

THEORY OF OPTICAL WAVES PROPAGATION IN GASEOUS MEDIA. BOUGUER LAW AND THE ABSORPTION COEFFICIENT

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This paper presents a derivation of the Bouguer law based on semiclassical electrodynamics. Within the framework of the relaxation theory an expression is obtained for the absorption coefficient. Contributions coming to the relaxation from the effect of spatial dispersion have been isolated and discussed.

1. INTRODUCTION

Derivation of the Bouguer law based on the fundamental electrodynamics principles enables one to track most important aspects of the theory of optical radiation interaction with gaseous medium and to obtain an expression for the absorption coefficient in the most general form. In this paper the problem is solved using a macroscopic approach to description of the interaction between the field and a substance, using electric susceptibility in material equations and fluctuational theorem. This theorem connects dissipative properties of a medium, being in thermodynamic equilibrium, with the spectral density of the equilibrium fluctuations of the polarization vector.

2. DERIVATION OF THE BOUGUER LAW

In the case of a stationary electromagnetic field and neglecting spontaneous and stimulated radiation, we can derive this law considering balance between energy, converted into the heat per unit time in a volume V of the medium and the energy inflow into this volume (Refs. 1 and 2). The electromagnetic field at a point \mathbf{r} at the moment t is presented by the complex vector $\mathbf{E}(\mathbf{r}, t)$ and the polarization of the medium by the complex vector $\mathbf{P}(\mathbf{r}, t)$. For the amount of energy, converted into the heat per unit time in the volume V , we obtain

$$Q(\mathbf{R}) = \int_V d^3\rho \lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T dt \frac{1}{2} \operatorname{Re} \{ \mathbf{E}(\mathbf{R} + \rho, t) \mathbf{j}^*(\mathbf{R} + \rho, t) \}, \quad (1)$$

where

$$\mathbf{j}(\mathbf{r}, t) = \partial \mathbf{P}(\mathbf{r}, t) / \partial t \quad (2)$$

is the current density (it is assumed that the medium consists of electrically neutral particles). The parametric dependence on \mathbf{R} shows that the volume V is localized near the point with the radius vector \mathbf{R} .

Introducing Fourier components of the field and polarization, formula (1) is reduced to the following form:

$$Q(\mathbf{R}) = \frac{V}{2} \operatorname{Im} \sum_r \omega_r \sum_{i=\{x,y,z\}} E_i(\mathbf{R}; \mathbf{k}_r, \omega_r) P_i^*(\mathbf{R}; \mathbf{k}_r, \omega_r). \quad (3)$$

The polarization is related to the incident field and in gaseous media that are in thermodynamic equilibrium. This relation may be expressed by the formula from Ref. 1

$$P_i(\mathbf{R}; \mathbf{k}_r, \omega_r) = \sum_{i=\{x,y,z\}} \chi_{ij}(\mathbf{k}_r, \omega_r) E_j(\mathbf{R}; \mathbf{k}_r, \omega_r), \quad (4)$$

where $\chi_{ij}(\mathbf{k}_r, \omega_r)$ is the tensor of linear electric susceptibility. Its dependence on the wave vector and frequency results from spatial and time dispersion, respectively. If the field is too weak to influence the statistical distributions in the medium, then $\chi_{ij}(\mathbf{k}_r, \omega_r) = \chi(\mathbf{k}_r, \omega_r) \delta_{ij}$ and formula (1) takes the following form

$$Q(\mathbf{R}) = \frac{V}{2} \sum_r \omega_r \chi''(\mathbf{k}_r, \omega_r) |E(\mathbf{R}; \mathbf{k}_r, \omega_r)|^2, \quad (5)$$

$\chi''(\mathbf{k}_r, \omega_r)$ is the imaginary part of the susceptibility. By introducing energy density of the wave with the wave vector \mathbf{k}_r and frequency ω_r at the point \mathbf{R} ,

$$W(\mathbf{R}; \mathbf{k}_r, \omega_r) = (1/4\pi) |E(\mathbf{R}; \mathbf{k}_r, \omega_r)|^2, \quad (6)$$

we reduce formula (3) to the form

$$Q(\mathbf{R}) = -4\pi V \sum_r \omega_r \chi''(\mathbf{k}_r, \omega_r) W(\mathbf{R}; \mathbf{k}_r, \omega_r). \quad (7)$$

From this we obtain that the amount of energy, converted into heat from the wave with the wave vector \mathbf{k}_r and the frequency ω_r , is

$$Q(\mathbf{R}; \mathbf{k}_r, \omega_r) = -4\pi V \omega_r \chi''(\mathbf{k}_r, \omega_r) W(\mathbf{R}; \mathbf{k}_r, \omega_r). \quad (8)$$

Let us now calculate the energy influx from this electromagnetic wave into the volume V which is then

dissipated in it. It can easily be done if the volume V is presented by parallelepiped with the cross section Σ and the length l . This parallelepiped is oriented along the wave propagation direction. In this case the flux through the lateral face is zero, and we can find the value sought, which we designate by $\Phi(\mathbf{R}; \mathbf{k}_r, \omega_r)$. The value sought is designated as the difference between the wave energy, flowing out of the volume V per unit time through the cross section at the point $\mathbf{R} + \mathbf{l}$ of the path, and the amount of energy, flowing into the volume V at the same time through the cross section at the point \mathbf{R} , that is,

$$\Phi(\mathbf{R}; \mathbf{k}_r, \omega_r) = c\{W(\mathbf{R} + \mathbf{l}; \mathbf{k}_r, \omega_r) - W(\mathbf{R}; \mathbf{k}_r, \omega_r)\}\Sigma. \quad (9)$$

Equating Eq. (9) to Eq. (8) we obtain

$$\Delta_{\mathbf{k}}W(\mathbf{R}; \mathbf{k}, \omega)/l = -4\pi\omega\chi''(\mathbf{k}_r, \omega)W(\mathbf{R}; \mathbf{k}, \omega), \quad (10)$$

where for simplicity of the subscript r is omitted and we denote the increment of wave energy density along the direction \mathbf{k} of its propagation at the path of the length l as $\Delta_{\mathbf{k}}W(\mathbf{R}; \mathbf{k}, \omega)$. Assuming that the medium is not too dense and the field is attenuated at the paths of the pathlength on the order of the wavelength only slightly, we can proceed to limit $l \rightarrow 0$ in Eq. (10) under the condition that $l \gg 1/|\mathbf{k}|$. As a result, we obtain

$$\partial W(\mathbf{R}; \mathbf{k}, \omega)/\partial l = \alpha(\mathbf{k}, \omega)W(\mathbf{R}; \mathbf{k}, \omega). \quad (11)$$

This formula is the Bouguer law in a differential form, where the absorption spectral coefficient is $\alpha(\mathbf{k}, \omega) = (4\pi\omega/c)\chi''(\mathbf{k}, \omega)$. If we consider the propagation of the field to takes place along one of the reference axis, then we can introduce the ordinary derivative instead of the partial derivative with respect to direction. In this case the Bouguer law takes the form

$$dW(\mathbf{R}; \mathbf{k}, \omega) = \alpha(\mathbf{k}, \omega)W(\mathbf{R}; \mathbf{k}, \omega)dl, \quad (12)$$

in which the law is usually used. Here the dependence on the wave vector \mathbf{k} is informal and in the general case has to be preserved.

3. THE ABSORPTION COEFFICIENT

Dissipative properties of the medium are determined by the imaginary part of the susceptibility and related to the equilibrium fluctuations of the medium polarization vector. This relation is described by the fluctuational-dissipational Callen-Velton theorem.¹² Using this theorem, the absorption coefficient can be expressed in terms of the correlation function

$$\alpha(\mathbf{k}, \omega) = \frac{4\pi\omega}{c\hbar} \tanh \frac{\hbar\omega\beta}{2} \int_{-\infty}^{+\infty} \psi(\mathbf{k}, \tau) e^{i\omega\tau} d\tau, \quad (13)$$

where $\psi(\mathbf{k}, \tau)$ is the correlation function

$$\psi(\mathbf{k}, \tau) = (1/2)\text{Tr}\{\tilde{\rho}[P_z^+(\mathbf{k}, \tau) + \text{h.c.}]\}, \quad (14)$$

in which averaging over medium states is presented as spur over states of all the particles in the volume V ; $\tilde{\rho}$ is the equilibrium density matrix, corresponding to the Hamiltonian H , h.c. means that it is necessary to add the term Hermitian conjugated to the previous one. The projection of the polarization vector on the z axis, fixed in space, is determined by the following formulas

$$P_z(\mathbf{k}, \tau) = e^{iH\tau/\hbar} P_z(\mathbf{k}) e^{-iH\tau/\hbar}, \quad (15)$$

$$P_z(\mathbf{k}) = \frac{1}{V} \int_V d^3\rho P_z(\mathbf{R} + \rho) e^{-i\mathbf{k}\rho}. \quad (16)$$

Use of these formulas and invariant property of the spur relative to cyclic permutation of operators after presentation of the polarization as a collection of point dipoles in the volume V and after integration over the volume gives for the correlation function

$$\begin{aligned} \psi(\mathbf{k}, \tau) = & \\ = & \frac{1}{2V^2} \left\{ \sum_s \sum_p d_z^{(s)} e^{-iH_{\mathbf{k}}(\rho_s)\tau/\hbar} \tilde{\rho}_{\mathbf{k}}(\rho_s, \rho_p) d_z^{(p)} e^{iH\tau/\hbar} + \text{h.c.} \right\}, \end{aligned} \quad (17)$$

where $H_{\mathbf{k}}(\rho_s) = \exp(-i\mathbf{k}\rho_s)H\exp(-i\mathbf{k}\rho_s)$, $\rho_{s(p)}$ is the radius vector of a dipole $s(p)$. Note then that all the multipliers under sum sings, except for the first multiplier, are the solution to the evolution equation of the form

$$\partial x(\tau)/\partial \tau = - (i/\hbar)\{H_{\mathbf{k}}(\rho_s)x(\tau) - x(\tau)H\} \quad (18)$$

with the initial condition $x(-\infty) = \tilde{\rho}(\rho_s, \rho_p)d^{(p)}$, by introducing a superoperator $\hat{L}_{\mathbf{k}}(\rho)$ and assuming formally that

$$\hat{L}_{\mathbf{k}}(\rho_s)x(\tau) = - (i/\hbar)\{H_{\mathbf{k}}(\rho_s)x(\tau) - x(\tau)H\}, \quad (19)$$

and after integration over time under assumption of the adiabatic field switching on in the far past and adiabaticity of its switching off in the far future, we obtain for the absorption coefficient

$$\begin{aligned} \alpha(\mathbf{k}, \omega) = & \frac{4\pi\omega}{c\hbar} \tanh \frac{\hbar\omega\beta}{2} \frac{1}{2V^2} \times \\ \times & \text{ImTr} \left\{ \sum_s \sum_p d_z^{(s)} \left[\omega - \hat{L}_{\mathbf{k}}(\rho_s) \right]^{-1} \left[\tilde{\rho}_{\mathbf{k}}(\rho_s, \rho_p) d_z^{(p)} \right] + \text{h.c.} \right\}. \end{aligned} \quad (20)$$

We can divide the right part of this formula into two parts, corresponding to the same and different indices s and p . The first case belongs to the monomolecular absorption, which we will use below, and the second one belongs to the bimolecular absorption. For simplicity we assume that an optically active gas consists of particles of one kind and its density is much lower than the density of particles of a buffer gas. Thus we can consider each molecule absorbing the radiation as a molecule, being in a thermostat of a buffer gas. Then after transition to thermodynamic limit we obtain

$$\alpha_1(\mathbf{k}, \omega) = \frac{4\pi\omega\eta_s}{ch} \tanh \frac{\hbar\omega\beta}{2} \frac{1}{2} \times \\ \times \text{ImTr} \left\{ d_z [\omega - \hat{L}_k(\rho_s)]^{-1} [\tilde{\rho}_k(\rho) d_z] + \text{h.c.} \right\}, \quad (21)$$

where η_s is the density of an optically active gas.

4. EXCLUSION OF THERMOSTAT VARIABLES

Following Ref. 3 and introducing only necessary changes, connected with the allowance for spatial dispersion, we separate the relaxation part and exclude thermostat variables.

Hamiltonian of the problem has the following form

$$H = H_0^s + H_{tr}^s + H^b + H^{sb}, \quad (22)$$

where H_0^s describes internal motion and rotation of a molecule absorbing radiation (with all possible interactions between them); H_{tr}^s describes its translational motion, H^b is the Hamiltonian of a thermostat; and H^{sb} is the Hamiltonian of all the interactions between the absorbing molecule and a thermostat. Because of commutativity of $\exp(i\mathbf{k}\rho)$ with all the components in Eq. (22) except for H_{tr}^s , the transformed Hamiltonian $H_k(\rho)$ has the form

$$H_k(\rho) = H_0^s + H_{tr}^s(\mathbf{k}, \rho) + H^b + H^{sb}, \quad (23)$$

where $H_{tr}^s(\mathbf{k}, \rho) = \exp(-i\mathbf{k}\rho) H_{tr}^s \exp(i\mathbf{k}\rho)$. Because of linearity, the Liouville operators \hat{L} and $\hat{L}_k(\rho)$ have similar structures. Keeping this in mind, we can rewrite the resolvent from Eq. (21) in the following form

$$\frac{1}{\omega - \hat{L}_k(\rho)} = \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho) - \hat{L}^{sb}} = \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho)} \times \\ \times \left[1 + \hat{M}(\omega; \mathbf{k}, \rho) \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho)} \right], \quad (24)$$

where

$$\hat{L}_0(\mathbf{k}, \rho) = \hat{L}_0^s + \hat{L}_{tr}^s(\mathbf{k}, \rho) + \hat{L}_b \quad (25)$$

and the relaxation superoperator introduced is

$$\hat{M}(\omega; \mathbf{k}, \rho) = \hat{L}^{sb} \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho) - \hat{L}^{sb}} (\omega - \hat{L}_0(\mathbf{k}, \rho)). \quad (26)$$

Averaging over variables of a thermostat, which will be designated by angular brackets, gives us the following form

$$\left\langle \frac{1}{\omega - \hat{L}_k(\rho)} \right\rangle = \frac{1}{\omega - \hat{L}_k^s(\rho)} \left[1 + \langle \hat{M}(\omega; \mathbf{k}, \rho) \frac{1}{\omega - \hat{L}_k^s(\rho)} \rangle \right] = \\ = \frac{1}{\omega - \hat{L}_k^s(\rho) - \langle \hat{M}_c(\omega; \mathbf{k}, \rho) \rangle}, \quad (27)$$

where

$$\hat{L}_k^s(\rho) = \hat{L}_0^s + \hat{L}_{tr}^s(\mathbf{k}, \rho), \quad (28)$$

and analog of Zwanzig relaxation operator^{3,4} is introduced as $\langle \hat{M}_c(\omega; \mathbf{k}, \rho) \rangle$ related to $\langle \hat{M}(\omega; \mathbf{k}, \rho) \rangle$ by the relationship

$$\langle \hat{M}_c(\omega; \mathbf{k}, \rho) \rangle = \\ = \langle \hat{M}(\omega; \mathbf{k}, \rho) \left[1 + \frac{1}{\omega - \hat{L}_k^s(\rho)} \langle \hat{M}(\omega; \mathbf{k}, \rho) \rangle \right]^{-1}. \quad (29)$$

The technique of expansion of the relaxation operator over powers of thermostat particle density was discussed in Ref. 3 in detail. In the first order corresponding to the approximation of binary interactions, it gives the form

$$\langle \hat{M}_c(\omega; \mathbf{k}, \rho) \rangle \rightarrow \eta_b \langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle, \quad (30)$$

where η_b is the particle density of a thermostat and $\langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle$ is the binary relaxation operator

$$\langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle = \langle \hat{L}_c \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho) - \hat{L}_c} (\omega - \hat{L}_0(\mathbf{k}, \rho)) \rangle, \quad (31)$$

\hat{L}_c is the Liouvillian of interaction of a molecule absorbing radiation and a particle of a thermostat.

Thus the monomolecular absorption coefficient takes the following form:

$$\alpha_1(\mathbf{k}, \omega) = -\frac{4\pi\omega\eta_s}{ch} \tanh \frac{\hbar\omega\beta}{2} \frac{1}{2} \text{ImTr}^s \left\{ d_z [\omega - \hat{L}_0^s - \hat{L}_{tr}^s(\mathbf{k}, \rho) - \eta_b \langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle]^{-1} [\tilde{\rho}_k(\rho) d_z] + \text{h.c.} \right\}, \quad (32)$$

Here spur is already taken only over states of the molecule absorbing radiation, these states may be internal, rotational or translational.

5. DISCUSSION

Spatial dispersion, when taken into account, formally results in appearance, according to Eq. (32), of the dependence of relaxation superoperator on the wave vector and translational coordinate of the molecule absorbing radiation. As a direct result, $\alpha_1(\mathbf{k}, \omega)$ automatically transforms in the absence of collisional broadening, into the absorption coefficient of the Doppler spectrum. Collisions result in the line broadening. Due to the dependence of the relaxation superoperator on the wave vector and translational coordinate, collisions also result in a static interrelation between the Doppler and collisional mechanisms what result, for example, in deviations of an isolated line shape from the Voigt profile.

Binary relaxation superoperator $\langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle$ can be divided into two parts.

$$\begin{aligned} \langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle = & \langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle - \\ & - \langle \hat{m}_c(\omega; \mathbf{k}, \rho) [\hat{L}_{tr}^s(\mathbf{k}, \rho) / \omega - \hat{L}_0^s] \rangle, \end{aligned} \quad (33)$$

where

$$\langle \hat{m}_c(\omega; \mathbf{k}, \rho) \rangle = \hat{L}_c \frac{1}{\omega - \hat{L}_0(\mathbf{k}, \rho) - \hat{L}_c} (\omega - \hat{L}_0), \quad (34)$$

and $\hat{L}_0 = \hat{L}_0^s + \hat{L}^b$. The first part describes both the collisional relaxation and the change in Doppler shift due to collisions (and, as a result, shape of the Doppler spectrum). The second part of the correlation term reflects the presence of a connection between the changes in velocity of a molecule absorbing radiation and collisional broadening. The correlation term disappears in the absence of one of these factors. A more detailed analysis of these questions needs for a separate investigation.

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