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MACROSCOPIC APPROACH TO EFFECTS OF RADIATIVE INTERACTION OF ATOMS AND MOLECULES

V. A. ALEKSEEV, A. V. VINOGRADOV, and I. I. SOBEL'MAN

P. N. Lebedev Physics Institute, U.S.S.R. Academy of Sciences

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1. INTRODUCTION

THE radiation of an aggregate of N oscillators (atoms and molecules) localized in a volume with linear dimensions $a \ll ƛ$ (where $ƛ = \lambda/2 = c/\omega$) and λ is the wavelength) is characterized by a number of specific features connected with the so-called cooperative effect, i.e., with the existence of collective oscillations due to the interaction of the oscillators via their common radiation field.

The nature of this effect is easiest to explain with classical oscillators as an example (charge e, mass m, natural frequency ω_0). It is well known that the radiation of electromagnetic waves is accompanied by a reaction of the radiation field on the charges, i.e., by the appearance (occurrence) of radiation-friction forces. In the case when $a \ll ƛ$ the radiation-friction force acting on each oscillator of the system is equal to (see, for example [1]

$$\mathbf{F} = (2e/3c^3)\dddot{\mathbf{D}}, \quad \mathbf{D} = e\sum_i \mathbf{r}_i, \tag{1.1}$$

where $\mathbf{D}$ is the total dipole moment of the system. Therefore the equation of motion of each of the oscillators in the external field $\mathbf{E}^0$ is

$$\ddot{\mathbf{r}}_i - (2e/3mc^3)\dddot{\mathbf{D}} + \omega_0^2\mathbf{r}_i = (e/m)\,\mathbf{E}^0. \tag{1.2}$$

Multiplying each of these equations by e and summing over all the oscillators of the system, we obtain an equation of motion for $\mathbf{D}$:

$$\ddot{\mathbf{D}} - N(2e^2/3mc^3)\dddot{\mathbf{D}} + \omega_0^2\mathbf{D} = N(e^2/m)\,\mathbf{E}^0. \tag{1.3}$$

From this it is easy to find the radiation spectrum of the system

$$I(\omega) \backsim |\mathbf{D}_\omega|^2 \backsim |\omega_0^2 - \omega^2 - i\omega N\gamma_0|^{-2}, \quad \gamma_0 = 2e^2\omega^2/3mc^3. \tag{1.4}$$

For one isolated oscillator, as is well known, we have

$$I(\omega) \backsim |\omega_0^2 - \omega^2 - i\omega\gamma_0|^{-2}; \tag{1.5}$$

here γ_0 is the constant of the radiative damping of the oscillator.

It is seen from (1.3) and (1.4) that the oscillations of the total dipole moment of the system in question, owing to the interaction of the oscillators via their common radiation field, attenuate by a factor N faster than the oscillations of one isolated oscillator. Accordingly, (1.4) contains the collective radiative width $N\gamma_0$.

It is easy to show that the same result is obtained by an elementary analysis of quantum radiators.

Let us consider a system of N identical atoms. The ground state of such a system is described by the wave function

$$\Psi_0 = \varphi_0(1)\,\varphi_0(2)\,\ldots\,\varphi_0(N), \tag{1.6}$$

where $\varphi(i)$ is the wave function of the i-th atom. The first excited level of the system, corresponding to excitation of one of the atoms, is N-fold degenerate (we assume for simplicity that the levels of one atom are not degenerate), and the states belonging to this level can be described either by wave functions of the type

$$\Psi_1^{(i)} = \varphi_0(1)\,\varphi_0(2)\,\ldots\,\varphi_1(i)\,\ldots\,\varphi_0(N), \tag{1.7}$$

or by symmetrized linear combinations of these functions. If all the atoms are localized in a volume $V \ll \lambda^3$, then the interaction of the system with the electromagnetic field can be written in the form

$$\mathscr{H}' = (e/mc)\sum_i \mathbf{p}_i\mathbf{A}(\mathbf{r}_i) \approx (e/mc)\,\mathbf{A}\sum_i \mathbf{p}_i,$$

where $\mathbf{p}_i$ is the momentum of the atomic electron and $\mathbf{A}$ is the vector potential of the field. Since the operator $\mathscr{H}'$ is completely symmetrical with respect to permutations of the arguments i (the number of the atom) and the wave function of the ground state (1.6) is also fully symmetrical, the matrix element $\mathscr{H}'$ differs from zero only for transitions to a fully-symmetrical excited state

$$\Psi_1 = (1/\sqrt{N})\sum_i \Psi_1^{(i)}. \tag{1.8}$$

All the remaining linear combinations of the functions (1.7), orthogonal to the function (1.8), have a different symmetry. Therefore the matrix elements $\mathscr{H}''$ for the corresponding transitions are equal to zero. In other words, only the fully-symmetrical state (1.8) is connected with ψ_0 by a radiative transition.

The matrix element for the transition $\psi_0 \to \psi_1$ is

$$\langle\Psi_1|\mathscr{H}'|\Psi_0\rangle = (1/\sqrt{N})\sum_i\langle\Psi_1^{(i)}|(e/mc)\,\mathbf{A}\sum_j \mathbf{p}_j|\Psi_0\rangle = \sqrt{N}\,(e/mc)\,\mathbf{A}\mathbf{p}_{10}, \tag{1.9}$$

where $\mathbf{p}_{10}$ is the matrix element of $\mathbf{p}$ for one isolated atom. It is seen even from (1.9) that the radiative decay of the state (1.8) is N times faster than in the case of a single atom. The width of the emission spectrum, which can be easily determined by using the well known Weisskopf–Wigner method[2] (see [3] concerning this subject) is also N times larger than for the isolated atom.

The fact that radiating systems manifest collective properties is well known, and a number of concrete examples where this effect plays an important role can be cited. Thus, the effective cross section for the scattering of electromagnetic waves by a cluster of N electrons or by an atom containing N electrons is proportional to N in the case when $ƛ \ll a$ and proportional to N^2 if $ƛ \gg a$.[1]

The question of collective radiative damping has been also discussed many times in the literature in connection with a variety of problems (see, for example, [3-8]). There are, however, a number of problems connected with this effect, which either have not been discussed at all in the literature, or have not been considered quite fully. These include, in particular, the question of the radiative damping in the case of an infinite medium (in practice, in the case of volume $V \gg \lambda^3$).

Recently, careful investigations were made of the spectral-line broadening of noble-gas atoms at low pressures.[9-13] The results of these investigations were interpreted by the authors as evidence of the appearance of collective radiative damping. In fact, there are not sufficient grounds for such an interpretation of the experimental data obtained in [9-13]. This is easiest to show by resorting to the known properties of the dielectric constant of rarefied gases $\epsilon(\omega)$, i.e., by solving the problem of radiative damping within the framework of the macroscopic approach. As will be explained in Sec. 2, no increase of the radiative width is connected with the cooperative effect in infinite media.

The macroscopic approach to the problem of interest to us, used in Sec. 2 for the case of large volumes ($a \gg \lambda$), is perfectly natural. In the case of small volumes ($a \ll \lambda$), on the other hand, the situation is not so simple. The point is that in practically all the cited papers devoted to the cooperative effect the analysis was based on the microscopic approach, i.e., on allowance for the interaction via the radiative field directly in the equations of motion of the oscillators. This naturally raises the question as to whether the collective radiative effect is present in the general scheme of the macroscopic description of the processes of radiation and scattering of electromagnetic waves or whether the microscopic analysis is essential in principle. In other words, is it possible to take into account the cooperative effect starting from the equations of macroscopic electrodynamics and ascribing to the medium in a small volume ($a \ll \lambda$) the same values of the dielectric constant and the magnetic permeability $\epsilon(\omega)$ and $\mu(\omega)$ as in the case of an infinite medium?

This question is of interest for the following reasons. First of all, a negative answer to it would mean that a number of the results obtained by exactly solving the equations of macroscopic electrodynamics, such as the Mie theory for the scattering of electromagnetic waves by small particles, reflection from a layer of thickness $a \ll \lambda$, etc., must be revised.

On the other hand, the microscopic approach is inevitably connected with the consideration of concrete models. Thus, for example, all the known published results concerning the influence of the cooperative effect on the emission spectrum of small volumes under thermal excitation pertain, in essence, to the case of a single isolated spectral line, corresponding to the transitions between nondegenerate levels. The foregoing pertains also to Dicke's well-known paper,[4] which contains the most complete analysis of different manifestations of radiative coupling.

The main content of the present article is a comparison between the microscopic and macroscopic descriptions of the effect of radiative coupling in small and large volumes. The entire analysis is limited to conditions such that the substance is in the states of thermodynamic equilibrium, or when the radiation is due to thermal excitation. We therefore do not consider at all other aspects of the theory of the cooperative effect, such as radiation echo (see [4,14]). As applied to the conditions in question, it is shown that the macroscopic approach permits a complete description of the cooperative effects. Moreover, within the framework of this approach, the limits of applicability of the approximations that must be made in the microscopic analysis, become clear.

2. RADIATIVE DAMPING IN UNBOUNDED MEDIA

The theory of collective radiative damping, developed in [4] for systems with linear dimensions $a \ll \lambda$, cannot be generalized directly to the case of unbounded media. At the same time, the question of the possible manifestation of this effect arises in a large number of physical problems. Thus, for example, in a series of recent studies by Kuhn, Vaughan, and Lewis,[9-13] they investigated in detail the broadening of a number of spectral lines of noble-gas atoms. The density dependence of the width turned out to be in very good agreement with the theory of shock broadening. At the same time, for very small densities these investigations led to a somewhat unexpected result. The radiative width of a number of lines, obtained by extrapolating the measured widths to zero density, turned out to differ from the theoretical ones or from those determined by other methods. The authors point to the cooperative effect as a possible cause of the observed discrepancy.[15] This conclusion is based on reasons analogous to those discussed in Sec. 1 above, as applied to the case of small volumes ($V \ll \lambda^3$), and on the results in [7], where the radiative damping constant γ, corresponding to the p → s-transition in a system of two atoms separated by an arbitrary interatomic distance R was calculated. At the initial instant $t = 0$, one atom is in the p-state and the second in the s-state. The damping constant γ depends on the projection m of the momentum of the excited atom on the z-axis which is directed along the vector **R**. In the case when $m = 0$ we have

$$\gamma_\sigma = \gamma_0 \{1 + [3/(kR)^3] (\sin kR - kR \cos kR)\}.$$

For $m = \pm 1$,

$$\gamma_\pi = \gamma_0 \{1 + [3/2 (kR)^3] (-\sin kR + kR \cos kR + (kR)^2 \sin kR)\}.$$

With decreasing R we get $\gamma_{\sigma,\pi} \to 2\gamma_0$. When R increases, γ_π differs from γ_0 by a quantity on the order of $\gamma_\pi - \gamma_0 \sim (\sin kR/kR)\gamma_0$, i.e., this difference decreases very slowly. This circumstance is the primary cause of the difficulty of generalizing the results of [7] to the case of a gas in a large volume, since one cannot limit oneself to allowing for nearest-neighbor interactions only.

The most general approach to our problem is to consider the connection of such characteristics of the medium as the absorption and emission spectra with the properties of the dielectric constant of the medium $\epsilon(\omega)$.

As is well known, both the dissipation of electromagnetic energy in a medium and the thermal radiation of a medium can be expressed directly in terms of $\epsilon(\omega)$. Knowing $\epsilon(\omega)$, we can also determine the Einstein spectral coefficients for spontaneous emission $a_{ik}(\omega)$ per atom of the medium (with allowance for the interaction between the atoms):

$$\mathrm{Im}\{[\varepsilon(\omega)-1]/[\varepsilon(\omega)+2]\}=(\pi^2/3)(c/\omega)^3\sum_{i,k}a_{ik}(\omega)[(g_i/g_k)n_k-n_i], \quad (2.1)$$

where g_i, g_k, and n_i, n_k are the static weights and the populations of the levels i and k ($E_i > E_k$),

$$\int a_{ik}(\omega)\,d\omega=A_{ik}=\frac{2\omega^2e^2}{mc^3}\frac{g_k}{g_i}f_{ki}, \quad (2.2)$$

A_{ik} is the Einstein integral coefficient, and f_{ki} is the oscillator strength of the transition $k \rightarrow i$.

The summation on the right-hand side of (2.1) extends over all possible transitions capable of making a contribution to the considered spectral region. For an isolated spectral line (in the case of sufficiently low densities) we can retain on the right-hand side of (2.1) only one term. In this case the frequency dependence of the coefficient $a_{ik}(\omega)$ can be obtained if the function $\epsilon(\omega)$ is known.

Thus, the problem of calculating the emission spectrum, and by the same token of clarifying the role of the cooperative effect, reduces to the calculation of the dielectric constant. This problem was discussed many times in the literature (see, for example, the book [16]), and this enables us to employ known results. However, before we proceed to discuss these results, let us show that by calculating $\epsilon(\omega)$ in the microscopic theory of dispersion, the radiative interaction of the atoms, which is responsible for the cooperative effect in the case of small volumes, is completely taken into account.

Let us consider again the model of classical oscillators. This model makes it possible to establish all the main features of the manifestation of the radiative coupling in small and large volumes. All the results can be generalized without difficulty to the case of quantum systems. The equations of motion of the i-th oscillator (i.e., one of the oscillators of the medium), with allowance for the recreation of its own radiation field and the fields of all the remaining oscillators, written for the Fourier component of the dipole moment $\mathbf{d}_\omega^{(i)} = e\mathbf{r}_\omega^{(i)}$, is of the form

$$\mathbf{d}_\omega^{(i)}[-\omega^2-i\omega(\gamma_0+\Gamma)+\omega_0^2]=\frac{e^2}{m}\sum_{i\neq j}\mathrm{rot\,rot}\frac{e^{i\frac{\omega}{c}|\mathbf{R}_i-\mathbf{R}_j|}}{|\mathbf{R}_i-\mathbf{R}_j|}\mathbf{d}_\omega^{(j)}+\frac{e^2}{m}\mathbf{E}_\omega^{(0)}, \quad (2.3)$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are the coordinates of the centers of inertia of the oscillators, the constant Γ characterizes the possible electromagnetic-energy dissipation processes due to any other factor not represented in the right-hand side of the system (2.3).

If the oscillators are localized in a volume $V \ll \lambda^3$, and therefore the conditions $(\omega/c)|\mathbf{R}_i - \mathbf{R}_j| \ll 1$, are satisfied for all values of i and j, then the right-hand side of (2.3) can be expanded in a series of powers of $(\omega/c)|\mathbf{R}_i - \mathbf{R}_j|$. Retaining in this expansion only the first nonvanishing imaginary term, which, as it turns out, corresponds to allowance for the radiative-friction forces in the approximation (1.1),

$$\mathrm{rot\,rot}\frac{e^{i\frac{\omega}{c}|\mathbf{R}_i-\mathbf{R}_j|}}{|\mathbf{R}_i-\mathbf{R}_j|}\mathbf{d}_\omega^{(j)}\simeq i\frac{2}{3}\left(\frac{\omega}{c}\right)^3\mathbf{d}_\omega^{(j)}, \quad (2.4)$$

we obtain

$$\mathbf{d}_\omega^{(i)}[-\omega^2-i\omega\Gamma+\omega_0^2]=i\omega\gamma_0\mathbf{D}_\omega+\frac{e^2}{m}\mathbf{E}_\omega^{(0)}, \quad (2.5)$$

where $\mathbf{D}_\omega$ is the Fourier component of the total dipole moment of the system. Summing (2.5) over all N oscillators of the system, we get

$$\mathbf{D}_\omega[-\omega^2-i\omega(N\gamma_0+\Gamma)+\omega_0^2]=N(e^2/m)\mathbf{E}_\omega^{(0)}. \quad (2.6)$$

This equation, like (1.3), contains the collective radiative width.

Let us recall now the method used to calculate the dielectric constant $\epsilon(\omega)$ with the aid of the system (2.3), (see [16] on this subject). Let us consider Eq. (2.3) without an external field. We average the right-hand side of (2.3) over the coordinates of the oscillators $\mathbf{R}_j$, assuming that each of the oscillators has an equal probability of being at any point in space, regardless of the locations of the other oscillators, including the oscillator i. Then

$$\sum_{j\neq i}=\lim_{V\to\infty}(N-1)\frac{1}{V}\int_\delta d\mathbf{R}_j\,\mathrm{rot}_{\mathbf{R}_i}\mathrm{rot}_{\mathbf{R}_i}\frac{e^{i\frac{\omega}{c}|\mathbf{R}_i-\mathbf{R}_j|}}{|\mathbf{R}_i-\mathbf{R}_j|}\mathbf{d}_\omega(\mathbf{R}_j), \quad (2.7)$$

where N = nV, and n is the oscillator concentration; the symbol δ at the integral sign denotes that the integration should be carried out over the region $|\mathbf{R}_i - \mathbf{R}_j| > \delta \rightarrow 0$. Using, further, the relation (see [16])

$$\int_\delta d\mathbf{R}'\,\mathrm{rot}_\mathbf{R}\mathrm{rot}_\mathbf{R}\frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\mathbf{d}_\omega(\mathbf{R}')=\mathrm{rot}_\mathbf{R}\mathrm{rot}_\mathbf{R}\int d\mathbf{R}'\frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\mathbf{d}_\omega(\mathbf{R}')-\frac{8\pi}{3}\mathbf{d}_\omega(\mathbf{R}),$$

we obtain an integral equation for $\mathbf{d}_\omega(\mathbf{R})$:

$$\mathbf{d}_\omega(\mathbf{R})=n\alpha_0\,\mathrm{rot\,rot}\int d\mathbf{R}'\frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\mathbf{d}_\omega(\mathbf{R}')-\frac{8\pi}{3}n\alpha_0\mathbf{d}_\omega(\mathbf{R}); \quad (2.8)$$

Here α_0 is the polarizability of one isolated oscillator

$$\alpha_0=(e^2/m)[\omega_0^2-\omega^2-i\omega(\gamma_0+\Gamma)]^{-1}. \quad (2.9)$$

If we seek the solution of (2.8) in the form of plane waves $\mathbf{d}_\omega(\mathbf{R}) \sim \exp i\kappa\mathbf{R}$, then it is easy to obtain a dispersion equation connecting κ with ω:

$$1=n\alpha_0\frac{4\pi\kappa^2}{\kappa^2-(\omega/c)^2}-\frac{8\pi}{3}n\alpha_0. \quad (2.10)$$

Putting $\kappa^2 = \epsilon(\omega)\,\omega^2/c^2 = \epsilon(\omega)k^2$ in (2.10), we obtain the well-known Lorentz–Lorenz formula for $\epsilon(\omega)$:

$$(\varepsilon-1)/(\varepsilon+2)=(4\pi/3)n\alpha_0=n(e^2/m)[\omega_0^2-\omega^2-i\omega(\gamma_0+\Gamma)]^{-1}. \quad (2.11)$$

Formula (2.11) was obtained for the case of an ideal gas. As was shown by Klimontovich and Fursov [17] in the case of an arbitrary medium the radiative damping is determined by the constant

$$\gamma_{\mathrm{rad}}=\gamma_0\overline{\Delta N^2}/N,$$

where $\overline{\Delta N^2}$ and N are respectively the mean square fluctuation and the average number of particles in a definite element of the body volume. For an ideal gas, as is well known, $\overline{\Delta N^2}/N = 1$ and $\gamma_{\mathrm{rad}} = \gamma_0$. If we eliminate completely the possibility of fluctuations, by putting $\overline{\Delta N^2} = 0$, then, as can be seen from the foregoing formula, there is no radiative damping at all:

$$\frac{3}{4\pi}\frac{\varepsilon-1}{\varepsilon+2}=n\frac{e^2}{m}\frac{1}{\omega_0^2-\omega^2-i\omega\Gamma}. \quad (2.12)$$

Thus, in a homogeneous medium of isotropic oscillators (without fluctuations) the interaction of oscillators via the radiation field leads not to an increase of the radiative width, as is in the case of a small volume, but to complete cancellation of the radiative damping. This result, first obtained by Mandel'shtam,[18] is closely connected with the well known fact that a homogeneous medium does not scatter electromagnetic waves.

The presence of fluctuations leads to scattering, and in an ideal gas the intensity of the scattering by the density fluctuations is equal to the sum of the intensities of scattering by each of the isolated oscillators. Simultaneously, $\epsilon(\omega)$ is determined by formula (2.11), i.e., it has the same form as if there were no interaction of the oscillators via the radiation field at all.

In (2.3) above we did not take into account the motion of the oscillators. Generalization of these equations to the case of moving oscillators does not change the results of interest to us in any way.

From the foregoing statements concerning the connection between the Einstein spectral coefficients $a(\omega)$ and the function $\epsilon(\omega)$, it follows that in an unbounded medium there is no increase of the radiative width as a result of the interaction of the oscillators via the common field of radiation. The radiative width remains exactly the same as in the case of an isolated oscillator. Thus, the effect whereby the radiative damping increases as a result of the coupling of the oscillators is peculiar only to small volumes $V \ll \lambda\!\!\!^{-3}$, and, as will be shown below, is connected with peculiarities of the scattering of light by small volumes.

As to the anomalous behavior of the line width in the spectra of noble gases at low densities, observed in [9-13], it is apparently due to some other causes which have no bearing on the cooperative effect (see [19]).

3. SCATTERING OF ELECTROMAGNETIC WAVES BY SMALL PARTICLES. THERMAL RADIATION

Let us consider a spherical volume V whose radius a satisfies the condition $a \ll \lambda\!\!\!^{-}$, filled with classical isotropic oscillators *. In accordance with the statements made in Sec. 2 above, the dipole oscillations of such a volume should be characterized by a radiative-damping constant proportional to the total number of oscillators $N = nV$ in the volume; this in principle can be manifest in various radiative processes. It is convenient to start the analysis of such effects with the problem of the scattering of electromagnetic waves.

If an external monochromatic field with amplitude $\mathbf{E}^0_\omega$ is incident on the system, then Eq. (2.6) for the Fourier component of the total dipole moment $\mathbf{D}_\omega$ takes the form

$$\mathbf{D}_\omega[-\omega^2 - i\omega(N\gamma_0 + \Gamma) + \omega_0^2] = (e^2/m) N\mathbf{E}^0_\omega. \tag{3.1}$$

From this we can readily find the polarizability α_V of the volume:

$$\alpha_V = \frac{e^2}{m}\frac{nV}{\omega_0^2 - \omega^2 - i\omega(\Gamma + nV\gamma_0)}. \tag{3.2}$$

Knowing the polarizability α_V, we can find the total effective cross section σ_V (usually called the attenuation cross section) and the effective scattering cross section σ'_V:

$$\sigma_V = 4\pi k\,\mathrm{Im}\,\alpha_V = 6\pi\lambda\!\!\!^{-2}\frac{nV\gamma_0(nV\gamma_0 + \Gamma)\omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2(\Gamma + nV\gamma_0)^2}, \tag{3.3}$$

$$\sigma'_V = \frac{8\pi}{3}k^4|\alpha_V|^2 = 6\pi\lambda\!\!\!^{-2}\frac{(nV\gamma_0)^2\omega^2}{(\omega_0^2 - \omega^2)^2 + \omega^2(\Gamma + nV\gamma_0)^2}. \tag{3.4}$$

Let us express now the polarizability α_V in terms of the dielectric constant ϵ from (2.12), using, as is customarily done in the theory of light scattering by small particles, the same formula as in the case of a static field:[20] *

$$\alpha_V^{st} = \frac{3}{4\pi}\frac{\varepsilon - 1}{\varepsilon + 2}V = \frac{e^2}{m}\frac{nV}{\omega_0^2 - \omega^2 - i\omega\Gamma}. \tag{3.5}$$

The difference between formulas (3.5) and (3.2) lies precisely in the fact that (3.2) contains the collective radiative width $nV\gamma_0$. From the fundamental point of view, this difference is quite significant. The point is that the polarizability α_V should satisfy the inequality

$$\mathrm{Im}\,\alpha_V \geqslant 2k^3|\alpha_V|^2/3, \tag{3.6}$$

which is the consequence of the so-called optical theorem for dipole scattering, which relates the total cross section with the forward scattering amplitude. The physical meaning of (3.6) lies in the fact that the total cross section cannot be smaller than the scattering cross section α'_V (see (3.3) and (3.4)). It is easy to verify that the polarizability (3.2) does satisfy the condition (3.6), whereas (3.5) can lead to a contradiction.

Further, inasmuch as $\mathrm{Im}\,\alpha_V \le |\alpha'_V|$, it follows also from (3.6) that $|\alpha_V| \le 2k^{-3}/3$. Therefore

$$\sigma'_V \leqslant 6\pi\lambda\!\!\!^{-2}, \quad \sigma_V \leqslant 6\pi\lambda\!\!\!^{-2}. \tag{3.7}$$

The quantity on the right-hand side of (3.7) is the well known theoretical limit for the dipole-scattering cross section. It is easy to verify that the scattering cross section σ'_V calculated with the aid of (3.5) likewise does not satisfy this condition in the general case. On the other hand no difficulties arise in the case (3.2).

Let us consider therefore the problem of calculating α_V within the framework of macroscopic electrodynamics in somewhat greater detail.

Let the oscillator density, and consequently ϵ, depend on the coordinate R, and in such a way that $\epsilon(\mathbf{R}) = \mathrm{const} \neq 1$ in the volume V, and outside this volume $\epsilon(\mathbf{R})$ tends smoothly but quite rapidly to unity. We solve the scattering problem using the Maxwell equation

$$\mathrm{rot}\,\mathrm{rot}\,\mathbf{E}_\omega + (\omega^2/c^2)\,\varepsilon(\mathbf{R})\,\mathbf{E}_\omega = 0. \tag{3.8}$$

It is convenient to change over from the differential equation (3.8) to the equivalent integral equation

$$\frac{\varepsilon(\mathbf{R}) + 2}{3}\mathbf{E}_\omega(\mathbf{R}) = \int_\delta d\mathbf{R}'\,\frac{\varepsilon(\mathbf{R}') - 1}{4\pi}\,\mathrm{rot}_\mathbf{R}\,\mathrm{rot}_\mathbf{R}\frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\mathbf{E}_\omega(\mathbf{R}') + \mathbf{E}^0_\omega(\mathbf{R}), \tag{3.9}$$

where $\mathbf{E}^0_\omega(\mathbf{R})$ is the incident wave. We denote the quantity on the left-hand side of (3.9) by $\mathbf{G}_\omega(\mathbf{R})$:

$$\mathbf{G}_\omega(\mathbf{R}) = [\varepsilon(\mathbf{R}) + 2]\,\mathbf{E}_\omega(\mathbf{R})/3. \tag{3.10}$$

*Here and throughout we confine ourselves for simplicity to nonmagnetic substances with $\mu = 1$.

*It should be recalled that the motion of particles localized in the volume $V \ll \lambda\!\!\!^{-3}$ does not lead to a Doppler broadening of the spectral lines, and therefore $\epsilon(\omega)$ should not take the Doppler effect into account.

The vector $\mathbf{G}_\omega(\mathbf{R})$ satisfies an equation that follows directly from (3.9):

$$\mathbf{G}_\omega(\mathbf{R}) = \int\limits_\delta d\mathbf{R}' \frac{3}{4\pi} \frac{\varepsilon(\mathbf{R}')-1}{\varepsilon(\mathbf{R}')+2} \,\mathrm{rot}_\mathbf{R}\, \mathrm{rot}_\mathbf{R} \frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|} \mathbf{G}_\omega(\mathbf{R}') + \mathbf{E}^0_\omega(\mathbf{R}). \quad (3.11)$$

In solving this equation, we use precisely the same approximation as in the solution of the system (2.3), carrying out an expansion, similar to (2.4), of the integrand

$$\mathrm{rot}\,\mathrm{rot}\left[\frac{e^{i\frac{\omega}{c}|\mathbf{R}-\mathbf{R}'|}}{|\mathbf{R}-\mathbf{R}'|}\mathbf{G}_\omega(\mathbf{R}')\right] \approx i\,\frac{2}{3}\left(\frac{\omega}{c}\right)^3 \mathbf{G}_\omega(\mathbf{R}'). \quad (3.12)$$

In addition, we assume that inside the volume in question the field $\mathbf{G}_\omega(\mathbf{R}')$ does not change significantly. Then

$$\mathbf{G}_\omega(\mathbf{R}) = \frac{\mathbf{E}^0_\omega}{1 - i(3/4\pi)[(\varepsilon-1)/(\varepsilon+2)](2/3)(\omega/c)^3 V}. \quad (3.13)$$

Using the relation $\mathbf{d}_\omega = (\epsilon - 1)\mathbf{E}_\omega/4\pi$, and also (3.10) and (3.13), we can express $\mathbf{d}_\omega$ and $\mathbf{D}_\omega = V\mathbf{d}_\omega$ in terms of $\mathbf{E}^0_\omega$. Further, putting $\mathbf{D}_\omega = \alpha_V \mathbf{E}^0_\omega$, we obtain the polarizability of α_V:

$$\alpha_V = \frac{(3/4\pi)[(\varepsilon-1)/(\varepsilon+2)]V}{1 - i(3/4\pi)[(\varepsilon-1)/(\varepsilon+2)](2/3)(\omega/c)^3 V} = \frac{\alpha_V^{st}}{1 - i(2/3)(\omega/c)^3 \alpha_V^{st}}. \quad (3.14)$$

If we substitute in this formula ϵ from (2.12), then the resulting expression coincides exactly with (3.2), i.e., with the polarizability of the volume α_V, calculated from the microscopic equation (2.3) with allowance for the effects of collective radiative damping.

Thus, this effect falls entirely within the usual macroscopic approach. The fact that the second term in the denominator of (3.14) determines the correction precisely for the effect of the collective radiation damping is seen also from the following simple reasoning. After determining in the first approximation the dipole moment of the system with the aid of the quasistatic approximation $\mathbf{D}_\omega = \alpha_V^{st}\mathbf{E}_\omega^{(0)}$, we can refine this expression by adding to $\mathbf{E}$ the radiation field of the dipole $\mathbf{E}_\omega^{rad}$ calculated with the aid of (1.1):

$$\mathbf{D}_\omega = \alpha_V^{st}[\mathbf{E}_\omega + (2/3c^3)\,\dddot{\mathbf{D}}_\omega]. \quad (3.15)$$

From this we get

$$\mathbf{D}_\omega = \frac{\alpha_V^{st}}{1 - i(2/3)(\omega/c)^3\alpha_V^{st}} \mathbf{E}_\omega, \quad (3.16)$$

i.e., we again arrive at formula (3.14).*

Formulas (3.14) are, evidently, much more general than (3.2), inasmuch as the derivation of these formulas does not involve any model of the oscillators (atoms or molecules) of the medium. Thus, in the case of an atomic gas it is possible to use in lieu of (2.12) the well known expression for

$$\frac{3}{4\pi}\frac{\varepsilon-1}{\varepsilon+2} = \frac{e^2}{m}\sum_{i,k} f_{ik}\left(n_k - \frac{g_k}{g_i}n_i\right)\int \frac{F_{ik}(\omega')\,d\omega'}{(\omega_{ik}-\omega')^2 - \omega'^2 - i\omega'\Gamma}. \quad (3.17)$$

The function $F_{ik}(\omega')$ describes the line broadening not connected with energy dissipation, i.e., with inelastic collisions. For example, the function $F_{ik}(\omega')$ can specify the intensity distribution in a line broadened as a result of the Holtsmark or Weisskopf broadening mechanisms.

Let us proceed to clarify the limits of applicability of the obtained formulas. The main question that arises here is whether it is at all possible to obtain a situation whereby the effect of the collective radiative broadening plays an essential role and at the same time remain valid the approximation used in the derivation of (3.14). The point is that in deriving these formulas we virtually had to assume (the field $\mathbf{G}_\omega(\mathbf{R}')$ was taken outside the integral sign) that the dimensions of the volume in question are small not only compared with the wavelength in vacuum $\lambda = c/\omega$, but also compared with the wavelength in the medium or with the depth of penetration $\delta \sim (c/\omega)1/\sqrt{|\epsilon|}$. This therefore raises the question as to whether the condition $(2/3)k^3\alpha_V^{st} \gtrsim 1$ does not lead automatically to the inequality $\delta < a$, when the dipole approximation itself becomes meaningless.

It is seen from (3.14) that the second term in the denominator becomes of the order of or larger than unity, and simultaneously $\delta > a$ at such values of ϵ which satisfy the conditions

$$|(\varepsilon-1)/(\varepsilon+2)| \gg 3(\lambda/a)^3/2, \quad \sqrt{|\varepsilon|} < \lambda/a. \quad (3.18)$$

It is easy to see that these conditions are compatible. Let us consider by way of an example ϵ from (2.12). The first of these conditions is realized when the inequalities $|\omega - \omega_0| \lesssim nV\gamma_0$ and $\Gamma < nV\gamma_0$ are satisfied. It is easy to verify that in this case $\delta \approx \lambda \gg a$. It should be noted, however, that when $nV\gamma_0 > \Gamma$ the depth of penetration δ in the frequency region $|\omega - \omega_0 + \pi n\lambda^3\gamma_0| \lesssim \Gamma$ becomes smaller than a. Then, as is well known,[20-24] the principal role is assumed not by electric dipole scattering but by magnetic dipole scattering.

The question of applicability of the approximation used in the derivation of (3.14) will be discussed again after we consider the problem of reflection of electromagnetic waves from a thin layer. In this case the microscopic equation (2.3) also leads to the appearance of a collective radiative width, and the corresponding macroscopic Maxwell's equations admit of an exact solution in a simple analytic form. Consequently, the estimates of the limits of applicability become clearer.

It follows from the foregoing that the necessary condition for the appearance of the cooperative effect is smallness of the dissipative width compared with $nV\gamma_0$. This condition is not sufficient. Nowhere in the foregoing did we take into account the possibility of broadening of the spectral lines as a result of elastic collisions and of collisions accompanied by exchange of excitation quanta (the so-called resonant broadening, or broadening due to its own pressure). It is evident that the cooperative effect can appear only in the case when the corresponding widths Γ' (in the general case the width of the distribution $F(\omega')$ in (3.17) are smaller than $nV\gamma_0$.

Let us estimate first the broadening due to the proper pressure. For resonant lines this broadening is connected with the dipole-dipole interaction of the atoms of the same species. In essence we were forced to take into account the corresponding terms in the interaction of the oscillators in the system (2.3), without confining ourselves only to the first imaginary term in the expansion (2.4). It was also necessary to take into account the motion of the oscillators. The role of the di-

*G. A. Askar'yan called our attention to the possibility of deriving formula (3.16) in this manner.

pole-dipole interaction, however, has been thoroughly investigated.* In gases of not too high density, for an atomic transition with an oscillator strength f, this interaction leads to a broadening

$$\Gamma' \approx (e^2/m\omega_0) fn = (3/2) n\gamma_0 f \lambda^3. \qquad (3.19)$$

For the case in question $f \approx 1$ and $V \ll \lambda^3$. From this we get $\Gamma' \gg nVf_0$. It can also be shown that for all atomic and molecular transitions, whether electric dipole, quadrupole, or magnetic dipole, the broadening due to the proper pressure is larger than the possible value of the collective radiative width. Therefore in gases in this density region where the estimate (3.19) is applicable, the cooperative effect cannot play any role whatever. With increasing density, the situation may be different. In any case, formula (3.19) is certainly not applicable to condensed media. Therefore the inequality $\Gamma' < nV\gamma_0$ may be satisfied in principle.

In concluding this section, let us stop to discuss briefly the process of thermal radiation by small volumes. Inasmuch as it was shown above that the macroscopic approach to the problem of scattering of electromagnetic waves by small volumes includes the description of the cooperative effect, there is no need for taking special account of this effect when calculating the intensity and the spectrum of the thermal radiation. It suffices to use the known results based on the Mie theory, and the general theory of equilibrium electric fluctuations.[24, 25]

4. REFLECTION FROM A THIN LAYER

Let us consider normal incidence (along the z-axis) of a wave on a homogeneous layer of thickness $a \ll \lambda$. Replacing the summation over j in the system (2.3) by integration, we can transform this system without any simplifications into (see also [26])

$$\mathbf{d}_\omega(z)\left[\omega_0^2-\omega^2-\frac{4\pi}{3}n\frac{e^2}{m}-i\omega\Gamma\right] = i2\pi n\frac{e^2}{m}k\int_0^a e^{ik|z-z'|}\mathbf{d}_\omega(z')\,dz' + \frac{e^2}{m}\mathbf{E}_\omega^0 e^{ikz}. \qquad (4.1)$$

Solving this equation in the approximation $\exp ikz \approx 1$, $\exp ik|z-z'| \approx 1$ and assuming that $\mathbf{d}_\omega(z')$ does not change significantly in the interval (0, a), we obtain for $0 \le z \le a$

$$\mathbf{d}_\omega\left[\omega_0^2-\omega^2-(4\pi/3)n\frac{e^2}{m}-i\omega\Gamma-i\omega 2\pi nak(e^2/m)\right]=(e^2/m)\,\mathbf{E}_\omega^0. \qquad (4.2)$$

Knowing the induced dipole moments of each of the oscillators of the medium (4.2), we can find the field produced by them at large distances from the layer (in the wave zone)

$$\mathbf{E}_\omega(z) = i2\pi kna\mathbf{d}_\omega\begin{cases} e^{ikz}, & z>a,\\ e^{-ikz}, & z<a.\end{cases} \qquad (4.3)$$

From this we can readily obtain the following expressions for the amplitude reflection and transmission coefficients R and D, respectively:

$$R=\frac{2\pi inake^2/m}{\omega_0^2-\omega^2-(4\pi/3)n(e^2/m)-i\omega[\Gamma+(3/4\pi)n\gamma_0 a\lambda^2]}, \qquad (4.4)$$

$$D=\frac{\omega_0^2-\omega^2-(4\pi/3)n(e^2/m)-i\omega\Gamma}{\omega_0^2-\omega^2-(4\pi/3)n(e^2/m)-i\omega[\Gamma+(3/4\pi)n\gamma_0 a\lambda^2]}. \qquad (4.5)$$

Thus, in this case the collective radiative width turns out to be equal to $3n\gamma_0 a\lambda^2/4\pi$, i.e., it is determined by the number of particles in the effective volume $3a\lambda^2/4\pi$.

Let us consider now the same problem, starting from the macroscopic Maxwell equations. Instead of the integral equation (3.9) we obtain for the one-dimensional problem being considered by us

$$\mathbf{E}_\omega(z)=\mathbf{E}_\omega^0 e^{ikz}+\frac{k}{2i}\int_0^a e^{ik|z-z'|}\mathbf{E}_\omega(z')[1-\varepsilon(z')]\,dz'. \qquad (4.6)$$

Solving this equation in the same approximation as (4.1), we obtain the field $\mathbf{E}_\omega(z)$ inside the layer

$$\mathbf{E}_\omega=\mathbf{E}_\omega^0/[1+i(ak/2)(1-\varepsilon)]. \qquad (4.7)$$

For the reflected and transmitted waves we have

$$\mathbf{E}_\omega^{\text{refl}}=e^{-ikz}\frac{k}{2i}\int_0^a e^{ikz'}\mathbf{E}_\omega(z')[1-\varepsilon(z')]\,dz', \qquad (4.8)$$

$$\mathbf{E}_\omega^{\text{trans.}}=e^{ikz}\left\{\mathbf{E}_\omega^0+\frac{k}{2i}\int_0^a e^{-ikz'}\mathbf{E}_\omega(z')[1-\varepsilon(z')]\,dz'\right\}. \qquad (4.9)$$

Hence

$$R=-i(ak/2)(1-\varepsilon)/[1+i(ak/2)(1-\varepsilon)]^{-1}, \qquad (4.10)$$

$$D=[1+i(ak/2)(1-\varepsilon)]^{-1}. \qquad (4.11)$$

For ϵ from (2.12), formulas (4.10) and (4.11) coincide with (4.4) and (4.5), i.e., the macroscopic approach again makes it possible to take full account of the effect of collective radiative damping.

It is easy to see that expressions (4.10) and (4.11) satisfy the exact normalization condition: the sum of the reflected flux, the transmitted flux, and the energy absorbed in the layer is equal to the incident flux

$$\frac{c}{4\pi}|\mathbf{E}_\omega^0|^2=\frac{c}{4\pi}|\mathbf{E}_\omega^0|^2(|R|^2+|D|^2)+\frac{\omega}{4\pi}\int|\mathbf{E}_\omega(z)|^2\,\mathrm{Im}\,\varepsilon(z)\,dz. \qquad (4.12)$$

Let us ascertain now the relation of formulas (4.10) and (4.11) to the exact formulas for the reflection and transmission coefficients. For a homogeneous layer (plane-parallel plate), as is well known[20-22]

$$R=r(1-e^{2ika\sqrt{\varepsilon}})/(1-r^2e^{2ika\sqrt{\varepsilon}}), \qquad (4.13)$$

$$D=(1-r^2)/(e^{-ika\sqrt{\varepsilon}}-r^2e^{ika\sqrt{\varepsilon}}), \qquad (4.14)$$

where

$$r=(1-\sqrt{\varepsilon})/(1+\sqrt{\varepsilon}). \qquad (4.15)$$

When $ka \ll 1$ and $ka\sqrt{|\epsilon|} \ll 1$ expressions (4.13) and (4.14) go over into (4.10) and (4.11). The second of these conditions means that the depth of penetration $\delta = \lambda/2\pi\sqrt{|\epsilon|}$ is large compared with the layer thickness a. On the other hand, the term $ak(1-\epsilon)/2$ in the denominators of (4.10) and (4.11) ceases to be negligibly small compared with unity if $|(ak/2)(1-\epsilon)| \gtrsim 1$.

Thus, the cooperative radiative effect plays an important role and is correctly described by formulas (4.10) and (4.11) in the region

$$(\lambda/2\pi a) \lesssim |\varepsilon| \ll (\lambda/2\pi a)^2. \qquad (4.16)$$

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*The most complete analysis is contained in [23].

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