ON THE METHOD OF GROUP INTEGRALS IN SCATTERING PROBLEMS

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Abstract

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ON THE METHOD OF GROUP INTEGRALS IN SCATTERING PROBLEMS

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A rigorous formulation of the problem of scattering of electromagnetic waves by statistical ensembles presupposes taking interference phenomena into account. Here the main difficulty consists in the fact that it is necessary simultaneously to take into account both the usual interaction between particles, specified by some potential, and the electrodynamic interaction, which is essentially connected with multiple scattering.

The purpose of the present work is to develop a scheme for applying the method of group integrals to such problems. Its advantage lies in the possibility of correctly introducing certain density approximations and, within these approximations, reducing the operation of averaging over the whole ensemble to averaging over a Mayer group.

1. Let there be a closed one-component isothermal system described by a canonical ensemble. Then the density matrix of the light scattered by such a system is given by the expression

$$\rho_{\alpha\beta} = \frac{1}{Z_N} \int_V \sum_{i,k=1}^{N} E_\alpha(\vec{r}_i, \vec{r}_1 \dots \vec{r}_{i-1}\vec{r}_{i+1} \dots \vec{r}_N \vec{r}) \times$$

$$\times E^*_\beta(\vec{r}_k, \vec{r}_1 \dots \vec{r}_{k-1}\vec{r}_{k+1} \dots \vec{r}_N \vec{r}) e^{-U/kT}\, d\{N\}. \qquad (1)$$

Here V is the volume of the system; N is the number of particles in it; Z_N is the configurational integral; $e^{-U/kT}$ is the Boltzmann factor; $\{N\}$ is the set of coordinates of all particles; $\vec{r}_j$ is the coordinate of the particle with number j; $\vec{r}$ is the coordinate of the observation point; E_α and E^*_β are components of the vector of the electric field scattered by particles with numbers i and k. These quantities, generally speaking, also depend on the coordinates of all the remaining $N-1$ particles.

Let

$$U = \sum_{\substack{l,m=1\\(l\neq m)}}^{N} u_{lm},$$

where u_{lm} is the potential of pair interaction, depending only on the distance between particles l and m. We expand the Boltzmann factor in products of group sums:

$$e^{-U/kT} = \sum_{(\sum jm_j = N)} \prod_j S_j(\{\lambda\}). \tag{2}$$

Here j is the order of the sum S_j; $\{\lambda\}$ is the set of coordinates of the particles belonging to the given group; m_j is the number of groups of j particles.

If the density of particles is such that the system is satisfactorily described by the equation of state up to the n-th virial coefficient, then one may take $j \leq n$. Suppose that the mean radius of the electrodynamic and "potential" interactions has one and the same order (this is fulfilled for a large class of real systems). Then phase correlation (coherence) will occur only between fields scattered by particles that belong to one and the same group. Consequently, E_α and E^*_β will depend on no more than $n+1$ arguments, and the integration in (1) may be carried out independently over each group.

Substitute the expansion (2) into (1), and, after carrying out the integration and separating the "pure" group integrals

$$b_j = \frac{1}{j!V} \int_V S_j d\{\lambda\}$$

from the integrals containing components of the scattered field, sum over all possible distributions of particles among groups compatible with the condition

$$\sum_{j=1}^{n} jm_j = N.$$

In doing so, the following possibilities must be considered:

1) Particle i belongs to a group of n_1 particles, particle k belongs to a group of n_2 particles.
2) Particles i and k fall into two different groups of n_1 particles.
3) Particles i and k belong to one and the same group of n_1 particles.

Denote by

$$\sum_{n_1,n_2=1}^{n} L_{n_1 n_2}$$

the contribution to $\rho_{\alpha\beta} Z_N$ obtained in the first and second cases (the calculation shows that the first case passes into the second when $n_1 = n_2$), and by

$$\sum_{n_1=1}^{n} M_{n_1}$$

the contribution corresponding to the third case. Then

$$L_{n_1 n_2} = n_1 n_2 \frac{N!}{(N - n_1 - n_2)!} V^2 C^{\alpha}_{n_1} C^{\beta *}_{n_2} Z_{N-n_1-n_2}, \tag{3}$$

where $C^{\alpha}_{n_1}$ and $C^{\beta *}_{n_2}$ are field components averaged over the groups,

$$C^{\alpha}_{l} = \frac{1}{l!V} \int E_{\alpha}(\vec{r}_i, \vec{r}_1 \ldots \vec{r}_l r) S_l d\vec{r}_1 \ldots d\vec{r}_l \tag{4}$$

and

$$Z_{N-n_1-n_2} = (N - n_1 - n_2)! \sum_{\left(\sum_{j=1}^{n} jm_j = N-n_1-n_2\right)} \prod_{j=1}^{n} \frac{(Vb_j)^{m_j}}{m_j!} \tag{5}$$

is the configurational integral of the system of $N - n_1 - n_2$ particles;

$$M_{n_1} = n_1^2 \frac{N!}{(N - n_1)!} V^2 d^{\alpha\beta}_{n_1} Z_{N-n_1}, \tag{6}$$

where

$$d^{\alpha\beta}_{l} = \frac{1}{l!V} \int_V E_{\alpha}(\vec{r}_i, \vec{r}_1, \ldots \vec{r}_l r) E^{*}_{\beta}(\vec{r}_k \vec{r}_1 \ldots \vec{r}_l r) S_l d\vec{r}_1 \ldots d\vec{r}_l \tag{7}$$

is the quadratic combination of field components averaged over the group, and Z_{N-n_1} is the configurational integral for a system of $N - n_1$ particles. Since the system is homogeneous, one may assume that $i, k < l$.

In M_{n_1} it is meaningful to single out a group of diagonal terms ($i = k$):

$$M'_{n_1} = n_1 \frac{N!}{(N-n_1)!} V^2 d'^{\alpha\beta}_{n_1} Z_{N-n_1}, \tag{8}$$

where

$$d'^{\alpha\beta}_l = \frac{1}{l!V} \int_V E_\alpha(\vec{r}_i, \vec{r}_1 \ldots \vec{r}_l r) E^*_\beta(\vec{r}_i, \vec{r}_1, \ldots \vec{r}_l r) S_l d\vec{r}_1 \ldots d\vec{r}_l.$$

Finally we have

$$\rho_{\alpha\beta} Z_N = \sum_{n_1,n_2=1}^{n} L_{n_1 n_2} + \sum_{n_1=1}^{n} M_{n_1}. \tag{9}$$

2. For an ideal gas $(n = 1,\ Z_N = V^N)$.

$$\rho_{\alpha\beta} = \rho^{(1)}_{\alpha\beta} + \rho^{(2)}_{\alpha\beta},$$

where

$$\rho^{(1)}_{\alpha\beta} = \frac{N}{V} \int_V E_\alpha(\vec{r}_1, \vec{r})\, E^*_\beta(\vec{r}_1, \vec{r})\, d\vec{r}_1 \tag{10}$$

is the density matrix of light scattered incoherently by each particle;

$$\rho^{(2)}_{\alpha\beta} = \frac{N(N-1)}{V^2} \int_V E_\alpha(\vec{r}_1, \vec{r})\, d\vec{r}_1 \int_V E^*_\beta(\vec{r}_2, \vec{r})\, d\vec{r}_2 \tag{11}$$

is the term corresponding to the interference that arises for a definite geometry of the surface of the scattering volume (^{2}).

If this surface is not fixed to within a wavelength, then $\rho^{(2)}_{\alpha\beta} = 0$, and for the dipole case the well-known Rayleigh scattering is obtained.

3. Let $n = 2$**.** Then the scattering is determined by the following quantities:

1) Diagonal terms $(i = k)$:

$$M'_1 = NV d'^{\alpha\beta}_1 Z_{N-1}, \qquad M'_2 = 2N(N-1)V^2 d'^{\alpha\beta}_2 Z_{N-2}. \tag{12}$$

2) The term corresponding to the correlation of the arguments of the quadratic functions of the field:

$$M_2 = 2N(N-1)V^2 d^{\alpha\beta}_2 Z_{N-2}. \tag{13}$$

3) Terms corresponding to the correlation of the arguments of the linear functions of the field:

$$L_{11} = N(N-1)V^2 C_1^{\alpha} C_1^{\beta *} Z_{N-2}, \qquad L_{21} = \frac{2N!}{(N-3)!} V^2 C_2^{\alpha} C_1^{\beta *} Z_{N-3},$$

$$L_{12} = \frac{2N!}{(N-3)!} V^2 C_1^{\alpha} C_2^{\beta *} Z_{N-3}, \qquad L_{22} = \frac{4N!}{(N-4)!} V^2 C_2^{\alpha} C_2^{\beta *} Z_{N-4}. \tag{14}$$

Using the estimate of the configuration integral by the enumeration method (^{1}), we obtain

$$Z_{N-l} \approx Z_N \frac{(N-l)!}{N!} t^l, \tag{15}$$

where t is the activity.

Substitution of (15) into (12)–(14) gives:

$$\begin{gathered}
\frac{1}{Z_N} M_1' = V d_1'^{\alpha\beta} t, \qquad \frac{1}{Z_N} L_{11} = V^2 C_1^{\alpha} C_1^{\beta *} t^2, \\
\frac{1}{Z_N} M_1' = 2V^2 d_2'^{\alpha\beta} t^2, \qquad \frac{1}{Z_N} L_{12} = 2V^2 C_1^{\alpha} C_2^{\beta *} t^3, \\
\frac{1}{Z_N} M_2 = 2V^2 d_2^{\alpha\beta} t^2, \qquad \frac{1}{Z_N} L_{21} = 2V^2 C_2^{\alpha} C_1^{\beta *} t^3, \\
\frac{1}{Z_N} L_{22} = 4V^2 C_2^{\alpha} C_2^{\beta *} t^4.
\end{gathered} \tag{16}$$

The expressions M_1' and L_{11}, to within the second virial coefficient, correspond to the preceding case. Since $S_2 = e^{-u_{12}/kT} - 1$, and for small densities $e^{-u_{12}/kT}$ coincides with the correlation function of second order, the term M_2 can be interpreted as a consequence of the correlation effect of the positions of the scattering particles (see also (^{3})).

We shall represent the integral C_2^{α} in the form

$$C_2^{\alpha} = \frac{1}{2!V} \int_V \widetilde{E}_{\alpha}(\vec{r}_1, \vec{r})\, d\vec{r}_1, \tag{17}$$

where

$$\widetilde{E}_\alpha(\vec{r}_1, \vec{r}) = \int_V E_\alpha(\vec{r}_1, \vec{r}_2, \vec{r})\, S_2\, d\vec{r}_2$$

is the field scattered by particle 1 of the group 1, 2, averaged over this group. It can be shown that $\widetilde{E}_\alpha(\vec{r}_1, \vec{r})$ also determines the non-averaged field scattered by an object with certain scattering properties different from the properties of the particles. Thus the terms $\frac{1}{Z_N} L_{n_1 n_2}$ and $\frac{1}{Z_N} M'_{n_1}$ may be interpreted, in a certain sense, as the density matrix of light scattered in a two-component ideal gas, one component of which consists of individual particles and the other of groups of two particles. The terms M'_1 and M'_2 are responsible for independent scattering on the elements of each of the components; the terms $L_{n_1 n_2}$ determine the "edge" effects.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.