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Abstract

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A VIRIAL EXPANSION IN THE PROBLEM OF ELECTROSTATIC POLARIZATION OF A MANY-BODY SYSTEM

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1. Let us place a system of N bodies, filling a volume V, in a homogeneous external electric field $\mathbf{E}_0$. Let $\langle \mathbf{E} \rangle$ and $\langle \mathbf{P} \rangle$ be the mean values of the electric field and polarization inside the system*. We shall be interested in the limiting value of the coefficient α in the relation

$$\langle \mathbf{P} \rangle = \alpha \langle \mathbf{E} \rangle \tag{1}$$

as $V \to \infty,\ N \to \infty,\ c = N/V = \text{const}$. (The polarizability α is a tensor. In what follows we shall denote tensors by Greek letters without tensor indices.) The aim of the work is to obtain an expansion of virial type:

$$\alpha = \sum_{s=1}^{\infty} c^s \alpha_s, \tag{2}$$

whose s-th term is expressed through the solution of the electrostatic problem for s bodies in the external field $\mathbf{E}_0$ and through the distribution function of s bodies.

The first term of such an expansion corresponds to neglecting the mutual influence of the polarizing bodies. The second term was obtained by Buckingham and Pople (^{1}) in considering the dielectric permittivity of a gas of classical nonpolar molecules.

In what follows, for simplicity, all N bodies are assumed identical.

2. Number the bodies by the index $i,\ 1 \le i \le N$. Let $\tilde{\pi}_1(1, 2, \dots, N)\mathbf{E}_0$ be the dipole moment of the first body in the presence of the remaining $N-1$ bodies. The numbers $1, 2, \dots$ denote the coordinates characterizing both the position and the orientation of the first, second, etc. bodies, while the same numbers with one prime $(1', 2', \dots)$ and with two primes $(1'', 2'', \dots)$ denote, respectively, the position and orientation of bodies.

We shall proceed from the following representation:

$$\begin{aligned}\tilde{\pi}_1(1,2,\dots,N) = \pi_1(1'') + \sum_{2\le i_2\le N} \pi_1(1,i_2) + \\ + \sum_{2\le i_2<i_3\le N} \pi_1(1,i_2,i_3) + \dots + \pi_1(1,2,\dots,N)\end{aligned} \tag{3}$$

The quantities $\pi_1(1,i_2,\dots,i_s)$ can be expressed through $\tilde{\pi}_1(1,i_2,\dots,i_s)$, if one considers relations (3) for $N = 1,2,\dots$ as equations for determining $\pi_1(1'')$, $\pi_1(1,2),\dots$. The solution of these equations gives

$$\begin{gathered}\pi_1(1'') = \tilde{\pi}_1(1''), \\ \pi_1(1,2) = \tilde{\pi}_1(1,2) - \tilde{\pi}_1(1''), \\ \pi_1(1,2,3) = \tilde{\pi}_1(1,2,3) - \tilde{\pi}_1(1,2) - \tilde{\pi}_1(1,3) + \tilde{\pi}_1(1'')\end{gathered}$$

* The averaging is performed over the ensemble of systems.

and so on. In general:

$$\begin{aligned}\pi_1(1,2,\dots,s) = \tilde{\pi}_1(1,2,\dots,s) - \sum_{2\le i_2<\dots<i_{s-1}\le s} \tilde{\pi}_1(1,i_2,\dots,i_{s-1}) + \\ + \sum_{2\le i_2<\dots<i_{s-2}\le s} \tilde{\pi}_1(1,i_2,\dots,i_{s-2}) - \dots + (-1)^{s-1}\tilde{\pi}_1(1'').\end{aligned} \tag{4}$$

An analogous representation for the field-strength tensor $\tilde{\varepsilon}(\mathbf{x} \mid 1,2,\dots,N)\mathbf{E}_0$ of the electric field at the point $\mathbf{x}$ has the form:

$$\begin{aligned}\tilde{\varepsilon}(\mathbf{x} \mid 1,2,\dots,N) = \delta + \sum_{1\le i_1\le N} \varepsilon(\mathbf{x} \mid i_1) + \\ + \sum_{1\le i_1<i_2\le N} \varepsilon(\mathbf{x} \mid i_1,i_2) + \dots + \varepsilon(\mathbf{x} \mid 1,2,\dots,N),\end{aligned} \tag{5}$$

where δ denotes the unit tensor $\delta^{\mu\nu}$, and

$$\begin{aligned}\varepsilon(\mathbf{x} \mid 1,\dots,s) = \tilde{\varepsilon}(\mathbf{x} \mid 1,\dots,s) - \sum_{1\le i_1<\dots<i_{s-1}\le s} \tilde{\varepsilon}(\mathbf{x} \mid i_1,\dots,i_{s-1}) + \dots \\ \dots + (-1)^{s-1} \sum_{1\le i_1\le s} \tilde{\varepsilon}(\mathbf{x} \mid i_1) + (-1)^s\delta.\end{aligned} \tag{6}$$

Averaging (3) and (5), we find the following expressions for

$$\langle \mathbf{P} \rangle = c\langle \tilde{\pi}_1(1,2,\dots,N)\rangle \mathbf{E}_0 \quad \text{and} \quad \langle \mathbf{E} \rangle = \langle \tilde{\varepsilon}(\mathbf{x} \mid 1,2,\dots,N)\rangle \mathbf{E}_0 :$$

$$\langle \mathbf{P} \rangle = \sum_{s\geq 1} c^s \pi_s \mathbf{E}_0; \tag{7}$$

$$\langle \mathbf{E} \rangle = \mathbf{E}_0 + \sum_{s\geq 1} c^s \varepsilon_s \mathbf{E}_0, \tag{8}$$

where

$$\pi_s = \frac{1}{(s-1)!}\int_V d1''\, d2 \dots ds\, F^{(N)}(1,2,\dots,s)\, \pi_1(1,2,\dots,s), \tag{9}$$

$$\varepsilon_s = \frac{1}{s!}\int_V d1\, d2 \dots ds\, F^{(N)}(1,2,\dots,s)\, \varepsilon(\mathbf{x} \mid 1,2,\dots,s), \tag{10}$$

and the distribution functions used by us, $F^{(N)}(1,2,\dots,s)$, are related to the probability dw of finding the first, second, ⋯, s-th body at the points $1,2,\dots,s$ by the relation

$$dw = c^{sF^{(N)}}(1,2,\dots,s)\,\frac{d1\, d2 \dots ds}{N(N-1)\dots(N-s+1)}.$$

To find the relation of interest to us between $\langle \mathbf{P} \rangle$ and $\langle \mathbf{E} \rangle$, we eliminate $\mathbf{E}_0$ from relations (7) and (8). Namely, substituting into (7)

$$\mathbf{E}_0 = \langle \mathbf{E} \rangle + \sum_{s\geq 1} c^s \beta_s \langle \mathbf{E} \rangle,$$

where

$$\beta_s = -\varepsilon_s - \sum_{t=1}^{s-1} \varepsilon_t \beta_{s-t}, \tag{11}$$

we obtain

$$\alpha_s = \pi_s + \sum_{t=1}^{s-1} \pi_t \beta_{s-t}. \tag{12}$$

3. Let us consider in more detail the first three coefficients a_s, and prove that, as $N \to \infty$, $V \to \infty$, $c = \text{const}$, these coefficients tend to finite limits. For $a_1 = \pi_1$ this is obvious, since π_1 does not depend on N. Therefore we begin with

Fig. 1

Figure 1: Fig. 1

$$a_2 = \pi_2 - \pi_1 \varepsilon_1 =$$

$$= \int d1'' \int_V d2 \{F^{(N)}(1,2)\pi_1(1,2) - F^{(N)}(1)F^{(N)}(2)\pi_1(1'')\varepsilon(1' \mid 2)\}. \tag{13}$$

Here, and also in the investigation of a_3, it is convenient to use the fact that the polarization of a finite number of bodies in an external field, at least for sufficiently large distances between the bodies, can be represented in the form of the following convergent series: the first term of the series is the polarization of isolated bodies in the external field; the polarization of a body in the $(n+1)$-st order is determined by the field of the remaining bodies, polarized in the n-th order. If such series are represented by graphs, then the image of $\pi(1,2)$ is Fig. 1a, and the image of $\varepsilon(\mathbf{x} \mid 2)$ is Fig. 1b.

Fig. 1

Let us return to a_2. All strongly connected graphs of Fig. 1a (for whose separation into two parts it is necessary to cut at least two lines) give, in the limit $V \to \infty$, a finite contribution to the integral (13), since each line in the graph has, as $|\mathbf{x}_{12}| \to \infty$, the order $|\mathbf{x}_{12}|^{-3}$, because it represents the field of an uncharged body ($|\mathbf{x}_{12}|$ is the distance between the first and second bodies). The remaining weakly connected graph $\pi_1(1,2)$ (with one line), as $|\mathbf{x}_{12}| \to \infty$, tends to

$$\pi_1(1'')\,\lambda(\mathbf{x}_{12})\,\pi_2(2''),$$

where the tensor

$$\lambda^{\mu\nu}(\mathbf{x}) = \frac{-\delta^{\mu\nu}|\mathbf{x}|^2 + 3x^\mu x^\nu}{|\mathbf{x}|^5}$$

describes the μ-th component of the field of a unit dipole directed along the ν-th axis. On the other hand, as $|\mathbf{x}_{12}| \to \infty$,

$$\varepsilon(1' \mid 2) = \lambda(\mathbf{x}_{12})\pi(2'') + O(|\mathbf{x}_{12}|^{-4})$$

and $F^{(N)}(1,2) - F^{(N)}(1)F^{(N)}(2) \to 0$, so that the weakly connected graphs also give a finite contribution to the integral (13).

Fig. 2

Figure 2: Fig. 2

Let us pass to

$$a_3 = \pi_3 - \pi_2\varepsilon_1 - \pi_1\varepsilon_2 + \pi_0\varepsilon_1\varepsilon_1. \tag{14}$$

Here π_s and ε_s are given by the integrals (8) and (9). The distribution functions $F^{(N)}(1, \dots, s)$, at large distances between the bodies, decompose into products of distribution functions of a smaller number of bodies, so that the proof of finiteness reduces to the investigation of $\pi_1(1, \dots, s)$, $s \leq 3$, and $\varepsilon(x \mid 1, \dots, s)$, $s \leq 2$. These quantities, in turn, are represented by the sum of all possible connected graphs (for whose separation into two parts it is necessary to cut at least one line). As in a_2, all strongly connected graphs $\pi_1(1, 2, 3)$ give a finite contribution to a_3 as $V \to \infty$. Among the weakly connected graphs we shall single out those in which the line of the external field enters the third body, and divide them into 4 groups (see Fig. 2): *a*—the third and second bodies are weakly connected, the second and first strongly; *b*—the third and first bodies are weakly connected, the first and second strongly; *c*—the second and third bodies …

are strongly connected, and the first is weakly connected with one of them; *d*—the third body is weakly connected with the second, and the second with the first—this group contains one graph.

It is easy to see that the graphs of the integrand π_3 of the type in Fig. 2a, for $|\mathbf{x}_{23}| \to \infty$, are compensated by those strongly connected graphs π_2 in which the line of the external field enters the second body, if in ε_1 one takes $\mathbf{x} = 2'$. Graphs of the type in Fig. 2b, for $|\mathbf{x}_{12}| \to \infty$, are compensated by graphs π_2 with the line of the external field entering the first body, if in ε_1 one sets $\mathbf{x} = 1'$. In the same way, graphs of the type in Fig. 2c are compensated by correspondingly chosen graphs of the expression $\pi_1\varepsilon_2$ (in Fig. 3 are shown graphs $\varepsilon(\mathbf{x} \mid 2, 3)$ with the line of the external field entering the third body). Finally, the graphs of the type in Fig. 2d, which occur in each of the four terms on the right-hand side of (14), mutually compensate one another.

Fig. 2

An analogous consideration can be carried out for the graphs $\pi_1(1, 2, 3)$, in which the line of the external field enters the second body.

Let us note that, whenever speaking of the compensation of graphs having a weak-connection line, it must be borne in mind that the compensation along this line occurs with accuracy up to $O(|\mathbf{x}_{ij}|^{-4})$. This, however, is sufficient for the convergence of the corresponding integrals.

Fig. 3

Figure 3: Fig. 3

Thus, as $V \to \infty$, α_3 also proves to be finite. By the same method one can prove the finiteness of the higher coefficients α_s.

Fig. 3

Let us note that for spherically symmetric bodies, as is not difficult to show,

$$\alpha_2 = \int d2\, F(1,2)\{\pi_1(1,2) - \pi_1 \lambda(\mathbf{x}_{12})\pi_1\}, \tag{15}$$

where π_1 is the polarizability of an isolated body.

4. If point dipoles with polarizability χ, which may or may not be isotropic, are taken as the bodies, then from (2) and (12) one can obtain series in powers of χ ([2]), expanding the tensors α_s in χ. The proposed method is also useful in calculating the dielectric permittivity of an emulsion ([3]).

All that has been set forth carries over without change to problems of static conductivity, magnetic permeability, or thermal conductivity of a matrix system,* owing to the identity of the equations describing these problems with the equations of electrostatics.

Of great interest is the derivation of a virial expansion in the problem of wave scattering by a system of many bodies. This question, however, has not yet been solved.

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* That is, of a homogeneous medium—the matrix—with inhomogeneous inclusions.