

## CLASSICAL AND WAVE MECHANICAL THEORY OF RAYLEIGH SCATTERING

By

L. JÁNOSSY

CENTRAL RESEARCH INSTITUTE OF PHYSICS, BUDAPEST

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The theory of the incoherent scattering of light by a volume of gas is discussed. It is shown that the wave mechanical treatment contains difficulties; the scattering process cannot be accounted for alone by the density fluctuation of an ensemble of atoms described by a collective wave function.

### Introduction

The passage of an electromagnetic wave through a gas can be treated satisfactorily by classical theory. The atoms of the gas are forced to oscillate under the influence of the electromagnetic field acting upon them. The superposition of the radiation emitted by the atoms upon the primary radiation field gives rise to the optical effects of refraction, also incoherent radiation is produced, which may be called the Rayleigh scattering.

The effect of refraction is obtained by averaging the effects of the atoms; a satisfactory treatment of these effects is obtained if one replaces the atoms by smoothed out polarizable material.

The incoherent scattering is caused by the microscopic fluctuations of the density which is obtained considering the atoms to be concentrated packets distributed at random.

While the wave mechanical treatment of refraction is quite straightforward (see e.g. [1]) — in connection with the incoherent scattering a peculiar problem arises. The scattered intensity is produced by isolated scattering centres distributed at random. In the wave mechanical description the atoms — even if they were concentrated at an initial moment into packets — are expected to diffuse rapidly. In fact the atoms of a gas enclosed into a box are expected, in the course of short time, to diffuse and ultimately to spread out with nearly uniform density over the whole of the volume of the container.

The question thus arises — is it possible at all to account for the incoherent scattering by pure wave mechanics — or is it necessary to add to wave mechanics other features (e.g. second quantisation) so as to account for phenomena which seem to arise from the action of atoms concentrated into small packets?

The question is certainly not trivial. Presently we show that the wave mechanical treatment of an ensemble of atoms leads to expect density fluctuations, which give rise to incoherent scattered radiation. However, the wave mechanical fluctuations differ from the classical fluctuations and they give rise to much smaller scattered intensity than the observed intensity (which agrees with the intensity calculated by the classical theory).

We show thus in this paper that the wave mechanical theory of incoherent scattering is not caused simply by the wave mechanically expected density fluctuation of a gas. This negative result in itself seems to be of interest. We hope to come back to the full wave mechanical treatment of the process in a later publication.

### Part I

#### *The classical theory of incoherent scattering*

A wave incident on an ensemble of atoms produces harmonic oscillations of the atoms. The oscillations are in phase with the incident radiation, therefore there are strict phase relations between the dipole fields the individual atoms give rise to.

The phase relations between the fields of the oscillating atoms give rise to beams of intensities comparable with that of the incident radiation. These coherent beams together with the primary radiation give rise to the refracted beam.

In most directions, however, the fields of the dipoles have random phases. Indeed, consider the radiation field in a point  $P$  far outside the volume of the gas and also outside the region of the optical beam. The distances of the individual atoms from  $P$  have random values and thus in spite of the existing phase relations the fields arrive with random phases in  $P$ . Thus the individual fields are incoherent and the total intensity in  $P$  fluctuates rapidly around a value

$$J_S \sim NJ_A, \quad (1)$$

where  $N$  is the number of atoms in the gas and  $J_A$  the intensity of secondary radiation emitted by one atom.

Further from electromagnetic theory it follows that

$$J_A \sim \alpha^2 J_0, \quad (2)$$

where  $J_0$  is the intensity of the primary beam and  $\alpha$  the dynamical polarisability of one atom.

The refractive index of the gas is obtained considering the coherent part of the radiation fields of the atoms. The well-known theory of this phenomenon leads to

$$n^2 - 1 = 4\pi\alpha N/V. \quad (3)$$

From (1) and (2) we have

$$J_S = \beta N \alpha^2 J_0, \quad (4)$$

where  $\beta$  is a geometrical factor the value of which is obtained from the detailed calculation. Thus measuring the refractive index  $n$  and the intensity  $J_S$  of the incoherently scattered radiation, the number  $N$  of scattering centres can be determined from (3) and (4).

#### *A remark on the light of the sky*

We note that the determination of  $J_S$  supposes the individual atoms to be sources of secondary radiation which radiate independently into the vicinity of the gas. The theory of Rayleigh considered the scattered radiation emitted by small dust particles — and this theory was applied to explain the light intensity of the sky. It was realized later that the sky light is not produced by dust particles but is a scattering on the spatial fluctuations of the density of air. According to (1) this fact can also be formulated by saying that the sky light is due to the scattering on the individual gas atoms themselves, which play the role of the dust particles of the original concept.

#### *The method of virtual lattices*

The simple classical consideration giving the intensity  $J_S$  of incoherently scattered radiation can be carried out by a method different from that given above. The latter method is mathematically identical with the former, therefore it leads necessarily to the same result. This method is useful in connection with the wave mechanical aspects of the problem.

The radiation induced by an outer field on an ensemble of  $N$  atoms can be treated by supposing the atoms to be scattering centres of linear dimensions small compared with  $\lambda$  the wave length of the incident light. The ensemble of atoms can alternatively be replaced by a medium of dynamical polarizability

$$\kappa(\mathbf{r}) = \kappa \varrho(\mathbf{r}),$$

where  $\varrho(\mathbf{r})$  is the relative density of the medium, thus

$$\int \varrho(\mathbf{r}) d^3\mathbf{r} = N. \quad (5)$$

Supposing the atoms to be points with position vectors  $\mathbf{r}^{(n)}$  we have

$$\varrho(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{r}^{(n)}), \quad (6)$$

where  $\delta(\mathbf{r})$  is the three-dimensional Dirac  $\delta$ -function. More generally we may suppose

$$\varrho(\mathbf{r}) = \sum_n \delta^*(\mathbf{r} - \mathbf{r}^{(n)}), \quad (7)$$

where  $\delta^*(\mathbf{r})$  is a function with large positive values in the vicinity of  $\mathbf{r} = 0$ , vanishing outside. Thus (6) describes the density of an ensemble of atoms each spread into a small vicinity of a point  $\mathbf{r}^{(n)}$ .

The polarization density produced by a field can be taken as

$$\mathbf{P} = \alpha\varrho(\mathbf{r}) \mathbf{E}.$$

The current density induced by the field is thus

$$\mathbf{i} = \frac{1}{c} \dot{\mathbf{P}} = -\frac{1}{c^2} \alpha\varrho \ddot{\mathbf{A}},$$

where  $\mathbf{A}$  is the vector potential of the total field acting on the medium. Thus in case of a periodic field

$$\mathbf{i} = -\frac{\alpha\varrho}{\lambda^2} \mathbf{A} \quad \text{with } \lambda = c/\Omega \quad (8)$$

(here  $\Omega$  is the circular frequency of the radiation). The field emitted by the oscillating medium can be derived from a vector potential

$$\mathbf{A}_S(\mathbf{r}, t) = -\frac{\alpha}{\lambda^2} \int \frac{\varrho(\mathbf{r}') \mathbf{A}(\mathbf{r}', t')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}'; \quad (9)$$

here  $t' = t - |\mathbf{r} - \mathbf{r}'|/c$ . If the density  $\varrho(\mathbf{r})$  is of the form (6), then (9) leads to the same intensity of the scattered field as is obtained from the classical consideration given further above. Instead of splitting  $\varrho(\mathbf{r})$  into the densities

$$\varrho^{(n)}(\mathbf{r}) = \delta^*(\mathbf{r} - \mathbf{r}^{(n)}) \quad (10)$$

of the individual atoms, we express the densities by Fourier series. For this purpose we consider the gas to be enclosed into a cubic box with sides  $L$ , thus we have

$$\varrho(\mathbf{r}) = \sum_{\nu} \varrho_{\nu} e^{i\mathbf{k}_{\nu} \cdot \mathbf{r}}, \quad (11)$$

$$\varrho_{\nu} = \frac{1}{L^3} \int \varrho(\mathbf{r}) \exp\{-i\mathbf{k}_{\nu} \cdot \mathbf{r}\} d^3 \mathbf{r},$$

where the  $\mathbf{k}_\nu$  are vectors with components

$$\mathbf{k}_\nu = \frac{2\pi}{L} \nu_1, \quad \frac{2\pi}{L} \nu_2, \quad \frac{2\pi}{L} \nu_3; \tag{12}$$

here  $\nu_1, \nu_2, \nu_3$  are integers.

Considering the densities of the individual atoms we have also

$$\begin{aligned} \varrho^{(n)}(\mathbf{r}) &= \sum_{\nu} \varrho_{\nu}^{(n)} e^{i\mathbf{k}_{\nu}\mathbf{r}}, \\ \varrho_{\nu}^{(n)} &= \frac{1}{L^3} \int \delta^*(\mathbf{r} - \mathbf{r}^{(n)}) e^{-i\mathbf{k}_{\nu}\mathbf{r}} d^3\mathbf{r}. \end{aligned} \tag{13}$$

In case of  $\delta$ -functions in place of  $\delta^*$  we have

$$\left. \begin{aligned} \varrho_{\nu}^{(n)} &= \frac{1}{L^3} e^{i\varphi_{\nu}^{(n)}}, \\ \varphi_{\nu}^{(n)} &= \mathbf{k}_{\nu}\mathbf{r}^{(n)}. \end{aligned} \right\} \tag{14}$$

where

Thus

$$\left. \begin{aligned} \varrho_0 &= N/L^3, \\ \varrho_{\nu} &= \frac{1}{L^3} \sum_n e^{i\varphi_{\nu}^{(n)}} \approx \frac{\sqrt{N}}{L^3} e^{i\varphi_{\nu}} \quad \text{if } \nu \neq 0. \end{aligned} \right\} \tag{15}$$

The right hand expression is obtained supposing the  $\varphi_{\nu}^{(n)}$  to have random values for  $n = 1, 2, \dots, N$ , in that case the sum of the  $N$  complex units  $\exp(i\varphi_{\nu}^{(n)})$  has an absolute value of the order of  $\sqrt{N}$  and has random phase.

Relation (15) can be made more precise taking the  $\varphi_{\nu}^{(n)}$  to be random variables and thus we can form expected values with respect to these variables; we have

$$\left. \begin{aligned} \langle \varrho_{\nu} \rangle &= 0 \\ \langle |\varrho_{\nu}|^2 \rangle &= N/L^3 \end{aligned} \right\} \quad \text{if } \nu \neq 0. \tag{16}$$

The concept of taking the  $\varphi_{\nu}^{(n)}$  as stochastic variables needs explanation.

Indeed, at a fixed time  $t$  and a fixed configuration  $\varrho(\mathbf{r})$  each Fourier coefficient has a definite numerical value. When we introduce nevertheless "expected" values this can be done for two reasons:

1) If the atoms are moving with thermal velocities, then the motions are slow as compared with the frequency of the incident radiation — however, in accord with (14) the thermal motion leads to rapid and independent changes of the  $\varphi_{\nu}^{(n)}$ . Thus the expected values of  $\varrho_{\nu}$  can be taken to be expected values

in short intervals of time which nevertheless are long as compared with the time of oscillation of the primary wave.

2) The phases  $\varphi_\nu^{(n)}$  vary strongly with  $\nu$ . Thus the expected values of  $\varrho_\nu$  can also be considered as the average values of the  $\varrho_\nu$  inside a small region of Fourier coefficients  $\delta_\nu$  around  $\nu$ .

### *Reflexion on virtual lattices*

The field of the scattered radiation can be decomposed to the contributions of the Fourier components

$$\varrho_\nu(\mathbf{r}) = \varrho_\nu e^{i\mathbf{k}_\nu \mathbf{r}} \quad (17)$$

of  $\varrho(\mathbf{r})$ . We may thus write

$$\mathbf{A}_S(\mathbf{r}, t) = \sum_\nu \mathbf{A}_\nu(\mathbf{r}, t). \quad (18)$$

Taking the field acting on the atoms to have a vector potential

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \exp \{i(\mathbf{K}\mathbf{r} - \Omega t)\}. \quad (19)$$

The vector potential of the scattered radiation field is thus, making use of (9) and inserting  $\varrho_\nu(\mathbf{r})$  in place of  $\varrho(\mathbf{r})$ :

$$\mathbf{A}_\nu(\mathbf{r}, t) = -\frac{\alpha \varrho_\nu \mathbf{A}_0}{\lambda^2} \int \exp \{i[(\mathbf{k}_\nu + \mathbf{K})\mathbf{r}' - \Omega(t - |\mathbf{r} - \mathbf{r}'|/c)]\} \frac{d^3 \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \quad (20)$$

The integral is to be extended over the volume of the gas. For points  $\mathbf{r}$  far outside the gas and also outside the optical beam the following approximations can be used: in the factor  $1/|\mathbf{r} - \mathbf{r}'|$

$$|\mathbf{r} - \mathbf{r}'| \sim r,$$

in the exponent

$$|\mathbf{r} - \mathbf{r}'| \sim r - \mathbf{r}'\mathbf{r}/r.$$

We find thus

$$\text{exponent} \approx i[(\mathbf{k}_\nu + \mathbf{K} - \mathbf{K}_0)\mathbf{r}' + K_0 r - \Omega t], \quad (21)$$

where

$$\mathbf{K}_0 = \frac{\Omega}{c} \frac{\mathbf{r}}{r}.$$

Inserting (21) into (20) and carrying out the integration over a cubic box with edges  $L_1, L_2, L_3$ ; we find thus in a good approximation

$$\mathbf{A}_\nu(\mathbf{r}, t) = \frac{\alpha \varrho_\nu \mathbf{A}_0 L^3}{\lambda^2 r} D_\nu(\mathbf{a}) e^{i(K_0 r - \Omega t)},$$

where

$$D_\nu(\mathbf{a}) = \frac{8 \sin\left(\frac{1}{2} \mathbf{aL}_1\right) \sin\left(\frac{1}{2} \mathbf{aL}_2\right) \sin\left(\frac{1}{2} \mathbf{aL}_3\right)}{(\mathbf{aL}_1)(\mathbf{aL}_2)(\mathbf{aL}_3)} \quad (22)$$

with

$$\mathbf{a} = \mathbf{k}_\nu + \mathbf{K} - \mathbf{K}_0 .$$

The expected value of the intensity of the radiation in the direction of the vector  $\mathbf{K}$  is thus proportional to

$$\langle |A_\nu(\mathbf{r}, t)|^2 \rangle = \frac{\alpha^2 \langle \rho_\nu^2 \rangle L^6}{\lambda^4 r^2} |D_\nu(\mathbf{a})|^2 |A_0|^2 . \quad (23)$$

We find with the help of (16) if we take  $|A_0|^2$  to be proportional to the primary intensity

$$J_\nu/J_0 = N \cdot \frac{\alpha^2}{\lambda^4 r^2} |D_\nu|^2 . \quad (24)$$

### *Rayleigh scattering as Bragg scattering*

So as to see the significance of the above considerations, we note that  $D_\nu(0) = 1$  and  $D_\nu(\mathbf{a})$  has a pronounced maximum in the vicinity of  $\mathbf{a} = 0$  [see (22)]. Appreciable intensities are thus obtained in directions  $\mathbf{K}$  so that  $\mathbf{a} \sim 0$ , i.e.

$$\mathbf{K} \sim \mathbf{K}_0 - \mathbf{k}_\nu . \quad (25)$$

The above relation has the form of the Bragg condition known in X-ray spectroscopy. The densities  $\rho_\nu(\mathbf{r})$  correspond to virtual lattices with lattice vectors  $\mathbf{k}_\nu$ . Only those lattices contribute appreciably to the scattered radiation for which (25) is satisfied. These lattices give reflexions into narrow cones pointing into definite directions.

The incoherently scattered radiation consists thus of the very numerous Bragg reflexions on the virtual lattices. The phases of the various reflexions are randomly distributed, therefore the reflected rays are incoherent and the intensities  $J_\nu$  arising from the reflexions can be added so as to obtain the total intensity. Thus the expected value  $\langle |A_\nu|^2 \rangle$  [see (23)] gives the intensity of radiation in a direction which depends on  $\nu$ .

We note further that the lattice corresponding to one particular  $\nu$ -value gives appreciable reflexion only if

$$|\mathbf{K}_0 - \mathbf{k}_\nu| \approx K = \Omega/c . \quad (26)$$

For  $\mathbf{k}_\nu$ -values for which (25) is not satisfied practically no reflexion takes place.

The  $\mathbf{k}_\nu$ -values satisfying (25) give radiation inside a cone with opening angle of the order of  $\sqrt{\lambda/L}$ . On the other hand lattices with neighbouring vectors  $\mathbf{k}_\nu$  give the maximum intensities in directions  $\mathbf{K}$  with angles of the order of  $\lambda/L$  between them. From this qualitative consideration we see that the Bragg reflexions overlap to a considerable extent.

### *Scattering on diffused atoms*

We see that the scattered intensity on the medium with density  $\varrho(\mathbf{r})$  depends only on the expected values of the absolute squares of the Fourier coefficients  $\varrho_\nu$ . Thus any density distribution  $\varrho(\mathbf{r})$  for which (16) holds will give the correct intensity distribution for the scattered radiation. We may therefore replace the  $\varrho^{(n)}(\mathbf{r})$  by  $\bar{\varrho}^{(n)}(\mathbf{r})$  so that

$$\bar{\varrho}^{(n)}(\mathbf{r}) = \sum \bar{\varrho}_\nu^{(n)} e^{i\mathbf{k}_\nu \mathbf{r}}, \quad (27)$$

with

$$\bar{\varrho}_\nu^{(n)} = \frac{1}{L^3} e^{i\bar{\varphi}_\nu^{(n)}}, \quad (28)$$

where the  $\bar{\varphi}^{(n)}$  have random values which may however differ arbitrarily from the  $\varphi_\nu^{(n)} = \mathbf{k}_\nu \mathbf{r}^{(n)}$ .

The  $\bar{\varrho}^{(n)}(\mathbf{r})$  thus obtained correspond to the densities of "diffused particles". The  $\bar{\varrho}^{(n)}(\mathbf{r})$  because the original phase relations of the Fourier coefficients have been destroyed does, in general, not possess a pronounced maximum. Nevertheless the Fourier coefficients of

$$\bar{\varrho}(\mathbf{r}) = \sum \bar{\varrho}^{(n)}(\mathbf{r})$$

have the form (15), i.e.

$$\begin{aligned} \bar{\varrho}_0 &= N/L^3, \\ \bar{\varrho}_\nu &= \frac{1}{L^3} \sum e^{i\bar{\varphi}_\nu^{(n)}} \approx \frac{\sqrt{N}}{L^3} e^{i\bar{\varphi}_\nu}, \quad \nu \neq 0 \end{aligned} \quad (29)$$

where the  $\bar{\varphi}_\nu$  differ from the  $\varphi_\nu$ , but the modified phases have still random values.

From the above considerations it follows that

$$\begin{aligned} \langle \bar{\varrho}_\nu \rangle &= \langle \varrho_\nu \rangle = 0, \\ \langle |\bar{\varrho}_\nu|^2 \rangle &= \langle |\varrho_\nu|^2 \rangle = N/L^3, \quad \nu \neq 0. \end{aligned} \quad (30)$$

We see thus that the particles if they "diffuse", they produce a change of distribution in accord with

$$\varrho(\mathbf{r}) \rightarrow \bar{\varrho}(\mathbf{r}) \quad (31)$$



and the distribution of the scattered radiation is not affected. More precisely, the expected values of the scattered intensities in various directions remain unaffected by the change (31).

The diffusion process (31) has some similarity to the wave mechanical diffusion of a packet — one might suspect therefore that the scattered intensity of radiation which is not affected by the “classical diffusion” (31) might also remain unaffected by wave mechanical diffusion. This is, however, in general not the case, as will be seen in Part II.

## Part II

### *Wave mechanical determination of the incoherent scattering intensity*

Using results of former publications [1] we can suppose, that the intensity scattered by an ensemble of atoms with dynamical polarizability  $\alpha$  is the same as the intensity scattered according to classical theory by a medium of polarizability

$$\kappa(\mathbf{r}) = N\alpha\rho(\mathbf{r}), \quad (32)$$

where  $\rho(\mathbf{r})$  is the density of the quantum mechanical ensemble of atoms. More precisely, considering an ensemble of  $N$  H-atoms supposing the state of the ensemble to be described by a wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2; t)$  where

$$\mathbf{r}_n = \mathbf{r}_n^{(1)}, \mathbf{r}_n^{(2)}, \dots, \mathbf{r}_n^{(N)} \quad n = 1, 2$$

the suffix  $n = 1$  referring to proton,  $n = 2$  to electron coordinate vector; the upper indices refer to the various atoms. The density of the  $k$ -th electron can thus be written

$$\rho^{(k)}(\mathbf{r}) = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2; t)|^2 \delta(\mathbf{r}_2^{(k)} - \mathbf{r}) d^{3N} \mathbf{r}_1 d^{3N} \mathbf{r}_2, \quad (33)$$

where the  $\delta$ -function is used to express in a concise manner that integration is to be carried out over  $6N-3$  variables, i.e. all the variables except the components of the coordinate vectors of the  $k$ -th electron. (The proton densities can be worked out in a similar fashion; however, we may neglect the contribution of the protons to the radiation.)

Because of symmetry we have

$$\rho_2^{(1)}(\mathbf{r}) = \rho_2^{(k)}(\mathbf{r}), \quad k = 2, 3, \dots, N$$

thus the density appearing in (32) can be taken as

$$\rho(\mathbf{r}) = N\rho_2^{(1)}(\mathbf{r}). \quad (34)$$

There exist a large number of wave functions  $\Psi$  which satisfy the wave equation representing the ensemble of  $N$  H-atoms. We have dealt with the difficulty of choice of the wave function elsewhere [2].

### *Particular wave functions*

In a former paper [3] we have dealt with the emission of photons by the ensemble of  $N$  atoms corresponding to a volume of gas enclosed in a cubic box with sides  $L$ . Two types of wave functions were found both describing an ensemble of atoms with momenta  $\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$  of translational motion. These wave functions were built each of two body H-wave functions. Both types of wave functions thus constructed lead to the emission of photons of the same manner as it was found in the case of a single atom enclosed in a box (see [3]). Thus both wave functions lead to a process which appears to be the independent emission of photons by individual atoms.

The first of the two wave functions thus considered corresponds to a constant electron density. In the latter state (if realized in nature) the ensemble would behave as a perfect crystal and no incoherently scattered radiation was to be expected. This type of wave function (as was pointed out in [3]) must be expected to describe a rather unstable configuration in which the energy is concentrated into kinetic energy and energy of excitation without radiation energy. The latter configuration does not seem therefore to represent the state which is realized in nature; this conclusion is further confirmed by the fact that the state produces no incoherent scattered intensity.

The second type of wave function which appears to be more suitable to represent the emission of photons by independent atoms is of the following type.

Consider

$$\Psi^{(v)}(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}; t) = F_v(\mathbf{R}) \varphi_v(\mathbf{s}) e^{-i\omega_v t}, \quad (35)$$

a normalized solution of the two body wave equation giving a stationary state of an H-atom enclosed into a box such that  $\mathbf{R}$  is the coordinate vector of the centre of gravity and  $\mathbf{s}$  the coordinate vector pointing from the proton to the electron.

The wave function (35) thus represents an H-atom with some translational momentum  $\mathbf{p}_v$  in the ground state or in an excited state with energy  $E_v$ .

We form the linear combination of  $N$  wave functions of the form (35), i.e.

$$\Psi = \sum_{v=1}^N c_v \Psi^{(v)}, \quad |c_v| = 1/\sqrt{N}. \quad (36)$$

Further write

$$\Psi_{KL} = \Psi_{KL}(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}; t) = \Psi_{KL}^{(2)}(\mathbf{r}_K^{(1)}, \mathbf{r}_L^{(2)}; t). \quad (37)$$

Thus  $\Psi_{KL}$  is the  $2N$ -body wave function which happens to depend only on one proton coordinate  $\mathbf{r}_K^{(1)}$  and one electron coordinate  $\mathbf{r}_L^{(2)}$ .

The wave function used in [3] is thus

$$\Psi = \frac{1}{\sqrt{N!}} \det \Psi_{KL}. \tag{38}$$

The electron density obtained from (38) with the help of (33) and (34) is found in a good approximation to be

$$\varrho(\mathbf{r}) = N |F(\mathbf{r})|^2 / L^3,$$

where

$$F(\mathbf{r}) = \sum_{(N)} c_\nu F_\nu(\mathbf{r}), \tag{39}$$

the sum is to be extended over the amplitudes of the  $N$  states occurring in the ensemble. So as to calculate the scattered intensity we have to determine the Fourier coefficients of the density  $\varrho(\mathbf{r})$ .

When calculating the Fourier coefficients of the density it is important whether or not the states  $k_\nu$  ( $\nu = 1, 2, \dots, N$ ) occupy all the states in a compact region of momentum space. Supposing this to be the case we take the  $\nu$  to take all the values where  $k_\nu^2 \leq k_{\max}^2$ ;  $k_{\max}^2$  has to be chosen so that the above condition should be satisfied by  $N$   $\mathbf{k}_\nu$  vectors. In the latter case we have with the help of (34) and (36)

$$\begin{aligned} \varrho_\nu &= N \sum_{\mu} c_{\mu+\nu} c_{\mu}^* / L^3, \\ \langle \varrho_\nu^2 \rangle &= N^2 \sum_{\mu\mu'} \langle c_{\mu+\nu} c_{\mu}^* c_{\mu'+\nu} c_{\mu'} \rangle / L^6. \end{aligned}$$

In the above sums the expected values of the terms with  $\mu \neq \mu'$  vanish. If the value of  $\nu$  is not too large, there remain about  $N$  non vanishing terms thus each equal to  $1/N^2$  so

$$\langle \varrho_\nu^2 \rangle = N/L^6.$$

Thus the Fourier coefficients of the wave mechanical density are equal to those obtained from the classical model. The wave function thus obtained gives therefore the correct intensity for the incoherent scattering.

*Some criticism of the above result*

In spite of the fact that the wave function given by (38) and (39) gives the correct intensity of incoherent scattering, we do not think that the above function is likely to be realized in nature. It seems very unlikely that the real

state of the gas is composed of all states  $\mathbf{k}_\nu$ , so that *all states*  $k_\nu < k_{\max}$  should occur with about equal amplitudes. It is more reasonable to consider a wave function of the form (39) so that the coefficients  $c_1, c_2, \dots, c_N$  correspond to wave numbers  $\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N$  each of them giving a harmonic contribution to the density but the values  $\mathbf{k}_\nu$  do by no means contain all the possible stationary states. We can thus write

$$c_\mu = \begin{cases} \gamma_\mu & \text{if } \mu \text{ represents one of the } N \text{ states} \\ & \text{occurring in the ensemble} \\ 0 & \text{otherwise.} \end{cases} \quad (40)$$

We have thus

$$\sum_{(N)} c_\nu F_\nu(\mathbf{r}) = \sum_\mu \gamma_\mu F_\mu(\mathbf{r}),$$

where on the right hand side a large fraction of the terms vanish.

We obtain e.g. something like a thermal distribution if we suppose that\*

$$\gamma_\mu = \begin{cases} 0 & \text{with a probability } 1 - p(\mu) \\ e^{i\varphi\mu/\sqrt{N}} & \text{with a probability } p(\mu) \end{cases} \quad (41)$$

$$p(\mu) = \frac{1}{2} N(2\alpha/\pi)^{3/2} e^{-\alpha\mu^2},$$

where  $\mu^2 = \mu_1^2 + \mu_2^2 + \mu_3^2$ ;  $\mu_1, \mu_2, \mu_3$  the components of  $\mu$ .

The Fourier expansion of the density is thus

$$\varrho(\mathbf{r}) = \sum_\lambda \varrho_\lambda e^{i\mathbf{k}_\lambda \mathbf{r}},$$

$$\varrho_\lambda = \sum_\mu \gamma_\mu \gamma_{\mu-\lambda}^*.$$

The expected value is

$$\langle \varrho_\lambda \rangle = 0, \quad \lambda \neq 0$$

because of the random phase factors of the  $\gamma_\mu$ . For the squares of the Fourier coefficients we find

$$\langle |\varrho_\lambda|^2 \rangle = \sum_{\mu, \mu'} \langle \gamma_\mu \gamma_{\mu-\lambda}^* \gamma_{\mu'} \gamma_{\mu'-\lambda} \rangle.$$

For  $\lambda \neq 0$  on the right only terms with  $\mu = \mu'$  are different from zero.

\* The kinetic energy of the system is thus found to be proportional to  $1/\alpha$ , thus  $\alpha$  is a parameter proportional to the reciprocal absolute temperature.

We find

$$\langle | \varrho_\lambda |^2 \rangle = \sum_\mu \langle | \gamma_\mu |^2 | \gamma_{\lambda-\mu}^2 | \rangle$$

and with the help of (41)

$$\langle | \varrho_\lambda |^2 \rangle = \frac{1}{2} (\alpha\pi)^{3/2} e^{-1/2 \alpha \lambda^2} N/L^6 .$$

Comparing the above value with the classical value we find the classical value  $N/L^6$  to be multiplied by a small factor, which gives the incorrect intensity of incoherent scattering — therefore we find a strong discrepancy with the classical result.

The density fluctuation thus calculated has a maximum in the region when

$$\alpha \lambda^2 \sim 1 .$$

In case of visible light  $\lambda \gg 1$  thus the maximum is found for  $\alpha \gg 1$ ; we see thus that even the maximum value of  $\langle | \varrho_\nu |^2 \rangle$  is much below the value  $N/L^6$  obtained from the classical theory. We see thus that the scattered light obtained from the consideration of the wave mechanical density fluctuation of the ensemble has an intensity proportional to  $N$  the number of atoms; however, the intensity has a strong temperature dependence and the calculated intensity is much smaller than the observed one at the temperature where the scattering is maximal.

The above result appears to be surprising at first sight. Indeed, we may consider a wave function which in the initial state  $t = 0$  leads to a density distribution  $\varrho(\mathbf{r})$  as given by (11) or  $\bar{\varrho}(\mathbf{r})$  given by (28). From the general considerations given in (1) we must expect that this distribution leads to the same Rayleigh scattering as is expected from classical theory. Therefore at least for a short time the configuration thus obtained leads indeed to the correct scattered intensity. However, the detailed calculation shows that the wave mechanical diffusion leads to changes, in the course of which the Fourier coefficients of the density  $\varrho(\mathbf{r})$  or  $\bar{\varrho}(\mathbf{r})$  change rapidly so that the amplitudes show a strong decreasing tendency. Therefore the initial configuration in which the density is of the form  $\varrho(\mathbf{r})$  or  $\bar{\varrho}(\mathbf{r})$  is according to wave mechanics an exceptional one which in the course of the diffusion shows a tendency of smoothing out until a state with very much smaller fluctuations is reached.

### Concluding remarks

The failure of the procedure might be attributed to the incorrect choice of the wave function of the ensemble. We do not think this very likely, because linear combinations of the wave functions we have chosen should in general

give fluctuations which are even more smoothed out than that of the wave function considered here.

The discrepancy pointed out here is one encountered (although not pointed out) in the original treatment of the Compton scattering by KLEIN and NISHINA [4]. In that work the correct Compton intensity of the scattered radiation is obtained by using wave functions of the free electrons which contain all possible momentum values with equal amplitudes. If the original configuration of the free electron were to be replaced in the treatment of KLEIN and NISHINA by a wave packet which contains a reasonable spectrum of frequencies, then a cross section much smaller than the observed one would be obtained.

It seems therefore that initial states with a constant spectrum of momenta have some physical significance the nature of which is, however, not obvious.

We think that the correct scattered intensity might be obtained by extending the consideration we have given here. A correct description might be obtained considering not simply the average fluctuation of the ensemble — but considering the avalanches which develop in an ensemble as the result of suitable thermal disturbances. We think of a process very alike the one considered for the emission of single photons in our previous papers. We hope to come back to this problem later.

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