} \times \ddot{\mathbf{d}}) \right\} = \frac{1}{R c^2} \left\{ \mathbf{s} \times (\mathbf{s} \times \ddot{\mathbf{d}}) \right\} \quad (137)$$

$$\mathbf{H}_R = -\frac{1}{R^2 c^2} (\mathbf{R} \times \ddot{\mathbf{d}}) = \frac{1}{R c^2} (\ddot{\mathbf{d}} \times \mathbf{s}) \quad (138)$$

Similarly, by Eqs (128) and (134), for the temporal flux of the dipole radiation emitted in an elementary angle $d\Omega$ in the direction defined by angle θ , we obtain

$$\frac{dS}{d\Omega} = \frac{1}{4\pi c^3} (\ddot{\mathbf{d}} \cdot \ddot{\mathbf{d}}) \sin^2 \theta \quad (139)$$

where the angle θ is between by the direction of the vector $\ddot{\mathbf{d}}$ and

the direction of observation \mathbf{s} ($\mathbf{d} \cdot \mathbf{s} = d \cos\theta$).

Integrating (139) over all angles θ and ϕ , we obtain

$$S_{ed} = \frac{2}{3c^3} (\ddot{\mathbf{d}} \cdot \ddot{\mathbf{d}}) \quad (140)$$

Then in the first approximation, the energy emitted in all directions is defined by the second derivative of the dipole moment $\mathbf{d}(t)$.

Electric quadrupole radiation Inserting (135) to Eqs.(125–126) we obtain the intensity of quadrupolar radiation as

$$\mathbf{E}_R = \frac{1}{3Rc^3} \left\{ \mathbf{s} \left[\mathbf{s} \times (\mathbf{s} \times \ddot{\mathbf{q}}) \right] \right\} \quad (141)$$

$$\mathbf{H}_R = \frac{-1}{3 R c^3} \left\{ \mathbf{s} \times (\mathbf{s} \cdot \ddot{\mathbf{q}}) \right\} \quad (142)$$

and similarly by Eq.(129)

$$\frac{dS}{d\Omega} = \frac{1}{36 \pi c^5} \left\{ (\mathbf{s} \cdot \ddot{\mathbf{q}} \cdot \ddot{\mathbf{q}} \cdot \mathbf{s}) - (\mathbf{s} \cdot \ddot{\mathbf{q}} \cdot \mathbf{s})^2 \right\} \quad (143)$$

After the isotropic averaging over all directions of the unit vector \mathbf{s} we obtain

$$\int (\mathbf{s} \cdot \mathbf{q} : \mathbf{q} \cdot \mathbf{s}) d\Omega = \frac{4\pi}{3} (\mathbf{q} : \mathbf{q}) \quad (144)$$

$$\int (\mathbf{s} \cdot \mathbf{q} \cdot \mathbf{s})^2 d\Omega = \frac{8\pi}{15} (\mathbf{q} : \mathbf{q}) \quad (145)$$

Then for the total flux of the quadrupolar radiation we get

$$S_{eq} = \frac{1}{45 c^5} (\ddot{\mathbf{q}}:\ddot{\mathbf{q}}) \quad (146)$$

Magnetic dipole radiation. Using Eqs (125– 126) in accordance with the approximation (136) for the magnetic dipole radiation we obtain

$$\mathbf{E}_R = \frac{1}{R c^2} (\mathbf{s} \times \ddot{\mathbf{m}}) \quad (147)$$

$$\mathbf{H}_R = \frac{1}{R c^2} \{ \mathbf{s} \times (\mathbf{s} \times \ddot{\mathbf{m}}) \} \quad (148)$$

$$\frac{dS}{d\Omega} = \frac{1}{4 \pi c^3} (\ddot{\mathbf{m}} \times \ddot{\mathbf{m}}) \sin^2 \theta \quad (149)$$

Then the flux of the magnetic radiation

$$S_{md} = \frac{2}{3c^3} (\ddot{\mathbf{m}} \cdot \ddot{\mathbf{m}}) \quad (150)$$

is defined in the same way as the flux for the electric dipole radiation (140). Assuming the harmonic behavior of multipoles in time and using (140), (146) and (150) we arrive at

$$\frac{S_{eq}}{S_{ed}} = \frac{1}{30c^2} \frac{(\ddot{\mathbf{q}} : \ddot{\mathbf{q}})}{(\ddot{\mathbf{d}} : \ddot{\mathbf{d}})} = \frac{1}{30} \left(\frac{\omega}{c} \right)^2 \frac{q^2}{d^2} \quad (151)$$

$$\frac{S_{md}}{S_{ed}} = \frac{(\ddot{\mathbf{m}} : \ddot{\mathbf{m}})}{(\ddot{\mathbf{d}} : \ddot{\mathbf{d}})} = \frac{m^2}{d^2} \quad (152)$$

3.4 Symmetric and antisymmetric light scattering in gases

In general the polarizability tensor $a_{ij}(\omega)$ depends on the frequency of the incident light. In the case of optically inactive molecules and in the absence of the electron dispersion and absorption, the tensor a_{ij} is real and symmetric $a_{ij} = a_{ji}$. More generally, however, the polarizability tensor is not symmetric and can be split into the symmetric part

$$a_{ij}^S = \frac{1}{2} (a_{ij} + a_{ji}) = a_{ji}^S \quad (153)$$

and the antisymmetric part

$$a_{ij}^A = \frac{1}{2} (a_{ij} - a_{ji}) = -a_{ji}^A \quad (154)$$

The symmetric part can be divided into the isotropic part $a \delta_{ij}$ and the anisotropic part (deviator)

$$D_{ij} = a_{ij}^S - a \delta_{ij} \quad (155)$$

with vanishing trace ($D_{ij} \delta_{ij} = 0$).

The symmetric part (isotropic + anisotropic) of the polarizability tensor is real, whereas the antisymmetric part is imaginary.

In the laboratory frame of axes xyz , the i -th component of the

induced dipole moment reads

$$d_i(t) = a_{ij}(\omega) E_j(t) \quad i, j = x, y, z \quad (156)$$

On the other hand the laboratory frame tensor components a_{ij} transform to the molecular frame ones by

$$a_{ij} = c_{i\alpha} c_{j\beta} a_{\alpha\beta} \quad (157)$$

where $c_{i\alpha}$ stands for the cosine of the angle between the i -th axis of the laboratory frame and the α -th axis of the molecular frame, and the following orthogonality relations hold

$$c_{i\alpha} c_{i\beta} = \delta_{\alpha\beta} \quad c_{i\alpha} c_{j\alpha} = \delta_{ij} \quad (158)$$

Let us define the second rank tensor

$$I_{ij}^R = \frac{1}{2c^4} \left\langle \ddot{d}_i(t) \ddot{d}_j(t)^* \right\rangle_{\Omega} = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \left\langle d_i d_j^* \right\rangle \quad (159)$$

which we call the light scattering tensor. Taking into account Eqs (156) and (159), we arrive at

$$I_{ij}^R = \frac{1}{2c^4} a_{\alpha\gamma} a_{\beta\delta}^* \left\langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} \right\rangle_{\Omega} E_k(\omega) E_l^*(\omega) \quad (160)$$

where the symbol $\langle \dots \rangle_{\Omega}$ stands for the equal probability averaging, in other words for the averaging over all possible orientations of axes of the molecular frame in respect to the laboratory frame (Kielich 1961):

$$\begin{aligned}
\langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} \rangle_{\Omega} &= \frac{1}{30} \left\{ (4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})\delta_{ij}\delta_{kl} \right. \\
&\frac{1}{2} (3\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - 2\delta_{\alpha\beta}\delta_{\gamma\delta}) (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + \\
&\left. \frac{5}{2} (\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}) \right\} \quad (161)
\end{aligned}$$

We define the symmetric part of the scattered intensity as

$$I_{ij}^S = \frac{1}{2} (I_{ij}^R + I_{ji}^R) \quad (162)$$

as well as its antisymmetric part

$$I_{ij}^A = \frac{1}{2} (I_{ij}^R - I_{ji}^R) \quad (163)$$

According to Eqs(153)–(155) we have

$$a_{ij} = a_{ij}^S + a_{ij}^A = a \delta_{ij} + D_{ij} + a_{ij}^A \quad (164)$$

and finally we arrive at

$$I_{ij}^S = \frac{1}{4} (S_{iso} + S_{aniso} - S_{anti}) (E_i E_j^* + E_j E_i^*) + \frac{1}{2} (3 S_{aniso} + S_{anti}) (E_i E_j^* - E_j E_i^*)$$

$$I_{ij}^A = \frac{1}{4} (S_{iso} - 5 S_{aniso} + S_{anti}) (E_i E_j^* - E_j E_i^*) \quad (166)$$

where

$$S_{iso} = \left(\frac{\omega}{c}\right)^4 a^2 \quad (167)$$

stands for the isotropic light scattering constant (factor?), whereas

$$S_{aniso} = \frac{1}{5} \left(\frac{\omega}{c}\right)^4 a^2 \kappa^2 \quad (168)$$

defines the anisotropic light scattering constant, moreover the symbol

$$\kappa^2 = \frac{D_{\alpha\beta} D_{\alpha\beta}}{6 a^2} = \frac{(3 a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta})}{18 a^2} \quad (169)$$

denotes the square of the optical anisotropy of the molecule. In the absence of the natural activity for molecules having polarizabilities

a_{11}, a_{22}, a_{33} along the three main axes by (169) we have

$$\kappa^2 = \frac{(a_{11} - a_{22})^2 + (a_{22} - a_{33})^2 + (a_{33} - a_{11})^2}{2(a_{11} + a_{22} + a_{33})^2} \quad (170)$$

which, for linear molecules, reduces to the anisotropy of Langevine (Eq.(?) already discussed in Section(III)).

In the particular case of optically isotropic molecules

$a_{11} = a_{22} = a_{33}$, then $\kappa = 0$ and the anisotropic light scattering constant (168) vanishes.

In systems composed of optically active molecules, besides the symmetric light scattering (165) (isotropic + anisotropic), the antisymmetric light scattering appears, defined by

$$S_{anti} = \frac{1}{6} \left(\frac{\omega}{c} \right)^4 (a_{\alpha\beta}^A) (a_{\alpha\beta}^A)^* \quad (171)$$

5. FUNDAMENTALS OF MOLECULAR-STATISTICAL THEORY OF LIGHT SCATTERING IN ISOTROPIC MEDIA

In normal conditions the isotropic medium light scattering theory can be completely described by the classical electrodynamics and the statistical mechanics. We consider the isotropic system of volume V composed of N -like anisotropic and polarizable molecules. In its center we choose the origin O of the laboratory frame coordinates $(X_i)_{i=1,2,3}$. To the center of each molecule of the system we fix the molecular frame. In the classical approach the positions and the orientations of molecules from the volume V are described by the continuous configurational variables $\tau = (\mathbf{r}, \Omega)$ where \mathbf{r} denote the positions whereas Ω denote the orientations of the molecules. (Fig.V.6).

4.1 Light scattering electric field

Let's consider the volume V illuminated by linearly polarized laser radiation with the electric field given by $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$. The electric field in the center of the p th molecule being at a distance \mathbf{r}_p from the center of the laboratory frame (X_i) reads

$$\mathbf{E}^{(p)}(t) = \mathbf{E}_0^{(p)} \exp[-i(\omega t - \mathbf{k}_0 \cdot \mathbf{r}_p)] \quad (172)$$

where

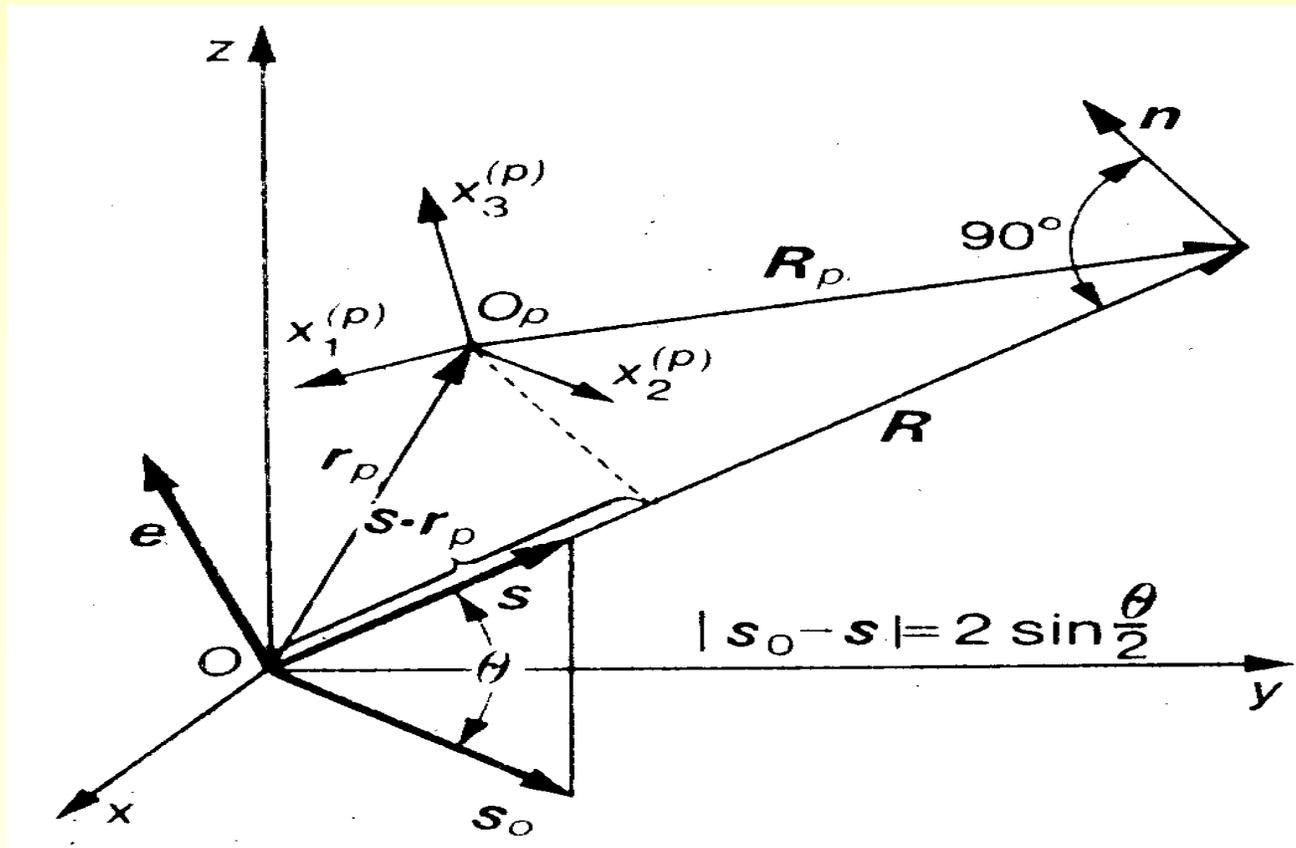
$$\mathbf{k}_0 = \frac{2\pi}{\lambda} \mathbf{s}_0 \quad (173)$$

denotes the wave-vector of the incident light with its direction of propagation given by \mathbf{s}_0 . The amplitude \mathbf{E} is always perpendicular to the vector \mathbf{s}_0 .

Fig. V.6

The electric field (172) induces in the p -th molecule (in the same way as in other molecules) the time dependent electric moment given by

$$\mathbf{d}^{(p)}(t) = \mathbf{d}^{(p)} \exp[-i(\omega t - \mathbf{k}_0 \cdot \mathbf{r}_p)] \quad (174)$$



Rysunek 7: The mutual orientation of the laboratory reference frame x, y, z in respect to the moving reference frame x_1, y_1, z_1 connected with the scattering light molecule p . Vectors s_0 and s give us the directions of the incident and scattered light.

We consider the electric dipolar radiation only; the one leading to the Rayleigh scattering of light. We take this radiation in the so-called wave zone i.e. at distances from the scattering system much larger than the wavelength of the light wave. In this case the electric field of the radiation scattered by the molecule p is given by (Heitler 1959)

$$\mathbf{E}_R^p(t) = -\frac{4\pi^2}{\lambda^2 R_p^3} \left\{ \mathbf{R}_p \times \left[\mathbf{R}_p \times \mathbf{d}^{(p)} \exp\left[-i\left(\omega t - \mathbf{k}_0 \cdot \mathbf{r}_p - \frac{2\pi}{\lambda} R_p\right)\right] \right] \right\} \quad (175)$$

where $\mathbf{R}_p = \mathbf{R} - \mathbf{r}_p$ denotes the vector going from the center of the molecule p to the point of observation, at a distance R_p from the center O of the laboratory coordinates (X_i). Since the distance of the observation point is large in comparison with the linear dimensions of the scattering volume as well as in comparison with

\mathbf{r}_p , we write

$$R_p = |\mathbf{R} - \mathbf{r}_p| = R - \mathbf{s} \cdot \mathbf{r}_p + \dots \quad (176)$$

where \mathbf{s} is the unit vector in the direction of observation $\mathbf{R} = \mathbf{s} R$ and denoting the direction of propagation of the scattered wave (Fig.V.6).]

If $R \gg r_p$, we can put R in Eq.(175) instead of R_p everywhere except in the argument of the exponential function, where, because of (176), we can put $R_p = R - \mathbf{s} \cdot \mathbf{r}_p$; then we have

$$\mathbf{E}_R^{(p)}(t) = -\frac{4\pi^2}{\lambda^2 R} \exp \left[i \left(\frac{2\pi}{\lambda} R - \omega t \right) \right] \left\{ \mathbf{s} \times \left[\mathbf{s} \times \mathbf{d}^{[p]} \right] \exp[i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_p] \right\} \quad (177)$$

where

$$\mathbf{k} = \frac{2\pi}{\lambda} \mathbf{s} \quad (178)$$

stands for the vector of the scattered light.

Due to Eq.(177) the total electric field scattered by all molecules of the scattering volume V reads

$$\mathbf{E}_R\left(t + \frac{R}{c}\right) = -\frac{4\pi^2}{\lambda^2 R} \left\{ \mathbf{s} \times [\mathbf{s} \times \mathbf{M} \exp[-i\omega t]] \right\} \quad (179)$$

The vector

$$\mathbf{M} = \sum_{p=1}^N \mathbf{d}^{(p)} \exp[(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}_p] \quad (180)$$

denotes the amplitude of the total electric dipolar moment induced in V by the electric field of the incident light wave.

4.2 Intensity of scattered light

We are interested now in the component of the scattered light passed through the analyser at the point of observation. We denote the direction of the light passing the analyzer by \mathbf{n} . Obviously, the vector \mathbf{n} is perpendicular to the observation vector $\mathbf{R} = \mathbf{s}R$ namely $\mathbf{n} \cdot \mathbf{s} = 0$. Then due to Eq(179), for the component of the vector \mathbf{E}_R in the direction \mathbf{n} we obtain

$$\mathbf{E}_R \cdot \mathbf{n} = \frac{4\pi^2}{\lambda^2 R} (\mathbf{M} \cdot \mathbf{n}) \exp[-i\omega t] \quad (181)$$

The component of the light scattered by V and passing through the analyzer is

$$I_{\mathbf{n}}^R = \frac{1}{2} \langle (\mathbf{E}_R \cdot \mathbf{n}) (\mathbf{E}_R \cdot \mathbf{n})^* \rangle_E \quad (182)$$

The star $*$ denotes the complex conjugate whereas E stands for the statistical averaging in the presence of the electric field \mathbf{E}

already discussed in Eq.(??) of Chapter IV.

Inserting (181) to (182) and using the tensorial notation we are in a position to write the fundamental equation for $I_{\mathbf{n}}$

$$I_{\mathbf{n}}^R = \frac{1}{2R^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle M_i M_j^* n_i n_j^* \right\rangle_E = \frac{1}{R^2} I_{ij}^R n_i n_j^* \quad (183)$$

where the subscripts i and j run over x, y, z .

Obviously, the electric moment \mathbf{M} depends on \mathbf{E} and τ ; we write $\mathbf{M} = \mathbf{M}(\tau, \mathbf{E})$. Usually, the intensity of the incident radiation is low, then we can assume that the induced dipole moment depends linearly on \mathbf{E}

$$M_i(\tau, E) = A_{ij} E_{0j} + \dots \quad (184)$$

where

$$A_{ij} = \left(\frac{\partial M_i}{\partial E_{0j}} \right)_{E=0} \quad (185)$$

stands for the optical polarizability tensor of the system of volume V .

Because of Eq.(184) for the spherical sample the light scattering tensor reads

$$I_{ij}^R = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \langle M_i M_j^* \rangle_E = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \langle A_{ik} A_{jl}^* \rangle E_{0k} E_{0l}^* \quad (186)$$

where the symbol

without any lower subscript denotes the statistical averaging in the ab

$$\langle Q \rangle = \frac{\int \dots \int Q(\tau, 0) \exp\left[-\frac{U(\tau, 0)}{k_B T}\right] d\tau_1 d\tau_2 \dots d\tau_N}{\int \dots \int \exp\left[-\frac{U(\tau, 0)}{k_B T}\right] d\tau_1 d\tau_2 \dots d\tau_N} \quad (187)$$

In the absence of the external field we can perform the isotropic

averaging on the left side of the tensor (186)

$$I_{ij}^R = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \langle A_{\alpha\gamma} A_{\beta\delta}^* \rangle \langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} \rangle E_{0k} E_{0l}^* \quad (188)$$

Taking into account Eq.(161) as well as the definitions (162) and (163) we again obtain the Eqs(162) and (??) but now with new light scattering constants suitable for arbitrary isotropic system.

Namely instead of Eq.(167) for one molecule now we have the isotropic light scattering constant for all N molecules of the system

$$S_{iso}(\mathbf{u}) = \frac{1}{9} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N \frac{\partial d_i^{(p)}}{\partial E_i} \frac{\partial d_j^{(q)}}{\partial E_j} \exp[-i\mathbf{u} \cdot \mathbf{r}_{pq}] \right\rangle \quad (189)$$

where $\mathbf{u} = \mathbf{k}_0 - \mathbf{k}$.

Similarly, instead of Eq.(165) the anisotropic light scattering

constant now has the form

$$S_{aniso}(\mathbf{u}) = \frac{1}{30} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N D_{ij}^{(p)} D_{ij}^{(q)} \exp[-i\mathbf{u} \cdot \mathbf{r}_{pq}] \right\rangle \quad (190)$$

where we introduce the deviator of the polarizability tensor of the *p*th molecule immersed in a system

$$D_{ij}^{(p)} = \frac{1}{2} \left(\frac{\partial d_i^{(p)}}{\partial E_{0j}} + \frac{\partial d_j^{(p)}}{\partial E_{0i}} \right) - \frac{1}{3} \delta_{ij} \left(\frac{\partial d_k^{(p)}}{\partial E_{0k}} \right) \quad (191)$$

shortly called a deviator.

The light scattering constant defining the antisymmetric scattering

is of the form (Kielich 1971)

$$S_{anti}(\mathbf{u}) = \frac{1}{24} \left(\frac{\omega}{c}\right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N \left(\frac{\partial d_i^{(p)}}{\partial E_{0j}} - \frac{\partial d_j^{(p)}}{\partial E_{0i}} \right) \left(\frac{\partial d_i^{(q)}}{\partial E_{0j}} - \frac{\partial d_j^{(q)}}{\partial E_{0i}} \right) \right\rangle \quad (192)$$

The parameter $\mathbf{u} \cdot \mathbf{r}_{pq}$ defines the scattered light phase difference between molecules p and q , where $\mathbf{r}_{pq} = \mathbf{r}_p - \mathbf{r}_q$ stands for the vector joining the centers of these molecules, and for the classical scattering it is of the form

$$|\mathbf{u}| = |\mathbf{k}_0 - \mathbf{k}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (193)$$

where θ stands for the angle between the incident and the scattered beams, shortly called the scattering angle (see Figs V.6 and V.7). The Eqs (165) and (166) together with Eqs (189)–(192) form the fundamentals of the statistical-molecular light scattering theory for

an arbitrary isotropic system.

4.3 The light scattering constants for molecules with intrinsic polarizability only

First we assume that molecules have only the polarizability independent of the fields of neighbor molecules as well as the external field. In this case, in the reference frame X_i the electric moment induced in the p th molecule by the electric field E_0 reads

$$d_i^{(p)} = a_{ij}^{(p)} E_{0j} \quad (194)$$

where $a_{ij}^{(p)}$ stands for the constant intrinsic optical polarizability of the p th molecule of the system. Taking into regard Eq.(194) Eqs (189) and (190) transform to

$$S_{iso}(\mathbf{u}) = \frac{1}{9} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_{ii}^{(p)} a_{jj}^{(q)} \exp[-i\mathbf{u} \cdot \mathbf{r}_{pq}] \right\rangle \quad (195)$$

$$S_{aniso}(\mathbf{u}) = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 a_{ij}^{(p)} a_{ij}^{(q)} - a_{ii}^{(p)} a_{jj}^{(q)}) \exp[-i\mathbf{u} \cdot \mathbf{r}_p] \right\rangle \quad (196)$$

For the following discussion it is convenient to relate the tensors $a_{ij}^{(p)}$ and $a_{ij}^{(q)}$ to the molecular reference frame

$$a_{ij}^{(p)} = c_{i\alpha}^{(p)} c_{j\beta}^{(p)} a_{\alpha\beta}^{(p)} \quad a_{ij}^{(q)} = c_{i\alpha}^{(q)} c_{j\beta}^{(q)} a_{\alpha\beta}^{(q)} \quad (197)$$

where where the cosine $c_{\alpha\beta}^{(pq)}$ stands for the cosine of the angle between the axis α and the axis β of the reference systems $X_{\alpha}^{(p)}$ and $X_{\beta}^{(q)}$ fixed respectively to the molecules p and q .

The tensor $a_{ij}^{(p)}$ defines the polarizability of the p – th molecule and for the optically inactive system, far from the absorption band this tensor is real and symmetric. Taking this into account we

write the real part of Eqs (195) and ??) as

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The isotropic scattering of light

We assume that all molecules of our system have the same polarizability, namely $a(p) = a(q) = a$. Then by Eq.(??) we obtain

$$S_{iso}(\mathbf{u}) = a^2 \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N + \sum_{p=1}^N \sum_{q \neq p}^N \cos(\mathbf{u} \cdot \mathbf{r}_{pq}) \right\rangle \quad (198)$$

where

$$a = \frac{1}{3} (a_{11} + a_{22} + a_{33}) \quad (199)$$

stands for the mean polarizability of the isolated molecule. Using the pair correlation function derived by Zernike and Prins (1927)

for X ray scattering by liquids, our equation (198) becomes

$$S_{iso}(\mathbf{u}) = a^2 \left(\frac{\omega}{c} \right)^4 \left\{ N + \rho^2 \int_V \int_V g(r_{pq}) \cos(\mathbf{u} \cdot \mathbf{r}_{pq}) d\mathbf{r}_p d\mathbf{r}_q \right\} \quad (200)$$

where $g(\mathbf{r}_{pq})$ denotes the probability of finding the molecule q in the infinitesimal volume $d\mathbf{r}_{pq}$ at the distance \mathbf{r}_{pq} from the molecule p being in the infinitesimal volume around \mathbf{r}_p

The infinitesimal volume around the molecule q for a fixed position of the molecule p can be written as. Then we can transform Eq(200) into

$$S_{iso}(\mathbf{u}) = a^2 \left(\frac{\omega}{c} \right)^4 N \left\{ 1 + 4\pi\rho^2 \int_V g(r_{pq}) \langle \cos(\mathbf{u} \cdot \mathbf{r}_{pq}) \rangle_{\Omega} r_{pq}^2 \right\} \quad (201)$$

Considering that

$$\langle \cos(\mathbf{u} \cdot \mathbf{r}_{pq}) \rangle_{\Omega} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \cos(ur_{pq} \cos \chi) \sin \chi d\chi d\psi = \frac{\sin(ur_{pq})}{ur_{pq}} \quad (202)$$

finally we find

$$S_{iso}(u) = a^2 \left(\frac{\omega}{c} \right)^4 N \{1 + G(u)\} \quad (203)$$

where $G(u)$ stands for the integral function introduced by Zernike and Prins (1927)

$$G(u) = 4\pi\rho \int_0^{\infty} \{g(r) - 1\} \frac{\sin ur}{ur} r^2 dr \quad (204)$$

For large values of u , where θ is large or λ is small (see Eq.(193)) the function $G(u)$ goes quickly to zero. Then the light scattering on liquids can be described similarly as for the light scattering on

gases:

$$S_{iso}^{gas} = a^2 \left(\frac{\omega}{c} \right)^4 N \quad (205)$$

This fact has been proved experimentally. For small values of u , that is when the linear dimensions of a molecule are small in comparison with the wavelength of the light λ , the interference factor goes to 1

$$\frac{\sin ur}{ur} = 1 - \frac{1}{6} (ur)^2 + \dots = 1 \quad \text{for } \lambda \gg r \quad (206)$$

then the function (204) takes the form

$$G_R = 4\pi\rho \int_0^\infty \{g(r) - 1\} r^2 dr \quad (207)$$

Therefore, for small scattering molecules (or small scattering

angles) the molecular isotropic light scattering constant reads

$$S_{iso} = a^2 \left(\frac{\omega}{c} \right)^4 N \gamma_R \quad (208)$$

where

$$\gamma_R = 1 + G_R = 1 + 4\pi\rho \int_0^\infty \{g(r) - 1\} r^2 dr \quad (209)$$

stands for the radial intermolecular correlation factor. This factor can be expressed as well in the thermodynamic form derived by Smoluchowski (1908) and Einstein (1910)

$$\gamma_R = \rho k_B T \beta_T \quad (210)$$

where

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (211)$$

denotes the isothermal compressibility of the system.

A comparison of Eqs (205) and Eqs (208) shows that for small scattering angles or large light wavelengths, the ratio of the isotropic scattering in liquid and in the perfect gas is given by the radial intermolecular correlation factor γ_R . On the other hand this factor is described by the isothermal compressibility of a liquid β_T . Since a and γ_R are the isotropic quantities, then S_{iso} really determines the isotropic light scattering. This scattering is caused mainly by the radial correlations of molecules, in other words by the density fluctuations, Smoluchowski (1908). When the molecules have the intrinsic polarizability only, (Eq.194), then the isotropic scattering does not depend on the symmetry of the molecules but only on their mean optical polarizability.

The anisotropic scattering of light

When molecules of the scattering volume are of the same kind and they are small in comparison with λ then we write Eq.(?? OK) in the form

$$S_{aniso} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 a_{\alpha\beta} a_{\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle \quad (212)$$

so S_{aniso} depends on the molecular anisotropy, given by the polarizability tensor $a_{\alpha\beta}$ as well as on the intermolecular orientation correlation. As has been shown, the isotropic scattering of light does not depend on the molecular anisotropy and, moreover, it is always nonzero. On the contrary, the anisotropic

light scattering, in this approximation of our theory vanishes, in the absence of molecular anisotropy. Then, for optically isotropic molecules, the polarizability tensor $a_{\alpha\beta}$ is reduced to the isotropic second rank tensor

$$a_{\alpha\beta} = a \delta_{\alpha\beta} \quad (213)$$

Taking into account

$$c_{\alpha\gamma}^{(pq)} c_{\alpha\delta}^{(pq)} = \delta_{\alpha\beta} c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)} = \delta_{\gamma\delta} \quad \delta_{\alpha\beta} \delta_{\alpha\beta} = 3 \quad (214)$$

and using Eq.(212) we can really prove that then $S_{aniso} = 0$. So the spherical molecules with the intrinsic polarizability only do not bring a contribution to the anisotropic light scattering.

When the molecular reference frame axes coincide with the

molecular main axes, then from Eq.(212) we obtain

$$S_{aniso} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 \sum_{s,t=1}^3 a_s a_t \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 \cos^2 \theta_{st}^{(pq)} - 1) \right\rangle \quad (215)$$

where θ_{st}^{pq} stands for the angle between the main axis s of the molecule p and the main axis t of the molecule q , whereas a_s is the polarizability in the direction of the sth main axis of the molecule.

In the case when molecules are symmetrical with respect the axis

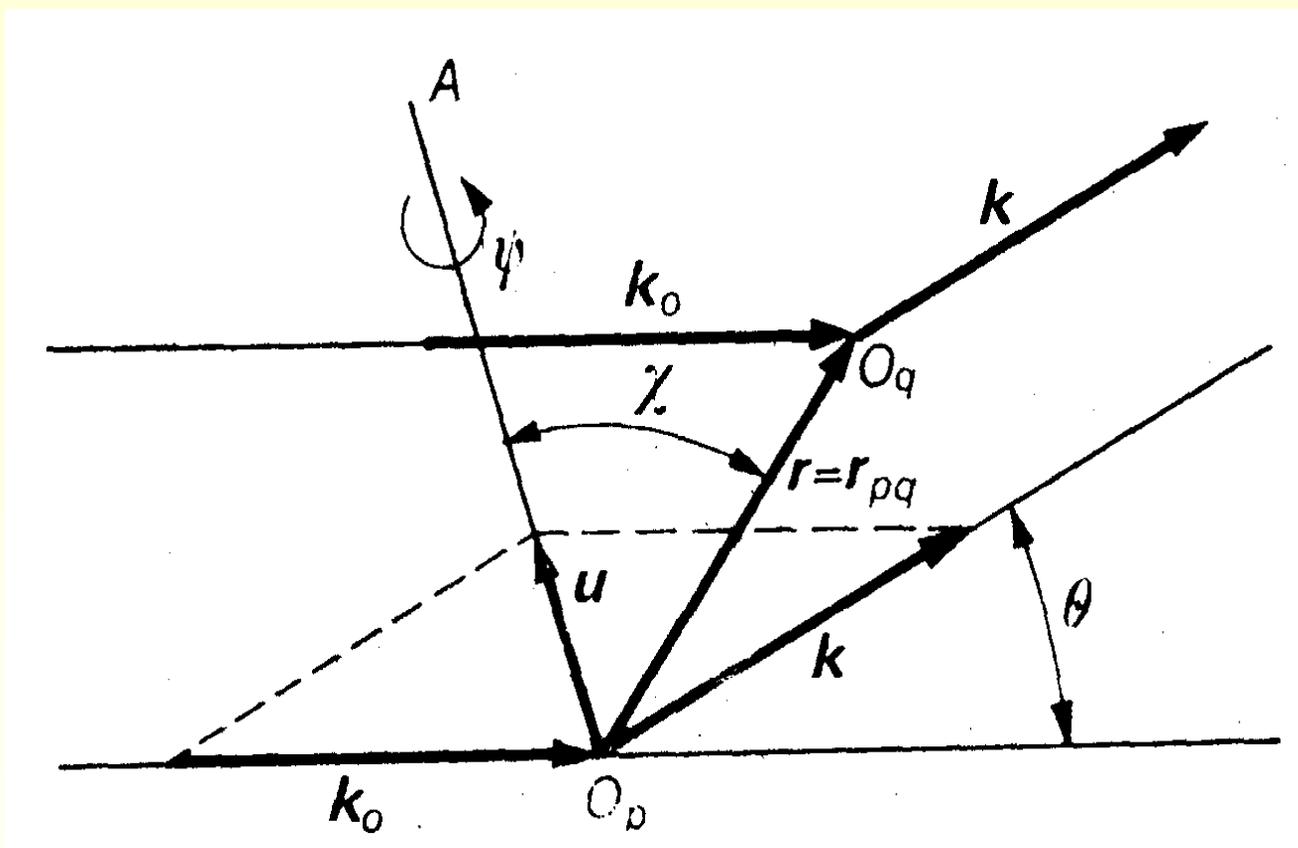
3, then $a_1 = a_2 \neq a_3$ and we rewrite Eq.(??) in the form

$$\begin{aligned}
 S_{aniso} &= \frac{1}{90} \left(\frac{\omega}{c} \right)^4 a_1^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N [3 (\cos^2 \theta_{11}^{(pq)} + \cos^2 \theta_{12}^{(pq)} + \cos^2 \theta_{21}^{(pq)} + \cos^2 \theta_{22}^{(pq)}) \right. \\
 &+ a_1 a_3 \left\langle \sum_{p=1}^N \sum_{q=1}^N [(3 \cos^2 \theta_{13}^{(pq)} + \cos^2 \theta_{23}^{(pq)} + \cos^2 \theta_{31}^{(pq)} + \cos^2 \theta_{32}^{(pq)}) \right. \\
 &\left. \left. + a_3^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N [(3 \cos^2 \theta_{33}^{(pq)} - 1) \right] \right\rangle \right\rangle
 \end{aligned}$$

Taking into account $c_{\alpha\gamma}^{(pq)} c_{\alpha\delta}^{(pq)} = \delta_{\gamma\delta}$ and denoting by $\theta_{pq} = \theta_{33}^{(pq)}$ the angle between the symmetry axes of p th and q - th molecule we obtain

$$\cos^2 \theta_{11}^{(pq)} + \cos^2 \theta_{12}^{(pq)} + \cos^2 \theta_{21}^{(pq)} + \cos^2 \theta_{22}^{(pq)} = 1 + \cos^2 \theta_{pq} \quad (217)$$

$$\cos^2 \theta_{13}^{(pq)} + \cos^2 \theta_{23}^{(pq)} + \cos^2 \theta_{31}^{(pq)} + \cos^2 \theta_{32}^{(pq)} = 2(1 - \cos^2 \theta_{(pq)}) \quad (218)$$



Rysunek 8: Determination of the phase difference between the scattered vectors of molecule p and q .

Then Eq.(216) is reduced to

$$S_{aniso} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 (a_3 - a_1)^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 \cos^2 \theta_{st}^{(pq)} - 1) \right\rangle \quad (219)$$

From this equation we note once more that when the molecules are optically isotropic $a_1 = a_3 = a$ the anisotropic scattering vanishes.

In a perfect gas all scattering molecules are independent of each other and in a given volume V they take all possible configurations with the same probability. In this case $\exp[-U(\tau)/k_B T] = 1$ and the statistical average given by Eq.(187) is reduced to the isotropic

average. Since now

$$S_{aniso} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 a_{\alpha\beta} a_{\gamma\delta} N \left\{ (3 \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\beta} \delta_{\gamma\delta}) + \sum_{p \neq q}^N (3 \langle c_{\alpha\gamma}^{(pq)} \rangle_{\Omega} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \right\} \quad (220)$$

then taking into account

$$\langle c_{\alpha\gamma}^{(pq)} \rangle_{\Omega} = \frac{1}{3} \delta_{\alpha\beta} \delta_{\gamma\delta} \quad \text{for } p \neq q \quad (221)$$

finally we obtain

$$S_{aniso}^{gas} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 (3 a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta}) N = \frac{1}{5} \left(\frac{\omega}{c} \right)^4 a^2 \kappa^2 N \quad (222)$$

We note that in a gas the anisotropic light scattering depends in the number N of molecules of the scattering volume as well as on its optical anisotropy given by Eq.(169). According to the

fluctuation theory, the key problem is the departure of the anisotropic molecules orientations from the chaotic distribution, so the fluctuations of the anisotropy and orientation leading to the appearance of optically inhomogeneous regions responsible for the anisotropic scattering of light.

From the results derived given by Eqs(212) and (215) we conclude that the anisotropic scattering in liquids composed of molecules with the intrinsic polarizability anisotropy is due to fluctuations of the optical anisotropy, closely dependent on the orientational (angular) intermolecular interactions. In gases the orientation and anisotropy fluctuations are totally incidental and independent of each other, whereas in liquids the mutual statistical dependence exist due to regions of temporary close range orientational and translational order.

The angular correlation parameter

Using the binary correlation function $g(\tau_p, \tau_q)$ we write the anisotropic scattering factor as (Kielich 1960)

$$S_{aniso} = \frac{1}{90} \left(\frac{\omega}{c} \right)^4 \left\{ (3 a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta}) N + a_{\alpha\beta} a_{\alpha\beta} \int \int (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)} - \delta_{\alpha\beta} \delta_{\gamma\delta}) g(\tau_p, \tau_q) d\tau_p, d\tau_q \right\} \quad (223)$$

For the particular case of axially symmetric molecules we obtain

$$S_{aniso} = \frac{1}{5} \left(\frac{\omega}{c} \right)^4 a^2 \kappa^2 N (1 + J_K) \quad (224)$$

where

$$J_K = \frac{\rho}{2V} \int \int (3 \cos^2 \theta_{pq} - 1) g(\tau_p, \tau_q) d\tau_p, d\tau_q \quad (225)$$

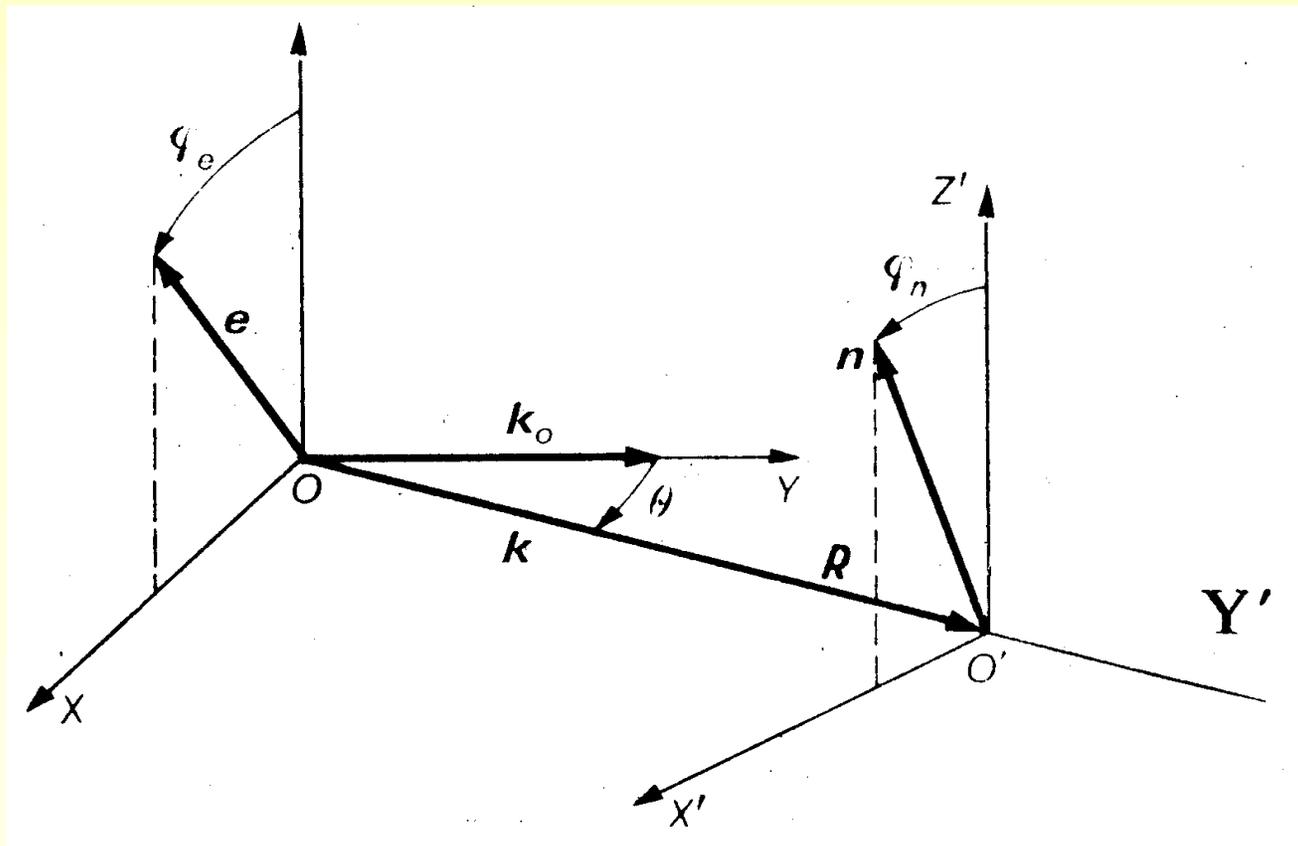
stands for the integral parameter describing the angular correlations of axially symmetric molecules. In the case of a perfect gas $g(\tau_p, \tau_q) = \frac{1}{\Omega^2}$ so the parameter J_K vanishes

$$J_K = \frac{N}{2\Omega^2} \int \int (3\cos^2\theta_{pq} - 1) d\tau_p, d\tau_q = 0 \quad (226)$$

In liquids and in real gases J_K is different from zero and can take positive as well as negative values. It means that clusters of molecules can increase as well as decrease the anisotropic scattering of light, depending on their configuration. The parameter J_K given by Eq.(225) appears as well in the expression for the magnetic birefringence (Kielich 1962).

5. THE DEPOLARIZATION RATIO AND THE RAYLEIGH CONSTANT

The following quantities characterizing intensity and polarization state of light are measured in the light scattering experiment: the depolarization ratio, the intensity and spectrum of the light scattered in certain direction (the scattering constant or the Rayleigh coefficient) as well as the amount of light scattered in all directions (the extinction coefficient). We calculate these quantities using Eqs(165) and (166) as well as Eqs.(189)–(192).



Rysunek 9: The mutual orientation of the molecular x', y', z' and the laboratory x, y, z reference frames.

We fix the reference frame system x, y, z at the center O of our scattering system, while the reference frame system x', y', z' at the

point O' of our observation. The plane biven by the propagating vectors \mathbf{k}_0 and \mathbf{k} of the incident and scattered beams is called the observation plane. For simplicity we assume that the observation plane is parallel to the xy plane and that the light is scattered within the angle θ in respect to the direction of the incident beam (Fig.V.8).

According to Eq.(165) the intensity of the symmetric light scattering reads

$$I_{\mathbf{n}}^S = \frac{I_0}{R^2} \left\{ (\mathbf{e} \cdot \mathbf{n})^2 S_{iso}(\mathbf{u}) + [3 + (\mathbf{e} \cdot \mathbf{n})^2] S_{aniso}(\mathbf{u}) \right\} \quad (227)$$

where $I_0 = \frac{E^* E}{2}$ - the intensity of incident light.

When the incident beam propagates along the y axis and we observe the scattering light along the y' axis making an angle θ with the y axis then the unit vectors \mathbf{e} and \mathbf{n} defining the

polarization vectors of the incident and the scattered radiation are given by where $\mathbf{x}, \mathbf{y}, \mathbf{z}$ and $\mathbf{x}', \mathbf{y}', \mathbf{z}'$ are the unit vectors of the respective reference frames.

$$\begin{aligned}\mathbf{e} &= \mathbf{x} \sin\varphi_e + \mathbf{z} \cos\varphi_e \\ \mathbf{n} &= \mathbf{x}' \sin\varphi_n + \mathbf{z}' \cos\varphi_n\end{aligned}\quad (228)$$

Since $\mathbf{x} \cdot \mathbf{z}' = \mathbf{x}' \cdot \mathbf{z} = 0$, $\mathbf{z} \cdot \mathbf{z}' = 1$ and $\mathbf{x} \cdot \mathbf{x}' = \cos\theta$ then we have

$$\mathbf{e} \cdot \mathbf{n} = \cos\varphi_e \cos\varphi_n + \sin\varphi_e \sin\varphi_n \cos\theta \quad (229)$$

For vibrations of the scattered light parallel to the observation plane $\phi_n = 90^\circ$ when $(\mathbf{e} \cdot \mathbf{n})^2 = \sin^2\varphi_e \cos^2\theta$ according to Eq.(227) we have

$$I_{\parallel}^R = \frac{I_0}{R^2} \left\{ \sin^2\varphi_e \cos^2\theta S_{iso}(\mathbf{u}) + [3 + \sin^2\varphi_e \cos^2\theta] S_{aniso}(\mathbf{u}) \right\} \quad (230)$$

In a similar way for perpendicular vibrations $\phi_n = 0^\circ$ we obtain

$$I_{\perp}^R = \frac{I_0}{R^2} \left\{ \cos^2 \varphi_e S_{iso}(\mathbf{u}) + [3 + \cos^2 \varphi_e] S_{aniso}(\mathbf{u}) \right\} \quad (231)$$

5.1 The depolarization ratio

The polarization state of the scattered radiation is studied examining, with the use of the analyzer, its perpendicular and parallel components. The depolarization ratio of the scattered radiation is defined as

$$D = \frac{I_{\parallel}^R}{I_{\perp}^R} \quad (232)$$

The symbols I_{\parallel}^S and I_{\perp}^S stand for the components of the scattered radiation with its electric field vibrations parallel and perpendicular with respect to the observation plane. Inserting Eqs (230) and (231) into Eq.(232) we obtain the general formula for the

depolarization ratio of the light scattered with the angle θ in respect to the direction of propagation of the incident beam

$$D = \frac{\sin^2\varphi_e \cos^2\theta S_{iso}(\mathbf{u}) + [3 + \sin^2\varphi_n \cos^2\theta] S_{aniso}(\mathbf{u})}{\cos^2\varphi_e S_{iso}(\mathbf{u}) + [3 + \cos^2\varphi_e] S_{aniso}(\mathbf{u})} \quad (233)$$

When the incident beam is linearly polarized with the electric vector perpendicular to the plane of observation , i.e. when $\phi_e = 0$, then Eq.(230) is of the form

$$D_{\perp} = \frac{3S_{aniso}(\mathbf{u})}{S_{iso}(\mathbf{u}) + 4S_{aniso}(\mathbf{u})} \quad (234)$$

Using Eq.(233) we can calculate the depolarization ratio for the case when the incident beam is unpolarized. In this case, taking into account equal probability of all directions of the vector \mathbf{e} in the plane perpendicular to \mathbf{k}_0 , we average $\cos^2\phi_e$ and $\sin^2\phi_e$ over

all possible values of ϕ_e

$$\langle \cos^2 \varphi_e \rangle = \frac{1}{2\pi} \int_0^{2\pi} \cos^2 \varphi_e d\varphi_e = \frac{1}{2} \quad \langle \sin^2 \varphi_e \rangle = \frac{1}{2}$$

Inserting these values into Eq.(233) for the natural incident beam we obtain

$$D_n = \frac{\cos^2 \theta S_{iso}(\mathbf{u}) + [6 + \cos^2 \theta] S_{aniso}(\mathbf{u})}{S_{iso}(\mathbf{u}) + 7 S_{aniso}(\mathbf{u})} \quad (235)$$

When the linear dimensions of molecules are small in comparison with the light wavelength then $S_{iso}(u)$ and $S_{aniso}(u)$ are independent of θ and for the right angle observations, Eq.(230) is reduced to

$$D_n = \frac{6 S_{aniso}}{S_{iso} + 7 S_{aniso}} \quad (236)$$

Comparing Eqs (234) and (236) we obtain a simple formula

connecting $D_{||}$ and D_{\perp}

$$D_n = \frac{2 D_{\perp}}{1 + D_{\perp}} \quad (237)$$

Inserting into Eq.(236) $S_{iso}(u)$ and $S_{aniso}(u)$ given by Eqs(208) and (212) we have the formula

$$S_{aniso} = \frac{6a_{\alpha\beta} a_{\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle}{90a^2 N \gamma_R + 7a_{\alpha\beta} a_{\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)} - \delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle} \quad (238)$$

valid to liquids of arbitrary symmetry complex molecules. When in Eq.(238) we neglect the radial and angular correlations, then we obtain the formula valid for gases

$$\frac{6(3 a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta})}{90a^2 + 7(3 a_{\alpha\beta} a_{\alpha\beta} - a_{\alpha\alpha} a_{\beta\beta})} \quad (239)$$

In the case of axially symmetric molecules Eq.(238) takes the form

$$D_n = \frac{6\kappa^2(1 + J_R)}{5(1 + G_R) + 7\kappa^2(1 + J_R)} \quad (240)$$

For the perfect gas, $G_R = 0$ and $J_K = 0$ then our equation is reduced to the Gans–Cabannes formula

$$D_n = \frac{6\kappa^2}{5 + 7\kappa^2} \quad (241)$$

We note that in the approximation considered, the systems composed of optically isotropic molecules with intrinsic polarizability only, do not depolarize the scattered light because for $\kappa = 0$ $D_n = 0$.

5.2 The Rayleigh light scattering constant

Adding together the components $I_{||}$ and I_{\perp} given by Eqs (230) and (231) describing the total light scattered in a given direction we obtain

$$I_{tot} = \frac{I_0}{R^2} \left\{ (1 - \sin^2 \phi_e \sin^2 \theta) S_{iso}(\mathbf{u}) + (7 - \sin^2 \phi_e \sin^2 \theta) S_{anis}(\mathbf{u}) \right\} \quad (242)$$

Note that this formula can be obtained in a different way with the use of Eq.(227) namely

$$I_{tot} = 2 \bar{I}_{\mathbf{n}} \quad (243)$$

where

$$\bar{I}_{\mathbf{n}} = \frac{1}{2\pi} \int_0^{2\pi} I_n d\phi_n \quad (244)$$

is the value of I_n , given by Eq.(227), averaged over all possible directions of the vector \mathbf{n} in the plane perpendicular to the

direction of the light scattered observation. In this case we have

$$\langle (\mathbf{e} \cdot \mathbf{n})^2 \rangle = \frac{1}{2} (\cos^2 \phi_e + \sin^2 \phi_e \cos^2 \theta) = \frac{1}{2} (1 - \sin^2 \phi_e \sin^2 \theta) \quad (245)$$

Then Eqs (243), (244) and (227) give directly Eq.(242). Our considerations show that Eq.(242) applies as well to the case when we observe the scattered light without analyser.

When the incident light is linearly polarized we usually consider two cases $\phi_e = 0^0$ and $\phi_e = 90^0$. Then we obtain

$$I_{tot}^{\perp} = \frac{I_0}{R^2} \{ S_{iso}(\mathbf{u}) + 7 S_{aniso}(\mathbf{u}) \} \quad (246)$$

$$I_{tot}^{\parallel} = \frac{I_0}{R^2} \{ \cos^2 \theta S_{iso}(\mathbf{u}) + (6 + \cos^2 \theta) S_{aniso}(\mathbf{u}) \} \quad (247)$$

In the case of the unpolarized incident radiation it is necessary to put in Eq.(242) $\langle \sin^2 \phi_e \rangle = 1/2$ instead of $\sin^2 \phi_e$. Then we obtain a general equation for the light scattered at the angle θ in respect to the propagation direction of the incident natural light

$$I_{tot}^n(\theta) = \frac{I_0}{R^2} \left\{ (1 + \cos^2 \theta) S_{iso}(\mathbf{u}) + (13 + \cos^2 \theta) S_{aniso}(\mathbf{u}) \right\} = \quad (248)$$

We define the light scattering constant also known as the Rayleigh coefficient in the following way

$$S_R = \frac{I_{tot} R^2}{I V} \quad (249)$$

where V is the volume of the scattering system.

The macroscopic electric field E inside a spherical sample with the

refractive index n is related to the electric field in a vacuum through

$$E = \frac{3}{n^2 + 2} E_0 \quad (250)$$

Consequently, for the intensities we obtain

$$I = \left(\frac{3}{n^2 + 2} \right)^2 I_0^2 \quad (251)$$

Now we rewrite our Rayleigh coefficient, Eq.(249), as follows

$$S_R = \left(\frac{n^2 + 3}{3} \right)^2 \frac{I_{tot} R^2}{I_0 V} \quad (252)$$

With the use of Eq.(242) giving us I_{tot} , we obtain the general

formula for the light scattering constant

$$\begin{aligned} S_R(\phi_e, \theta) &= \frac{1}{V} \left(\frac{n^2 + 3}{3} \right)^2 \left\{ (1 - \sin^2 \phi_e \sin^2 \theta) S_{iso}(\mathbf{u}) \right. \\ &\quad \left. + (7 - \sin^2 \phi_e \sin^2 \theta) S_{aniso}(\mathbf{u}) \right\} \end{aligned} \quad (253)$$

For the linearly polarized incident light with its electric field vector perpendicular to the observation plane, $\phi_e = 0^0$, Eq.(253) is of the form

$$S_R^\perp = \frac{1}{V} \left(\frac{n^2 + 3}{3} \right)^2 \{ S_{iso}(\mathbf{u}) + 7 S_{aniso}(\mathbf{u}) \} \quad (254)$$

We note that in this case the scattering constant does not depend on the scattering angle θ .

For the incident unpolarized light we obtain (Kielich 1960)

$$S_R = \frac{1}{2V} \left(\frac{n^2 + 3}{3} \right)^2 \left\{ (1 + \cos^2 \theta) S_{iso}(\mathbf{u}) + (13 + \cos^2 \theta) S_{aniso} \right\}$$

Then with the right angle observation in respect to the propagation direction of the incident unpolarized light we have

$$S_R(90^0) = \frac{1}{2V} \left(\frac{n^2 + 2}{3} \right)^2 (S_{iso} + 13 S_{aniso}) \quad (256)$$

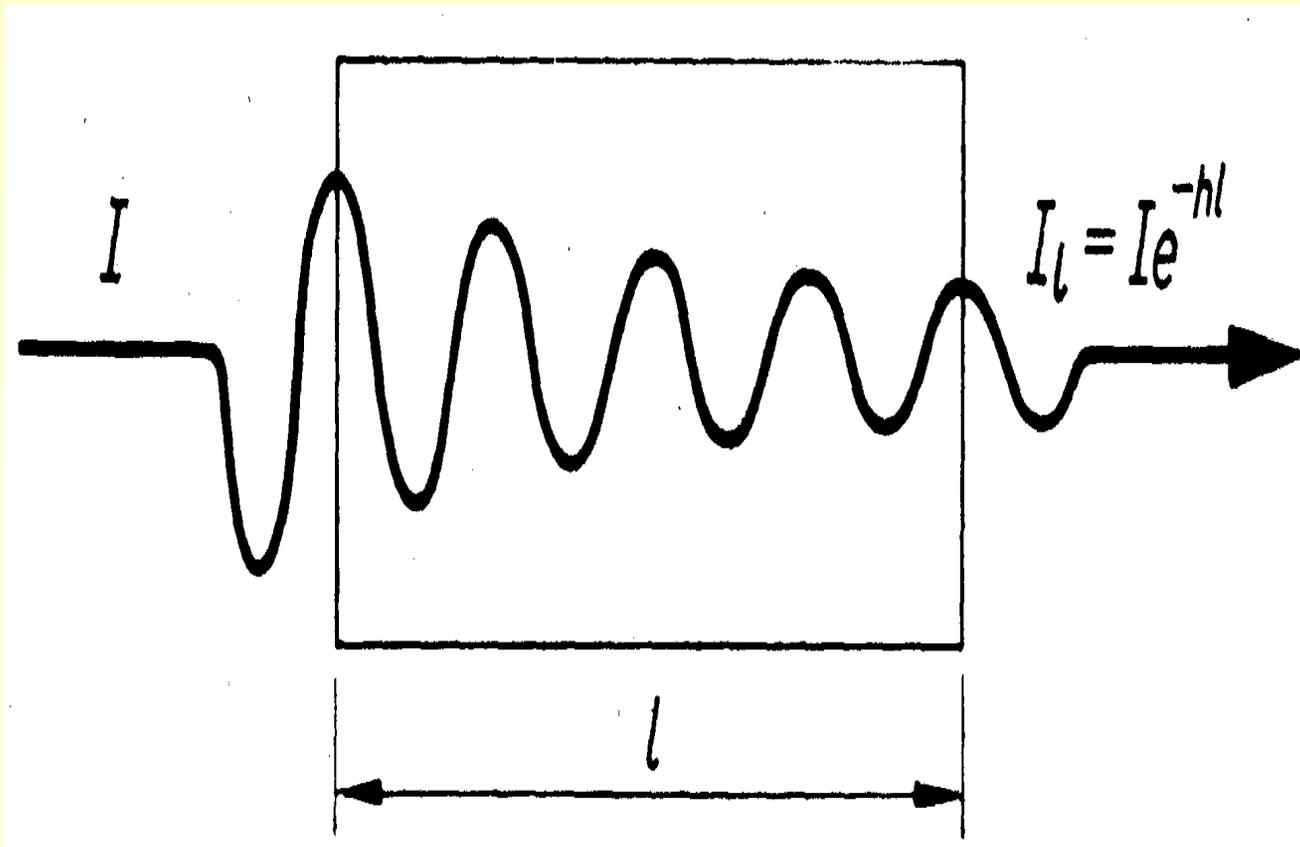
5.3 The extinction coefficient

Due to the light scattering process the light beam traveling through the medium diminishes (its reduction as a result of the absorption process is not considered here). The intensity of this

beam I after passing the distance l diminishes according to the Lambert's law (Fig. V.9):

$$I_l = I \exp(-h l) \quad (257)$$

In this formula the coefficient h describes attenuation of the incident light wave due to the light scattering process and is called the extinction coefficient or the opaque (opacity) coefficient of a system. The opacity coefficient is calculated as the ratio of the total light scattered in all directions with respect to the intensity of the incident light. We calculate the total intensity scattered in all directions integrating I_{tot} over the sphere surface of a radius R



Rysunek 10: The attenuation law for the light beam passing through the scattering system.

$$h = \frac{R^2}{IV} \int_0^\pi \int_0^{2\pi} I_{tot} \sin\theta \, d\theta \, d\phi_e \quad (258)$$

Taking into account Eq.(249) we obtain

$$h = \int_0^\pi \int_0^{2\pi} S_R(\phi_e, \theta) \sin\theta d\theta d\phi_e \quad (259)$$

Now with regard to Eq.(253) we have the general opacity coefficient formula (Kielich 1960)

$$h = \frac{\pi}{V} \left(\frac{n^2 + 2}{3} \right)^2 \int_0^\pi \left\{ (1 + \cos^2\theta) S_{iso}(\mathbf{u}) + (13 + \cos^2\theta) S_{aniso}(\mathbf{u}) \right\} \sin\theta d\theta \quad (260)$$

For small scattering molecules, in the absence of internal interference, the integration over θ gives

$$h = \frac{8\pi}{3V} \left(\frac{n^2 + 2}{3} \right)^2 (S_{iso} + 10 S_{aniso}) \quad (261)$$

5.4 The S_R and h values for particular cases

Inserting molecular factors given by Eqs (208) and (212) into Eqs (256) and (261), for gases and molecular liquids composed of arbitrary symmetry anisotropic molecules we obtain

$$S_R = \frac{4 \pi^4 (n^2 + 2)^2}{405 \lambda^4 V} \left\{ 90 a^2 N \gamma_R + 13 a_{\alpha\beta} a_{\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)}) \right\rangle \right. \quad (262)$$

$$h = \frac{128 \pi^5 (n^2 + 2)^2}{243 \lambda^4 V} \left\{ 9 a^2 N \gamma_R + a_{\alpha\beta} a_{\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 c_{\alpha\gamma}^{(pq)} c_{\beta\delta}^{(pq)}) \right\rangle \right. \quad (263)$$

Taking into account the Lorentz–Lorenz equation (7) for axially

symmetric molecules we have

$$S_R = \frac{\pi^2 (n^2 - 1)^2}{10 \lambda^4 \rho} \left\{ 5 (1 + G_R) + 13 \kappa^2 (1 + J_K) \right\} \quad (264)$$

$$h = \frac{8 \pi^3 (n^2 - 1)^2}{3 \lambda^4 \rho} \left\{ 5 (1 + G_R) + 2 \kappa^2 (1 + J_K) \right\} \quad (265)$$

where the correlation parameter J_K is given by Eq.(225).

These formulas differ from the King–Rocard equations (1928) only in their anisotropic part due to the angular correlations parameter J_K . For optically isotropic molecules ($\kappa = 0$) and our equations transform into the Smoluchowski–Einstein–Rocard relations

$$S_R = \frac{\pi^2 (n^2 - 1)^2}{2 \lambda^4} k_B T \beta_T \quad (266)$$

$$h = \frac{8 \pi^3 (n^2 - 1)^2}{3 \lambda^4} k_B T \beta_T \quad (267)$$

In the case of the perfect gas the relations given by Eqs (270) and Eqs (265) reduce to the Born–Cabannes formula

$$S_R = \frac{\pi^2 (n^2 - 1)^2}{10 \lambda^4 \rho} (5 + 13 \kappa^2) \quad (268)$$

$$h = \frac{8 \pi^3 (n^2 - 1)^2}{3 \lambda^4 \rho} (1 + 2 \kappa^2) \quad (269)$$

whereas Eqs (??) and (271) to the well known relations of Rayleigh

$$S_R = \frac{2 \pi^2}{\lambda^4 \rho} (n - 1)^2 \quad (270)$$

$$h = \frac{32 \pi^3}{3 \lambda^4 \rho} (n - 1)^2 \quad (271)$$

5.5 Relations between D , S_R and h According to the formulas derived for D , S_R and h , their calculations requires the knowledge of the radial as well as angular correlation parameters. Since these molecular parameters are rarely known, a frequently adapted procedure is to calculate D , S_R and h from experimental data. From Eq.(233) we have the ratio

$$\frac{S_{aniso}(u)}{S_{iso}(u)} = \frac{D_n(\theta) - \cos^2\theta}{6 - 7D_n(\theta) + \cos^2\theta} \quad (272)$$

giving the optical anisotropy of a system.

Inserting Eq.(272) to Eq.(255) we can write the $S_R(\theta)$ constant in one of these forms

$$S_R(\theta) = \frac{1}{2V} \left(\frac{n^2 + 2}{3} \right)^2 \frac{\{6 + 6D_n(\theta)\} \sin^2\theta}{\{6 - 7D_n(\theta)\} + \cos^2\theta} S_{iso}(\mathbf{u}) \quad (273)$$

$$S_R(\theta) = \frac{1}{2V} \left(\frac{n^2 + 2}{3} \right)^2 \frac{\{6 + 6 D_n(\theta)\} \sin^2 \theta}{D_n(\theta) - \cos^2 \theta} S_{aniso}(\mathbf{u}) \quad (274)$$

When we deal with the right angle scattering of the natural light then in the case of small scattering molecules we have

$$\frac{S_{aniso}}{S_{iso}} = \frac{D_n}{6 - 7 D_n} \quad (275)$$

$$S_R = \frac{1}{2V} \left(\frac{n^2 + 2}{3} \right)^2 \frac{6 + 6 D_n}{6 - 7 D_n} S_{iso} \quad (276)$$

$$S_R = \frac{1}{2V} \left(\frac{n^2 + 2}{3} \right)^2 \frac{6 + 6 D_n}{D_n} S_{aniso} \quad (277)$$

These equations give the following general relations

$$D_n(\theta) = D_n \left\{ 1 + \frac{1 - D_n}{D_n} \cos^2 \theta \right\} \quad (278)$$

$$S_R(\theta) = S_R \left\{ 1 + \frac{1 - D_n}{1 + D_n} \cos^2 \theta \right\} \quad (279)$$

$$h = \frac{8\pi}{3} \frac{2 + D_n}{1 + D_n} S_R \quad (280)$$

valid for the isotropic molecular system of arbitrary density and molecular structure. Analogous relations were obtained by Cabannes (1929) for the light scattered by individual molecules. When the isotropic light scattering coefficient S_{iso} is given by Eq.(208) then due to the Lorentz–Lorenz equation Eq.(7) we

obtain

$$S_{iso} = \frac{9V}{(4\pi)^2} \left(\frac{\omega}{c}\right)^4 \left(\frac{n^2 - 1}{n^2 + 2}\right)^2 k_B T \beta_T \quad (281)$$

and from Eqs (276) and (280) we have the Cabannes–King–Rocard formulas

$$S_R = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} \frac{6 + 6D_n}{6 - 7D_n} k_B T \beta_T \quad (282)$$

$$h = \frac{8\pi^3 (n^2 - 1)^2}{3\lambda^4} \frac{6 + 3D_n}{6 - 7D_n} k_B T \beta_T \quad (283)$$

without any molecular parameters. They can be obtained directly from experiment.

We calculate the Rayleigh isotropic and anisotropic light scattering

constants from the relations

$$S_R^{iso} = \frac{6 - 7 D_n}{6 + 6 D_n} S_R \quad (284)$$

$$S_R^{aniso} = \frac{13 D_n}{6 + 6 D_n} S_R \quad (285)$$

They result from Eqs (276) and (277).

6. ANISOTROPIC SCATTERING OF LIGHT BY FLUCTUATIONS OF MOLECULAR FIELDS

As we have just seen in condensed systems the isotropic as well as anisotropic light scattering takes place. However, the microscopic origin of these two types of scattering is quite different. Isotropic scattering of light defined by equation (189) is mainly due to

density fluctuations and has a global character, i.e. it appears in all systems. The anisotropic light scattering defined by equation (190) is related to asymmetric structure of the molecules and/or with statistical fluctuations of molecular fields. Then studies of anisotropic scattering reveal not only the data on the structure of molecules but first of all on the microscopic structure of scattering system.

In our hitherto discussion of the anisotropic light scattering constant (190) we assumed for simplicity that scattering molecules are linearly polarized (194) in an electric field \mathbf{E}_0 of the incident light. However, in a dense system besides \mathbf{E}_0 there is a molecular field $\mathbf{F}^{(p)}$ causing additional polarization of the molecule p

according to

$$d_i^{(p)} = a_{ij}^{(p)} \left(E_{0j} + F_j^{(p)} \right) \quad (286)$$

When inserting this induced moment into Eq.(191), defining the deviator of the polarizability tensor, we get

$$D_{ij}^{(p)} = D_{ij}^{(p)}(0) + \frac{1}{2} \left\{ a_{ik}^{(p)} \frac{\partial F_k^{(p)}}{\partial E_{0j}} + a_{jk}^{(p)} \frac{\partial F_k^{(p)}}{\partial E_{0i}} \right\} - \frac{1}{3} \delta_{ij} \left\{ a_{kl}^{(p)} \frac{\partial F_l^{(p)}}{\partial E_{0i}} \right\} \quad (287)$$

where

$$D_{ij}^{(p)} = a_{ij}^{(p)} - a_p \delta_{ij} \quad (288)$$

stands for the deviator of the polarizability tensor of the isolated molecule p in the absence of molecular fields.

It is easy to see now that when inserting deviator (287) to general equation (190) we obtain the constant of anisotropic light scattering (196) already discussed in Section 4. Now in the deviation tensor (287) we take into account subsequent terms connected with molecular field which fluctuations cause additional light scattering of a collective character.

5.1 Translational fluctuations

Consider first atomic liquid or molecular liquid composed of

optically isotropic molecules, then

$$a_{ij}^{(p)} = a_p \delta_{ij} \quad (289)$$

We note that in this case the deviator of the isolated molecule (288) vanishes and then Eq.(287) reads

$$D_{ij}^{(p)} = a_p \left\{ \frac{\partial F_i^{(p)}}{\partial E_{0j}} - \frac{1}{3} \delta_{ij} \frac{\partial F_k^{(p)}}{\partial E_{0k}} \right\} \quad (290)$$

which can be described by fluctuations of molecular fields as

$$D_{ij}^{(p)} = a_p \Delta \left(\frac{\partial F_i^{(p)}}{\partial E_{0j}} \right) \quad (291)$$

We arrived at the interesting results implying that for atoms or

optically isotropic molecules, the deviator of the polarizability tensor exists only if fluctuations of molecular fields take place in the liquid . Since the deviator is nonzero then the anisotropic light scattering constant (190) is nonzero as well, and reads (Kielich 1960)

$$S_{aniso} = \frac{1}{30} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p a_q \Delta \left(\frac{\partial F_i^{(p)}}{\partial E_{0j}} \right) \Delta \left(\frac{\partial F_i^{(q)}}{\partial E_{0j}} \right)^* \right\rangle \quad (292)$$

So in atomic fluids and/or in molecular fluids composed of optically isotropic molecules, the fluctuations lead to light scattering of an anisotropic character.

According to Kirkwood–Yvon equation (85) in the first

approximation we obtain

$$D_{ij}^{(p)} = -a_p \sum_{r=1}^N a_r T_{ij}^{(pr)} \quad (293)$$

leading to the following formula for the light scattering constant (292)

$$S_{aniso} = \frac{1}{30} \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{pqrs} a_p a_q a_r a_s T_{ij}^{(pr)} T_{ij}^{(qs)} \right\rangle \quad (294)$$

Binary radial correlations. According to the definition of the dipole interaction tensor, Eq.(93), formula (294) vanishes in the absence of molecular correlations ($p = q = r = s$). In order to get first nonzero result it is sufficient to assume binary interactions in Eq.(294). We have two possibilities, the first one assuming $p = q \neq r = s$ and the second one when $p = s \neq r = q$ both

giving equivalent contributions (since the molecule p polarizes the molecule q in the same way as the molecule q polarizes the molecule p). In this way by (294) in the binary approximation we obtain

$$S_{aniso} = \frac{2}{5} \left(\frac{\omega}{c} \right)^4 a^4 N \left\{ \left\langle r_{pq}^{-6} \right\rangle \right\} \quad (295)$$

where $\left\langle r_{pq}^{-6} \right\rangle$ is defined by Eq.(99).

Ternary radial correlations. Equation (294) consists not only of the just discussed binary correlations but also of ternary and quaternary ones. For ternary correlations we get four nonzero contributions when $p = q \neq r \neq s, p = s \neq r \neq q, r = q \neq p \neq s$ and $r = s \neq q \neq p$. Then we obtain

$$S_{aniz} = \frac{2}{5} \left(\frac{\omega}{c} \right)^4 a^4 N \left\{ \left\langle r_{pq}^{-3} r_{qs}^{-3} \right\rangle + \left\langle r_{pq}^{-3} r_{sp}^{-3} \right\rangle \right\} \quad (296)$$

where the parameters of ternary correlations are given by Eq.(100). As we can see from Eq.(??) as well as from figure V.4 the parameter $\langle r_{pq}^{-3} r_{qs}^{-3} \rangle$ can be positive or negative depending on the angle between the vectors \mathbf{r}_{pq} and \mathbf{r}_{qs} . Then the contribution Eq.(296), resulting from the ternary correlations can increase as well as decrease anisotropic scattering due to binary correlations (295). When three atoms tend to the asymmetric structure (vectors \mathbf{r}_{pq} and \mathbf{r}_{qs} being almost parallel forming angle between 0 and 54 degree or antiparallel, making an angle between 125 and 180 degree) then the parameter (100) is positive and enhances the anisotropic scattering. However, when almost symmetric ternary structures are formed (vectors \mathbf{r}_{pq} and \mathbf{r}_{qs} making angles between 54 and 125 degree) the parameter (42) is negative and weakens the anisotropic scattering. Obviously with increasing density the near neighbor structure of an atomic liquid tends to be increasingly

symmetric (higher than three body correlations have to be taken into account as well) leading to a decrease in the anisotropic scattering. The high pressure measurements of the depolarization ratio (Thibeau 1970. McTague 1971) confirm this conclusion.

6.2 Translational-orientational fluctuations.

For anisotropic molecules the molecular field is given by the expansion (87) of Section IV so then we have

$$\frac{\partial F_i^{(p)}}{\partial E_{0j}} = - \sum_{q=1}^N T_{ik}^{(pq)} a_{kj}^{(p)} + \sum_{q=1}^N \sum_{r=1}^N T_{ik}^{(pq)} a_{kl}^{(q)} T_{lm}^{(qr)} a_{mj}^{(r)} \dots \quad (297)$$

When inserting the first approximation of this expansion into (287)

for the deviator of a molecule immersed in a system we obtain

$$D_{ij}^{(p)} = D_{ij}^{(p)}(0) - \frac{1}{2} \sum_{r=1}^N \left\{ a_{ik}^{(p)} a_{lj}^{(r)} + a_{jk}^{(p)} a_{li}^{(r)} \right\} T_{kl}^{(pr)} + \frac{1}{3} \delta_{ij} \sum_{r=1}^N a_{ij}^{(r)} \quad (298)$$

As we have seen earlier, taking into account the nonzero approximation of the deviation tensor (298) leads to the light scattering due to polarizability anisotropy of molecules as well as to their angular interactions, Eqs (??) and (212). For atoms, $D_{ij}(0)$ vanishes and then the first approximation (298) is nonzero (293) and with the help of (190) leads to Eq.(294), the result describing the anisotropic light scattering due to translational fluctuations.

Now we consider the anisotropic light scattering by a system of anisotropic molecules and in the approximation of the deviator

(111) so in the case when translational and orientational fluctuations overlap. To simplify our calculations we assume that the molecules are of axial symmetry and are characterized by the polarizability tensor of the form Eq.(121). Then by Eq.(190) and Eq.(298) in the binary correlations approximation we obtain (Kielich, Lalanne 1972):

$$S_{aniso} = \frac{1}{5} \left(\frac{\omega}{c}\right)^4 a^2 \kappa^2 N \left\{ 1 + J_K + 4a \left[\frac{1 - \kappa}{\kappa} J_{RK} + 3(1 + \kappa) \right] \right\} \quad (299)$$

where two parameters J_{RK} and K_{RK} of the angular–radial molecular correlations are used

$$J_{RK} = \frac{\rho}{4V} \int \int (3 \cos^2 \theta_p + 3 \cos^2 \theta_q - 2) r_{pq}^{-3} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (300)$$

$$K_{RK} = \frac{\rho}{2V} \int \int (3 \cos\theta_{pq} \cos\theta_p \cos\theta_q - \cos^2\theta_{pq}) r_{pq}^{-3} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (301)$$

Now θ_p and θ_q stand for the angles between the vector \mathbf{r}_{pq} and the symmetry axes \mathbf{k}_p and \mathbf{k}_q , respectively.

In our Eq.(299) the angular correlation parameter J_K is given by Eq.(225). The two new parameters Eq.(300) and Eq.(301) are due to a coupling between the radial and the angular correlations.

Depending of the mutual interaction model of molecules, the parameters Eq.(225), Eq.(300) and Eq.(301) are positive or negative. According to Prins (1957) we have two extreme models of the near-neighbor structure in liquid:

a) paratropizm when molecules are parallel, then the parameters J_k , J_{RK} and K_{RK} are positive.

b) diatropizm when molecules are aligned perpendicularly, then the molecular parameters J_k , J_{RK} and K_{RK} are negative.

6.3 Influence of the size and shape of molecules

In the subsection 2.1 we have discussed the molecular refraction of liquids taking into account the molecular shape and dimensions.

We have introduced there the main effective polarizabilities given by Eq.(82). With the use of these polarizabilities the isotropic

(189) and the anisotropic (190) light scattering constants are of the form suitable for numerical calculations (Kielich, Pieczynska

1970, Burnham 1975)

$$S_{iso}^* = \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{a_1^* + a_2^* + a_3^*}{3} \right)^2 N \gamma_R \quad (302)$$

$$S_{aniso}^* = \frac{N}{90} \left(\frac{2\pi}{\lambda} \right)^4 \left\{ (a_1^* - a_2^*)^2 + (a_2^* - a_3^*)^2 + (a_3^* - a_1^*)^2 \right\} \quad (303)$$

Moreover we have the relations

$$S_{iso}^* = \left(\frac{n^2 + 2}{3} \right)^2 S_{iso} \quad (304)$$

$$S_{aniso}^* = \left(\frac{n^2 + 2}{3} \right)^2 S_{aniso} \quad (305)$$

With the use of these constants we calculate the Rayleigh

coefficient

$$S_R = \frac{1}{2V} (S_{iso}^* + 13 S_{aniso}^*) \quad (306)$$

as well as the depolarization ratio

$$D_n = \frac{6 S_{aniso}^*}{S_{iso}^* + 7 S_{aniso}^*} \quad (307)$$

The experimental values of S_R and D_n are collected in Table V.6, whereas the theoretical data computed with the use of (302)–(307) and (82) are given in Table V.7. We note that none of the models of the local field give a good agreement between the experiment and the theory. Especially large deviations are found for the Rayleigh coefficient. However, no agreement was expected mainly because in our formulas (302)–(307) the radial as well as angular correlations were not considered.

6.4 Determination of angular correlations

The anisotropic light scattering experiments permit measurements of the numerical value of the angular correlation parameter J_K given by Eq.(225). We have two ways of determining the value of J_K : one from the anisotropic light scattering measurements and the second one from the depolarization ratio measurements. The first method has been developed in Bordeaux (Bothorel 1968, Lalanne 1969) and consists in the measurements of the horizontal component of the scattered light for the vertically polarized incident radiation (Fig. V.10)

$$H_v = 3 S_{aniso} \left(\frac{n^2 + 2}{3} \right)^2 I_v \quad (308)$$

With the use of Eq(224) we obtain

$$H_v = \frac{3}{5} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 a^2 \kappa^2 N (1 + J_K) I_v \quad (309)$$

From this formula we get J_K provided that we know H_v (from measurements) as well as the molecular optical anisotropy (170).

From Eq.(236) for the depolarization ratio we have

$$S_{aniso} = \frac{S_{iso} D_n}{6 - 7 D_n} \quad (310)$$

Taking into account Eqs (224) and (256) we obtain

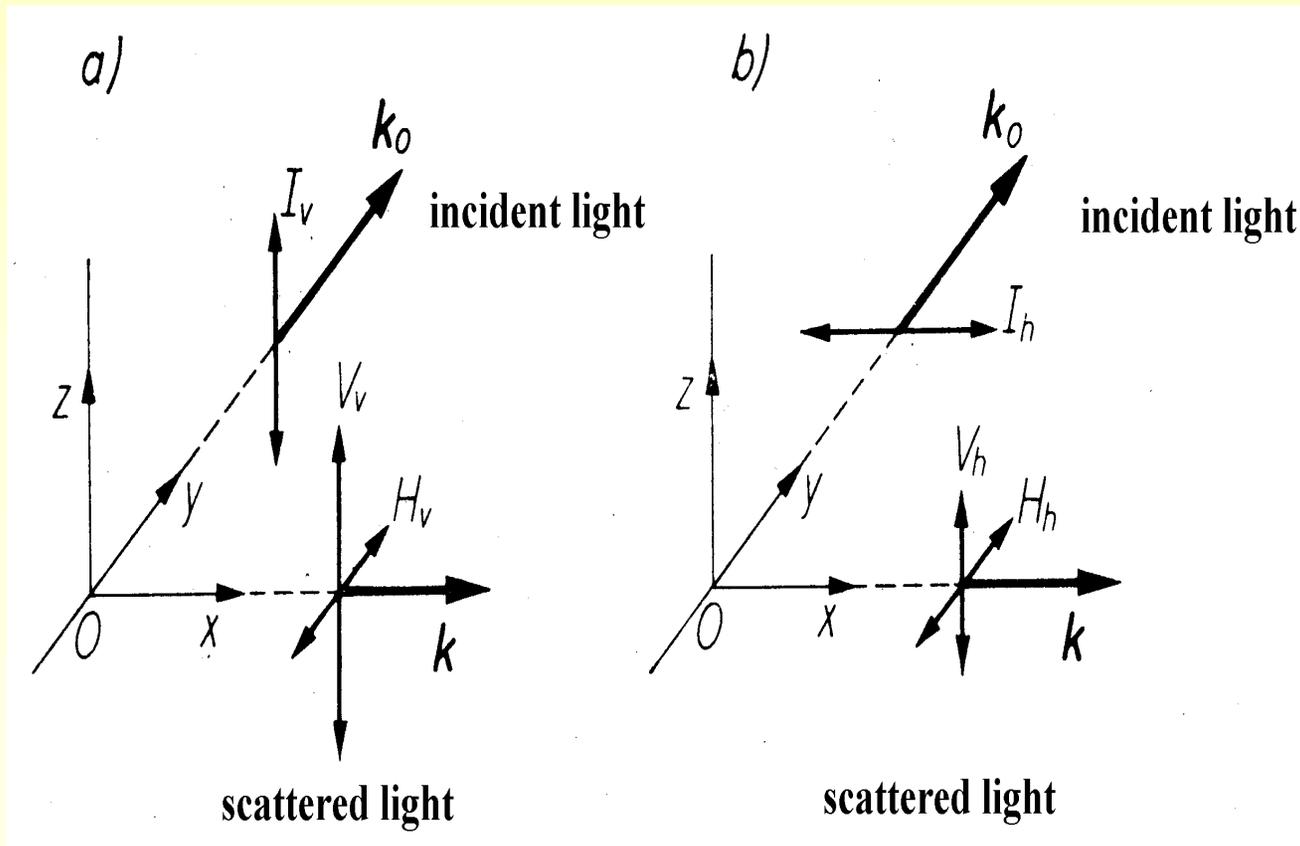
$$1 + J_K = \frac{10 D_n S_R^{iso}}{a^2 \kappa^2 (6 - 7 D_n)} \left(\frac{\lambda}{2\pi} \right)^4 \left(\frac{3}{n^2 + 2} \right)^2 \quad (311)$$

allowing us to get J_K provided that we know D_n and S_R^{iso} from measurements. When we do not know the Rayleigh constant directly from measurements, we can use Eq.(311)

$$S_R^{iso} = \frac{1}{2} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 a^2 \rho k_B T \beta_T \quad (312)$$

getting the particular formula

$$1 + J_K = \frac{5 \rho k_B T \beta_T D_n}{\kappa^2 (6 - 7 D_n)} \quad (313)$$



Rysunek 11: Different components of the scattered light.

where for the determination of the angular correlation parameter J_K we need only the experimental value of the depolarization ratio D_n and the isothermal compressibility parameter β_T . The values of

J_K calculated with the use of Eqs (311) and (313) are collected in Table V.8. The values of J_K obtained by different methods are given in Table V.9 for benzene and in Table V.10 for nitrobenzene.

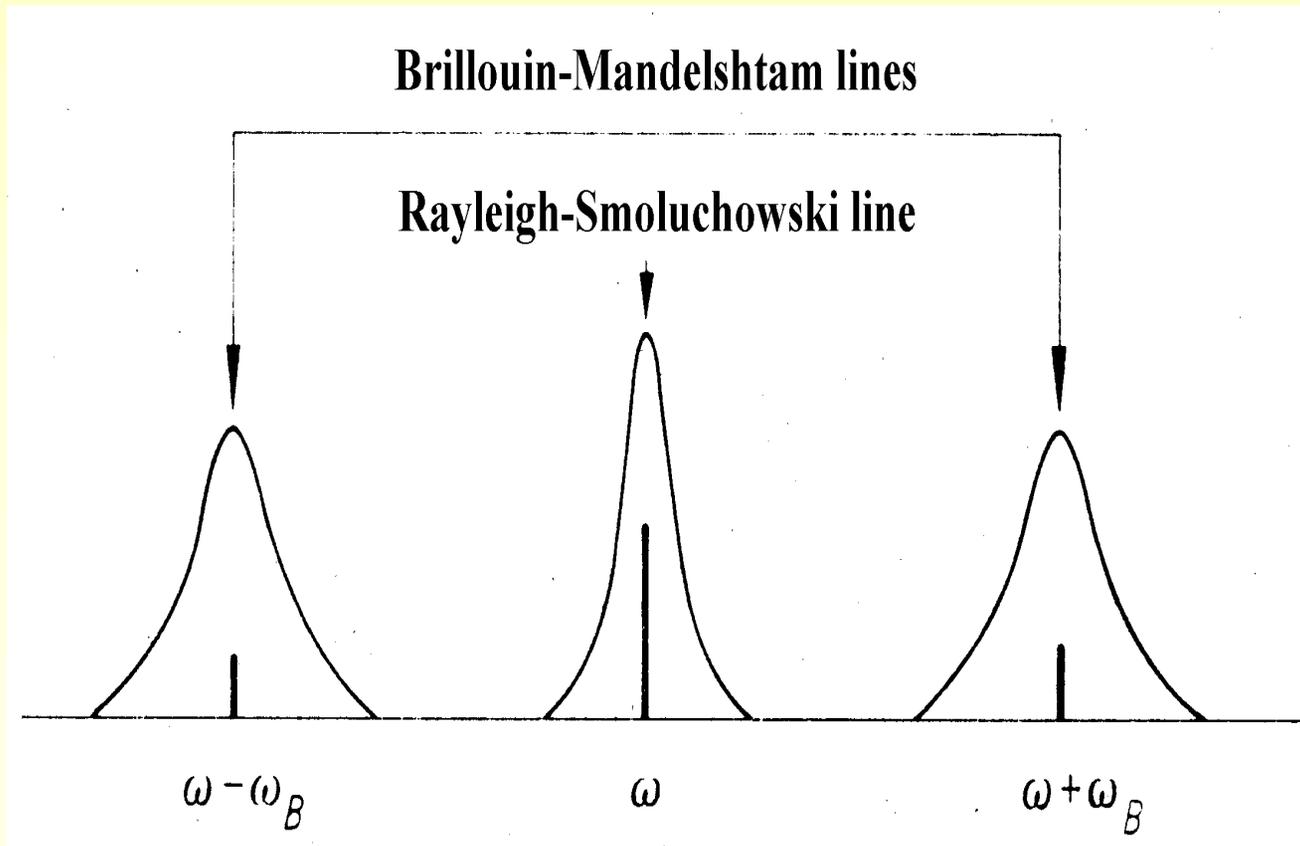
7. STUDIES OF SPECTRAL LINE STRUCTURE OF SCATTERED LIGHT

Up to now we have considered the integral light scattering intensity bearing information on the equilibrium structure of the system. Spectral studies of scattered light provide information about the dynamical structure of liquid due to molecular translational and orientational motions as well as collective motions. The frequency dependence $I(\omega)$ of the intensity of scattered radiation is described by hydrodynamic methods or microscopic methods of statistical

kinetics. In general, the molecular light scattering can be considered as a stochastic process (Smoluchowski 1908, Gabriel 1973).

The opportunities offered by the laser technique led to substantial progress in the light scattering studies, especially in the study of spectral line shape. Usually, the argon laser emitting the light of 4880 Å (of the frequency $4 \cdot 10^{15}$ Hz) is used as an incident light source. The frequency shift of the scattered light is of the range 10 to 10^{14} Hz. The frequency shift of 10 to 10^5 Hz corresponds to the Rayleigh scattering. The frequency changes of the Brillouin scattering are from the range 10^3 to 10^{10} Hz, whereas for the Raman scattering they lie between 10^{11} to 10^{14} Hz (Chu 1970). Several methods have been developed allowing measurements of

the scattered light frequency shifts from the respective range. We, however, are going now to explain the origin of the phenomena leading to the three types processes of light scattering, namely Rayleigh, Brillouin and Raman ones.



Rysunek 12: A spectrum of the light scattered by gaseous system.

7.1 Brillouin-Mandelsztam scattering in liquids

According to Smoluchowski (1908) density fluctuations in gases or

liquids lead to the molecular scattering of light. The other sources of the light scattering are fluctuations of other thermodynamic parameters of the system such as pressure, temperature, concentration as well as molecular orientation. Different statistical fluctuations change in time in a different way and modulate the spectrum of the scattered radiation accordingly. Then, by the Chinczin–Wiener theorem, the time changes of the intensity of scattered radiation follow the respective stochastic processes going on in the scattering system.

According to thermodynamics, the density fluctuations consist of adiabatic fluctuations (pressure fluctuations) and isobaric fluctuations (entropy fluctuations). The isobaric fluctuations lead to the central Rayleigh–Smoluchowski line of the intensity I_{RS} .

Moreover in the scattered light, symmetrically to the Rayleigh–Smoluchowski line, the density fluctuations bring about

two additional components (fig. V.11), predicted by Brillouin (1922) and Mandelsztam (1926). The Brillouin–Mandelsztam doublet of the intensity I_{BM} has been discovered in liquids by Gross (1930).

In the process of inelastic two-photon scattering the following rule of the energy conservation is fulfilled

$$\hbar\omega = \hbar\omega_0 \pm \hbar\Omega \quad (314)$$

together with the momentum conservation rule

$$\hbar\mathbf{k} = \hbar\mathbf{k}_0 \pm \hbar\mathbf{u} \quad (315)$$

According to these rules, the scattering of light involves in the inelastic collisions of the incident photon $\hbar\omega_0$ and the thermal excitation quantum $\hbar\Omega$ in which the scattered photon $\hbar\omega$ arouse

(see Eq.(314)). In a solid state the Raman scattering consists in interaction of photons and phonons –quanta of crystal lattice vibrations. In particular, the scattering on acoustical phonons is called the Brillouin– Mandelsztam process. It is possible as well the scattering of quanta of other collective excitations e.g. magnons, polaritons, crystal defects.

As it can be seen from figure V.12, the \mathbf{u} vector value depends on the scattering angle θ

$$u^2 = k_0^2 + k^2 - 2 k_0 k \cos\theta = (k - k_0)^2 + 4 k_0 k \sin^2 \frac{\theta}{2} \quad (316)$$

For a large value of the scattering angle, u is of the order of k_0 and k , whereas for small scattering angles Eq.(316) reduces to the form given by Eq.(193) since $k_0 \approx k = \frac{2\pi}{\lambda}$. This result is analogous to the Bragg conditions for X ray scattering.

Landau and Placzek have explained the simultaneous existence of three lines in the light scattering spectrum and have shown that their intensities obey the following relation

$$\frac{I_{RS}}{2 I_{BM}} = \frac{C_p - C_v}{C_v} = \frac{C_p}{C_v} - 1 \quad (317)$$

where C_p and C_v denote the heat capacity at a constant pressure and volume, respectively.

Numerous observations have shown that the value of $\frac{I_{RS}}{2 I_{BM}}$ is higher than that resulting from the theoretical relation of Landau–Placzek, Eq.(317). In order to explain this divergence Fabelinskij (1955) proposed the following formula

$$\frac{I_{RS}}{2 I_{BM}} = K \left(\frac{\alpha_p^2 T}{\rho C_p \beta_S} \right) \quad (318)$$

where

$$K = \frac{\left(\frac{1}{\alpha} \frac{\partial \epsilon}{\partial T}\right)_p^2}{\left(\rho \frac{\partial \epsilon}{\partial \rho}\right)_S^2} \quad (319)$$

with $\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ standing for the thermal volume expansion coefficient over constant pressure, whereas $\beta_p = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_S$ denotes the adiabatic compressibility coefficient.

For the thermal β_T and adiabatic β_S compressibility coefficients the following relation holds

$$\beta_T = \beta_S + \frac{\alpha_p^2 T}{\rho C_p} = \frac{C_p}{C_v} \beta_S \quad (320)$$

Then we can rewrite Eq.(318) in the form

$$\frac{I_{RS}}{2 I_{BM}} = K \left(\frac{\beta_T}{\beta_S} - 1 \right) = K \left(\frac{C_p}{C_v} - 1 \right) \quad (321)$$

different from Eq.(317) by the coefficient K given by formula (319). The value of K is generally higher than one e.g. for water $K=1.7$. The differences between Eqs (317) and (321) are much greater in the presence of dispersion, since K depends on frequency through the electric permittivity frequency dependence, $\epsilon(\omega)$. This problem has been studied by Fabielinskij (1955, 1968), Cummins (1966) and Mountain (1966).

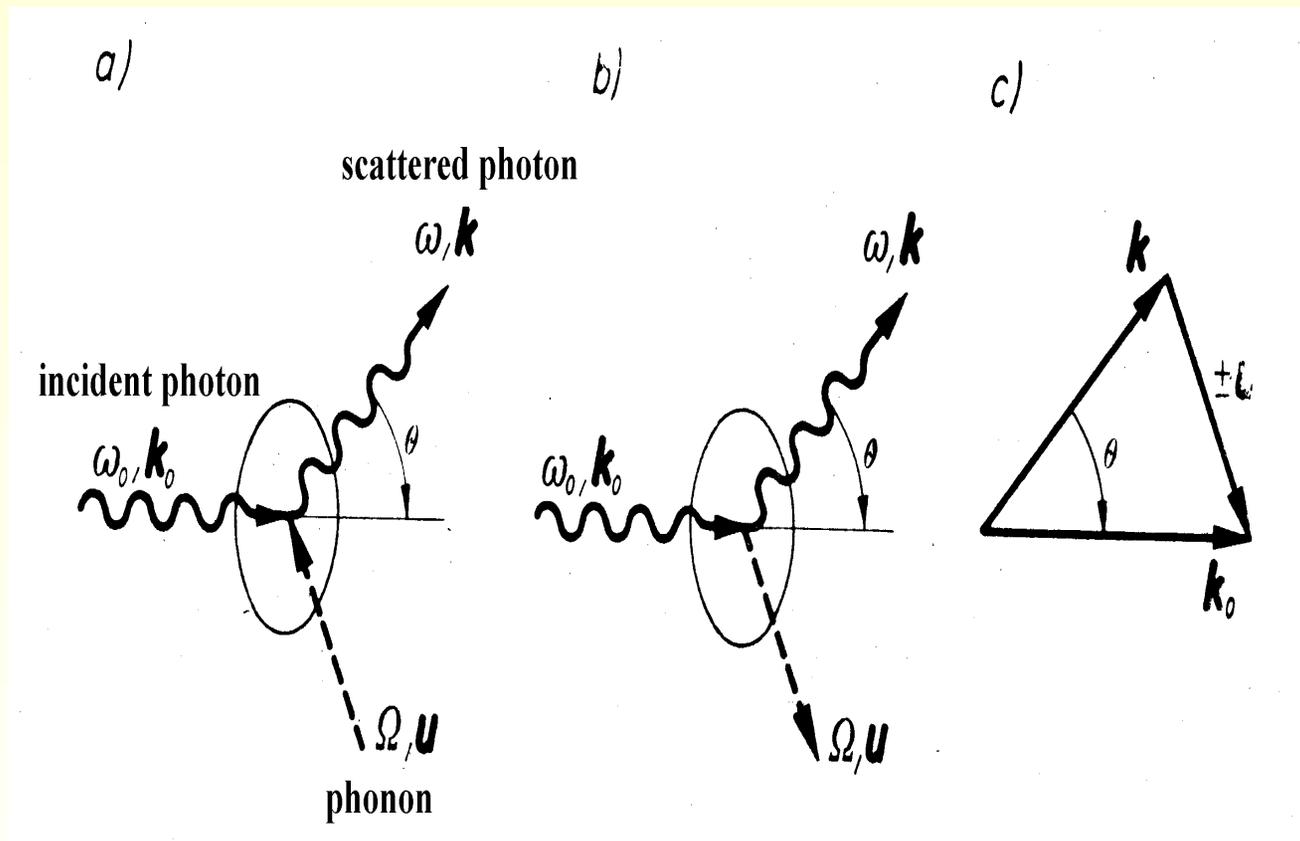
7.2 Doublet of depolarized light scattering spectrum

The Brillouin–Mandelstam doublet concerns the polarized light scattering component of isotropic systems. As far as this component is concerned, the broadening of the Rayleigh line as well as the Brillouin spectrum results from translational molecular motion. In order to get some information about molecular rotational motions, we have to study the depolarization of scattered radiation (see Fig.10)

Cabannes (1928) and Raman and Krishnan (1928) were the first to start the spectral study of the Rayleigh light scattering in liquids. Fabielinskij (1967) and Stoicheff (1968), who studied the fine structure of the molecular liquid light scattering spectra, with the help of the laser beam, reported on the existence of a doublet in the depolarized component of the scattering radiation. This doublet is observed in the spectrum of light scattered at an angle θ different than 0 and 180 degrees with special polarizations of the

incident and scattered beams respectively (Fig. V.12). This doublet is symmetric according to the zero frequency shift of the scattered intensity and its splitting is of the order of 0.5 GHz. The advantages of laser spectroscopy permitted observations of the doublet in light scattering spectra of several liquids composed of optically anisotropic molecules (Zajcev 1972, Tiganov 1972, Stegman 1973, Dardy 1973, Alms 1973, 1974, Enright 1974, Starunov 1974, Bucaro 1974, Bauer 1975, Searby 1975). The doublet light scattering angle dependence as well as its temperature and concentration (in the case of mixtures) dependence has also been examined. The fine structure investigation has substantially extended the already performed studies of the Rayleigh light scattering wings (Fabielskij 1968, Sabirov 1974, Kriwochiza 1974, Schwartz 1974). The light scattering spectra of synthetic and

biological macromolecular solutions (Pecora 1972, Peticolas 1972) and liquid crystals (Alms 1974, Gierke 1974, Flygare 1974, Pusey and Jakeman 1975) have also been investigated.



Rysunek 13: Kinematics of two-photon light scattering processes.

The existence of the depolarized light scattering doublet was predicted by Leontowicz (1941) with the use of the Maxwell hydrodynamical model of the liquid viscosity. The Leontowicz theory, however, describes the frequency shift of the Rayleigh line in the range of low temperatures only. Rytov(1957) extended the Leontowicz's theory and described the behavior of the Rayleigh wing for arbitrary temperature. The Leontowicz–Rytow theory is based on the assumption that the Rayleigh wing and its doublet is caused by anisotropy fluctuations and shear deformation of the liquid (deformacji scinania cieczy). For the Rayleigh wing far from the Brillouin–Mandelsztam doublet Leontowicz (1928) obtained the following form of the light scattered spectral distribution

$$I(\omega) = A \frac{k_B T}{\mu} \frac{\tau_B}{1 + \omega^2 \tau_B^2} \quad (322)$$

where A —constant, $\mu = \frac{\eta}{\tau_B}$ —sheer module (modul scinania??), η liquid viscosity and τ_B reorientation correlation time given by Eq.(??) of section IV. Then the spectrum of scattered light, Eq(322), is given by the Lorentz function.

The Leontowicz–Rytow theory gives the following formulas for the spectral shape of depolarized components of the light scattered by viscous liquid

$$V_h(\omega, \theta) = H_v(\omega, \theta) = 2B \left\{ \frac{\tau_B}{1 + \omega^2 \tau_B^2} \sin^2 \frac{\theta}{2} + \frac{\omega^2 \tau_B}{\omega^2 + (\omega^2 - \omega_T^2)} \right. \\ \left. (323) \right.$$

$$H_h(\omega, \theta = 90^0) = \frac{B}{2} \left\{ \frac{\tau_B}{1 + \omega^2 \tau_B^2} + \frac{3(\omega^2 - \omega_L^2)^2 \tau_B}{(\omega^2 - \omega_L^2)^2 + (\omega^2 - \omega_S^2)^2 \omega} \right\} \quad (324)$$

with

$$\omega_S^2 = \omega_L^2 + \frac{4}{3} \omega_T^2$$

where $\omega_L = u(\beta \rho)^{-1/2}$ stands for the frequency of longitudinal vibrations, $\omega_T = u \left(\frac{\mu}{\rho} \right)^{1/2}$ for the frequency of the transverse vibrations and u is given by Eq.193).

In Eq.(323) the first term gives the Lorentz contour and vanishes for $\theta = 0$ (forward scattering). The second term gives the doublet due to sheer waves (fale scinajace??) and can be composed of two Lorentz's contours. The doublet is absent where $\theta = 180^0$ (backward scattering) and it dominates in the depolarized

component, Eq.(323), for small scattering angles $\theta < 90^0$.

However, for $\theta > 90^0$ the first term of Eq.(323) of the Lorentz's function type predominates. The horizontal component, Eq.(324), exists only for $\theta = 90^0$ and its first part is of the Lorentz's function shape. The existence of the doublet is a consequence of the coupling between anisotropic fluctuations and longitudinal waves.

For the vertical component the Rytov theory gives

$$V_v(\omega) = \frac{4}{9} H_h(\omega) = \frac{16 B}{9} \frac{\tau_B}{1 + \omega^2 \tau_B^2} + \frac{[B_1 \omega_L^2 \omega_T^2 + (B_2 \omega_L^2 + E)]}{(\omega^2 - \omega_L^2)^2 + (\omega^2 \tau_B^2)^2} \quad (325)$$

Then the spectral distribution of scattered light strongly depends on the frequency of longitudinal ω_L as well as transversal ω_T vibrations, the relaxation time τ_B and phenomenological constants

B, B_1, B_2, B_3 .

In the frequency range of the spectrum far from its fine structure features Eqs (323–325) give the Rayleigh wing spectral distribution. Then because of $\omega_L \ll \omega$ and $\omega_T \ll \omega$ we have

$$V_h(\omega) = H_v(\omega) = H_h(\omega) = 2B \frac{\tau_B}{1 + \omega^2 \tau_B^2} \quad (326)$$

$$V_v(\omega) = \frac{8}{3} B \frac{\tau_B}{1 + \omega^2 \tau_B^2} = \frac{4}{3} H_h(\omega) \quad (327)$$

In this special case the depolarization ratio of unpolarized light does not depend on the frequency

$$D_n = \frac{H_v + H_h}{V_v + V_h} = \frac{6}{7} \quad (328)$$

Voltera (1969) took into account in thermodynamic Leontowicz's theory the coupling between molecular reorientation and sheer

waves due to thermal fluctuations. In this way for molecular liquids he got a better agreement between the theory and the high temperature light scattering spectral experimental results. Starunow and Fabielinskij (1974) carried out the analyze of structure of the scattered radiation spectrum with the use of Rytov's theory taking into account two anisotropic relaxation times. The hydrodynamic theory of spectral light scattering was developed by Chung (1971), Ailawadi (1971) and Lekkerkerker (1973).

7.3. Inelastic translational scattering by simple gases and liquids

It has been experimentally shown that simple gases (e.g. CH_4) and liquids (e.g. CCl_4) composed of optically isotropic molecules

depolarize the scattered radiation (Cabannes 1929). This phenomena can be described by the Silberstein's theory already given in Section III. By Eqs (??) and (??) derived there for the mean polarizability $a(r)$ and the anisotropy $\gamma(r)$ of the pair polarizability tensor of two atoms or molecules separated by r , we have

$$a(r) = \frac{1}{3} \left\{ a_{||}(r) + 2 a_{\perp}(r) \right\} = \frac{2 a (1 - a r^{-3})}{1 - a r^{-3} - 2 a^2 r^{-6}} \quad (329)$$

$$\gamma(r) = a_{||}(r) - a_{\perp}(r) = \frac{6 a^2 r^{-3}}{1 - a r^{-3} - 2 a^2 r^{-6}} \quad (330)$$

With the use of Eq.(241) for the depolarization ratio we obtain (Wolkensztain 1951)

$$D_n = \frac{6 \gamma(r)^2}{45 a(r)^2 + 7 \gamma(r)^2} \quad (331)$$

Then according to Eqs (329) and (330) we have

$$D_n = \frac{6 a^2 r^{-6}}{5 - 10 a r^{-3} + 12 a^2 r^{-6}} \quad (332)$$

As follows from this formula, the scattered light depolarization ratio of a real gas depends on the mean polarizability of its atoms and on the distance between them. Equation (332) applies to low density gases in which only pair collisions take place. In more compressed gases and in liquids many-body collisions should be considered as it was already said in Section 6.1.

In the inelastic light scattering the polarizability changes of (329) and (330) are important

$$\left\{ \frac{\partial a(r)}{\partial r} \right\}_{r=r_0} = - \frac{12 a^3 (2 r_0^{-7} - a r_0^{-10})}{(1 - a r^{-3} - 2 a^2 r^{-6})^2} r_0 \quad (333)$$

$$\left\{ \frac{\partial \gamma(r)}{\partial r} \right\}_{r=r_0} = - \frac{18 a^2 (r_0^{-4} - 2 a r^{-10})}{(1 - a r^{-3} - 2 a^2 r^{-6})^2} \quad (334)$$

Then the depolarization ratio reads (Wolkensztain 1951)

$$D'_n = \frac{6 (1 + 2 a^2 r_0^{-6})^2}{20 a^2 (2 r_0^{-3} - a r_0^{-6})^2 + 7 (1 + 2 a^2 r_0^{-6})^2} \quad (335)$$

Cabannes and Rousset (1940) for the first time compared these formulas with the experimental data finding significant disagreement for some molecules.

Levine and Birnbaum (1968) suggested that the polarizability changes mainly arise during collisions when the symmetry of the electronic structure of atoms and spherical molecules is distorted. For binary interactions these changes are anisotropic and lead to

the depolarization of the scattered radiation. Levine and Birnbaum assumed the following short range $a(r)$ and $\gamma(r)$

$$a(r) = A_1 \exp \{-b_1(r)\} \quad (336)$$

$$\gamma(r) = A_2 \exp \{-b_2(r)\} \quad (337)$$

implying that

1) $a(r) \rightarrow 2a$ when $r \rightarrow \infty$ moreover $a(r)$ has the finite value at $r \rightarrow 0$

2) $\gamma(r) \rightarrow 0$ when $r \rightarrow \infty$ and it takes the finite value at $r \rightarrow 0$

McTague and Birnbaum (1968, 1971) reported the first measurements of the depolarized light scattering in argon and krypton. This new type of the inelastic collision-induced light scattering as well as its spectral distribution were investigated in

several gases as a function of density and temperature (Birnbbaum 1968, 1971, Thibeau 1970, 1972, Lallemand 1970, Irwin and May 1972, Keijser 1974, Oksengorn 1974, Watson 1974, Shelton 1975, Barocchi 1975). The study has shown that the anisotropy of the induced pair polarizability of colliding atoms can be given by

$$6 a^2 r^{-3} + B r^{-p} \quad \text{Levine(1971)} \quad (338)$$

$$6 a^2 r^{-3} - \lambda \exp(-r/r_0) \quad \text{O'Brien(1973)} \quad (339)$$

where B, p, λ and r_0 are some constants characterizing electron clouds penetration. The term $6 a^2 r^{-3}$ results from the long range dipole–induced dipole Silberstain’s model whereas the second short range, DID independent term arises from the deformation of the electron cloud during collision. The numerical calculations of

collision–induced polarizabilities for pairs of helium, neon, argon and hydrogen have also been performed (Du Pré 1969, Levine 1972, O’Brien 1974, Harris 1974, Baron 1974, Lallemand 1974).

The light scattering due to the polarizability changes has been also observed in atomic liquids (McTague 1969, Gornal 1970, Simic-Glavaski 1971, Fleury 1973, Schoen 1975) and in simple molecular liquids (Bucaro 1971, Tabisz 1972, Ho 1973, Barocchi 1974, Bruining 1975, Trappeniers 1975).

The anisotropic light scattering intensity due to radial and/or molecular correlations is a function of density and reads in the form of expansion (Kielich 1962, 1971, McTague 1973)

$$I_A(\omega, \rho) = I_2(\omega) \rho^2 + I_3(\omega) \rho^3 + I_4(\omega) \rho^4 + \dots \quad (340)$$

where the subsequent terms are connected to binary, ternary and quaternary correlations, respectively. The individual terms of Eq.(340) have been calculated by several authors with the use of simple microscopic models (Kielich 1971, Levis 1972, Alder 1973, Berne 1973, Gelbart 1973, Mahan 1973, Mc Court 1973, Ralph 1974, Wozniak 1975). These models and details of the calculations are described in the review given by Gelbart (1974).

In fact the collisional inelastic light scattering considered is a new kind of translational Raman scattering (Birnbaum 1968, 1971, Gelbart 1973). The translational Raman scattering results from polarizability changes of atoms and/or molecules due to their collisions and/or interactions. Contrary to the translational Raman scattering, the ordinary Raman scattering is due to internal

molecular motion of multi-atomic molecule, its internal vibrational motions and the rotational motion.

Holzer (1974) reported the observation in gaseous CF_4 and SF_6 forbidden Raman transitions (vibrational bands) due to collisional scattering. The first theoretical explanation of this process was given by Samson (1975). Greytak (1969) investigated the spectrum of scattered radiation by liquid helium. The theory of this phenomena was given by Stephan (1969).

The hitherto observations of the translational Raman effect have shown its following frequency dependence

$$I(\omega) = I_0 \exp\left(-\frac{\omega}{\Delta}\right) \quad (341)$$

with Δ inversely proportional to the time of collision. The frequency range of these spectra ($10^{11} - 10^{13}$ Hz) corresponds to the collisional times of $10^{-14} - 10^{-12}$ s. According to the equation (340) the translational spectra strongly depend on gas density (or pressure) (Thibeau 1970). Studies of translational spectra have led to a new effective method of analysis of the intermolecular interaction, in particular their dynamics.

7.4 Spectral statistical–molecular theory of scattered light

The spectral statistical–molecular theory of light scattering applies the stochastic formalism of Van Hove (1954) and Mori (1955). Applying methods of the correlation function Ben–Reuven and Gershon (1969) formulated the spectral statistical theory of light

scattering which, in the case of the integrated intensity gives the results of Kielich (1960, 1967) and Pecora and Steele (1965). Ben-Reuven and Gershon applied their theory for the microscopic description of the depolarization of the Rayleigh wing. The theory of the Rayleigh wing depolarization was given by Pecora (1968), Andresen and Pecora (1971), Keyes and Kivelson (1971, 1972), Gershon and Oppenheim (1973), Keyes (1975) and Alms (1973). The consequent microscopic theory of the isotropic Rayleigh scattering was formulated by Gabriel (1973) in the stochastic approach. All these theories are not equivalent and there were a lot of discussion which one is the best for description of the light scattering spectra of anisotropic molecules. Not going into all these details we give here an outline of the formal statistical-molecular theory of light scattering spectra.

Analogously to the light scattering tensor, Eq.(186), we define for the time t

$$I_{ij}^R(t) = \frac{1}{2c^4} \left\langle \ddot{M}_i(t + t_0) \ddot{M}_j^*(t_0) \right\rangle \quad (342)$$

where the electric dipole moment induced by the laser field of the form $\mathbf{E}(t) = \mathbf{E}(0) \exp(-i\omega t)$ reads

$$M_i(t) = \sum_{p=1}^N a_{ik}[\tau_p(t)] E_{0k}(t) \exp[i\mathbf{u} \cdot \mathbf{r}_p(t)] \quad (343)$$

where $\tau_p(t) = \Omega_p(t)$, $\mathbf{r}_p(t)$ stands for the set of configurational variables defining the orientation $\Omega_p(t)$ and position $\mathbf{r}_p(t)$ of the molecule p at time t .

By the Wiener–Chinczin theorem we have

$$I_{ij}(t) = \int I_{ij}(\omega) \exp[-i\omega t] d\omega \quad (344)$$

where the spectral density of the light scattering tensor reads

$$I_{ij}(\omega) = \frac{1}{2\pi} \int I_{ij}(t) \exp[i\omega t] dt \quad (345)$$

In particular for the integrated intensity for the light scattering tensor we obtain

$$I_{ij} = \int I_{ij}(\omega) d\omega \quad (346)$$

According to Eqs (342) and (343) we write for t_0

$$I_{ij}(t) = \left(\frac{\omega}{c}\right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_{ik}[\tau_p(t)] a_{jl}^*[\tau_q(0)] \exp \{i \mathbf{u} \cdot [\mathbf{r}_p(t) - \mathbf{r}_q(0)]\} \right\rangle \quad (347)$$

where

$$I_{kl}^0(t) = \frac{1}{2} E_{0k}(t + t_0) E_{0l}^*(t_0) \quad (348)$$

is the incident light tensor at the moment of time t .

For simplicity, we assume that the polarizability tensor depends only on the orientational molecular variable $a_{ik}[\Omega_p(t)]$. It excludes from our considerations the changes of the polarizability tensor due to translational motion.

For $p = q$ the light scattering tensor, Eq.(347) describes the incoherent light scattered by a system of N statistically independent molecules. In other words it brings the light scattered by individual molecules of the system

$$I_{ij}^C = N \left(\frac{\omega}{c} \right)^4 \left\langle a_{ik}[\tau(t)] a_{jl}^*[\tau(0)] \exp \{i \mathbf{u} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]\} \right\rangle I_{kl}^0(t) \quad (349)$$

The second part of the tensor, Eq.(347), calculated for $p \neq q$ gives the coherent radiation scattered on the statistically correlated

molecules of the system.

$$I_{ij}^C = N \left(\frac{\omega}{c} \right)^4 \left\langle \sum_{q \neq p}^N a_{ik}[\tau_p(t)] a_{jl}^*[\tau_q(0)] \exp \{ i \mathbf{u} \cdot [\mathbf{r}_p(t) - \mathbf{r}_q(0)] \} \right\rangle \quad (350)$$

In order to perform the statistical averaging of Eqs (349) and (350) we have to know the distribution function $G(\mathbf{r}, \Omega, t)$ giving the changes of position and orientation of molecules in time. It is a subject of statistics of non-equilibrium states to search for functions of this kind. In the simplest case such a function is given by the free diffusion equation

$$\left(\frac{\partial}{\partial t} - D \Delta \right) G(\mathbf{r}, \Omega, t) = 0 \quad (351)$$

where D stands for the free diffusion coefficient.

The function $G(\mathbf{r}, \Omega, t)$ gives us the probability ...????!!!. For

statistically independent molecules we separate the distribution function $G(\mathbf{r}, \Omega, t)$ into the part $G_T(\mathbf{r}, t)$ describing translational motions and the part $G_R(\Omega, t)$ dealing with orientational motion.

$$G(\mathbf{r}, \Omega, t) = G_T(\mathbf{r}, t) G_R(\Omega, t) \quad (352)$$

Next we assume the two equations

$$\left(\frac{\partial}{\partial t} - D_T \Delta_r \right) G_T(\mathbf{r}, t) = 0 \quad (353)$$

$$\left(\frac{\partial}{\partial t} - D_R \Delta_\Omega \right) G_R(\Omega, t) = 0 \quad (354)$$

From these formulas we get separately two distribution functions $G_T(\mathbf{r}, t)$ and $G_R(\Omega, t)$, where Δ_r and Δ_Ω denote the radial and angular part of the Laplace operator, respectively.

Translational Brownian motion. The general solution of Eq.(353) is of the form given by Smoluchowski

$$G(r, t) = (4 \pi D_T t)^{-3/2} \exp \left(- \frac{r^2}{4 D_T t} \right) \quad (355)$$

where the translational diffusion coefficient is given by

$$D_T = \frac{k_B T}{W_r} \quad (356)$$

with W_r standing for the friction constant of a system. Taking the Stokes formula for the friction constant

$$W_r = 6 \pi r_0 \eta \quad (357)$$

of the translational motion of the r_0 radius sphere in a system of

the viscosity η for D_T we obtain

$$D_T = \frac{k_B T}{6 \pi r_0 \eta} \quad (358)$$

With these assumptions only the interference factor of Eq.(349) depends on \mathbf{r} , then by Eq.(355) we obtain

$$g(t) = \left\langle \exp \{i \mathbf{u} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]\} \right\rangle = \exp (-u^2 D_T t) \quad (359)$$

Assuming optically isotropic molecules and using Eq.(359) we reduce Eq.(349) to the form

$$I_{ij}^{IC}(t) = N a^2 \left(\frac{\omega}{c} \right)^4 g(t) I_{ij}(0) \quad (360)$$

Now we rewrite our function $g(t)$ in the form

$$g(t) = \exp \left(- \frac{t}{\tau_T} \right) \quad (361)$$

We define here the translational relaxation time

$$\tau_T = (u^2 D_T)^{-1} \quad (362)$$

Inserting Eq.(360) into Eq.(345) for the spectral density light scattering tensor by atoms or optically isotropic molecules we obtain

$$I_{ij}^{iso}(\omega) = \frac{1}{\pi} S_{iso}^{gas} I_{ij}^0 \frac{u^2 D_T}{\omega^2 + (u^2 D_T)^2} \quad (363)$$

where we use Eq.(205) for the isotropic light scattering constant. According to Eq.(363) our spectrum is of the Lorentz shape and can be transformed to

$$I_{ij}^{iso}(\omega) = \frac{1}{\pi} S_{iso}^{gas} I_{ij}^0 \frac{\tau_T}{1 + (\omega \tau_T)^2} \quad (364)$$

We note that the translational diffusion leads to very small frequency shifts of scattered light. To reveal such a small

frequency shifts the high resolution laser optical mixing technique is used. The translational spectra studied by optical mixing methods give us the information on the slow thermal molecular motions of times lower than 10^{-6} s.

Arecchi (1967) started studies of statistical properties of translational Brownian motion by the photon counting method using the He–Ne laser beam of 6328 Å. These investigations of the scattered light give information on the statistical properties of light as well as on the statistical properties of the scattering system (Shen 1967, Jakeman and Pike 1969, Mandel 1969, Di Porto 1969, Tartaglia and Chen 1973, Jakeman and Pusey 1975).

Rotational Brownian motion. The rotational diffusion equation

(354) has the general solution of the form ($l = 1, 2, \dots$)

$$G_R(\Omega, t) = \Omega^{-1} \sum_{lm} (2l + 1) Y_{lm}(\Omega) \exp\left(-\frac{t}{\tau_R^l}\right) \quad (365)$$

where Y_{lm} denotes the spherical harmonics function and

$$\tau_R^l = \frac{1}{l(l+1)D_R} \quad (366)$$

are the rotational relaxation time of the order l .

The rotational diffusion coefficient reads

$$D_R = \frac{k_B T}{W_R} = \frac{k_B T}{8 \pi r_0^3 \eta} \quad (367)$$

where we assumed the Stokes relation

$$W_R = 8 \pi r_0^3 \eta \quad (368)$$

for the rotational friction coefficient of a particle in a viscous system.

The Eq.(366) can be rewritten as

$$\tau_R^l = \frac{2 \tau_D}{l(l+1)} \quad (369)$$

where $\tau_D = \tau_R^1$ is the Debye's dipolar relaxation time given by Eq.(??) of Section IV.

Taking into account Eqs(352),(359) and (359)for the light scattering tensor components we obtain

$$V_v(t) = S_{iso}^{gas} g(t) I_v + \frac{4}{3} H_v(t) \quad (370)$$

$$H_v(t) = 3 S_{aniso}^{gas} g(t) \exp\left(-\frac{t}{\tau_B}\right) I_v \quad (371)$$

where the anisotropic light scattering constant is given by Eq.(222). Using Eqs (345) and (370) we obtain the formulas of Pecora (1968)

$$V_v(\omega) = \frac{1}{\pi} S_{iso}^{gas} \frac{u^2 D_T}{\omega^2 + (u^2 D_T)^2} I_v + \frac{4}{3} H_v(\omega) \quad (372)$$

$$H_v(\omega) = \frac{3}{\pi} S_{aniso}^{gas} \frac{u^2 D_T + 6 D_R}{\omega^2 + (u^2 D_T + 6 D_R)^2} I_v \quad (373)$$

We note that in the case of optically anisotropic molecules the light scattering depolarized component depends simultaneously on both translational and orientational motions.

In the simple Debye-Stokes model between the rotational and

translational diffusion coefficients are interrelated:

$$D_R = \frac{3}{4 r_0^2} D_T \quad (374)$$

so for molecules of small linear dimension

$$6 D_R \gg u^2 D_T \quad (375)$$

$$H_v(\omega) = \frac{3}{\pi} S_{aniso}^{gas} \frac{6 D_R}{\omega^2 + (6 D_R)^2} I_v \quad (376)$$

When we deal with the rotational diffusion only, the time dependent part of Eq.(365)

$$R_l(t) = \exp\left(-\frac{t}{\tau_R^L}\right) \quad (377)$$

in the frequency domain reads (Egelstaff 1970)

$$R_l(\omega) = \frac{1}{\pi} \frac{l(l+1) D_R}{\omega^2 + [(l(l+1) D_R)]^2} = \frac{1}{\pi} \frac{\tau_R^l}{1 + (\omega \tau_R^l)^2} \quad (378)$$

For $l = 2$ this function gives the depolarized spectrum, Eq(373).

For asymmetric molecules we write the diffusion equation in the form

$$\frac{\partial}{\partial t} G(\mathbf{r}, \Omega, t) = D_{ij} \nabla_i \nabla_j G(\mathbf{r}, \Omega, t) \quad (379)$$

where D_{ij} are the components of the free diffusion tensor. The general solution of Eq.(379) is highly complicated and takes the readable form only when the diffusion tensor is of the diagonal form (Favro 1960, Steele 1963). In particular, for molecules of cylindrical symmetry ($D_{11} = D_{22}$) the rotational part of the distribution

function, Eq.(365) depends on the relaxation times given by

$$\tau_m^l = \left\{ l(l+1) D_{11} + m^2 (D_{33} - D_{11}) \right\}^{-1} \quad (380)$$

For axially symmetric molecules we have only one depolarized line of the Lorentz type, Eq(376). The spectrum for molecules of low symmetry is a sum of Lorentz's type lines (Pecora 1968).

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