Local-field effects in nonlinear dielectrics

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In a system of identical nonlinear dielectric inclusions immersed in a uniform linear dielectric medium the mean polarization on a macroscopic length scale is related to the Maxwell field by a nonlocal and nonlinear constitutive equation. The method of statistical averaging and cluster expansion is used to derive a formally exact expression for the constitutive equation. The resulting cluster integrals are shown to be absolutely convergent, i.e., independent of the shape of the macroscopic sample in the thermodynamic limit. For a suspension of spherical inclusions a selection of terms leads to a nonlinear Clausius-Mossotti relation. Expressions are derived for the correlation corrections to this mean-field result. [S0163-1829(97)05216-8]

I. INTRODUCTION

The theory of the effective dielectric constant of a suspension of identical dielectric inclusions immersed in a medium with a linear dielectric constant has a long and distinguished history,[1,2] going back to contributions by Maxwell and Lorentz. An intrinsic difficulty of the theory is that the relationship between the electric polarization and the applied electric field is quite nonlocal. On the other hand, the existence of an effective dielectric constant implies that the relation between the polarization and the average electric field is local. It is the task of a statistical theory to show how the effective dielectric constant can be calculated from the microstructure of the suspension. Some years ago it was shown by Felderhof *et al.*,[3] following earlier work by Finkel'berg[4,5] and Jeffrey,[6,7] how this task can be accomplished, in principle, by the method of cluster expansion. In the following we develop a similar formalism for the macroscopic constitutive equation of a nonlinear dielectric.[8–10]

We allow arbitrary nonlinearity of the dielectric inclusions. In earlier work the case of weak nonlinearity was considered[11] and compared with the results of computer simulation.[12] It turned out that for a system of spherical inclusions the correlation corrections to the mean-field result were larger than in the linear case. For strong nonlinearity the effect of local fluctuations in the microstructure will be even more enhanced. It is known from computer simulations on fractal aggregates that the electric response is characterized by hot spots on the microscopic scale.[13] Hence the study of correlation corrections is particularly relevant for strongly nonlinear systems. The cluster expansion developed in the following, in principle, provides the necessary tool. For a system of spherical inclusions we derive a nonlinear Clausius-Mossotti relation.[14,15] Explicit expressions are found for the first few terms of the cluster expansion, involving two-particle and three-particle correlation functions. A study of these terms would yield valuable insight into the nature of the correlation corrections to the mean-field result.

As is well known, the problem of electrical or thermal conduction in a composite is mathematically identical to the dielectric one. However, our study has relevance beyond this particular class of problems. The theory can be applied to other transport phenomena, for example, to nonlinear elasticity or to wave propagation in a system with nonlinear scatterers. Harmonic generation can be taken into account. This opens the way to the study of local-field effects in nonlinear optics.[16–19] We have considered continuous systems in three dimensions, but the formal expressions of the cluster expansion can be applied in other dimensions and in systems with lattice structure.

II. FORMULATION OF THE PROBLEM

Our aim is to determine the effective properties of a nonlinear disordered dielectric system on a macroscopic length scale. On the microscopic length scale a particular configuration of the system consists of a large number N of identical, nonoverlapping inclusions distributed approximately uniformly in a large volume Ω. The configuration is characterized by the positions of centers $\{\mathbf{R}_1,\ldots,\mathbf{R}_N\}$ and, if the inclusions are not spherical, by a set of orientational variables $\{\Omega_1,\ldots,\Omega_N\}$. The inclusions are immersed in an infinite uniform background with dielectric constant ϵ_1. The dielectric response of a single inclusion, immersed in the background, to an applied electric field is assumed known. It is specified as a nonlinear and nonlocal dependence of the induced polarization $\mathbf{P}$ at the point $\mathbf{r}$ on the applied field $\mathbf{E}_0(\mathbf{r}')$. By definition the induced polarization $\mathbf{P}(1;\mathbf{E}_0) \equiv \mathbf{P}(1;\mathbf{r};\mathbf{E}_0(\mathbf{r}'))$ is nonvanishing only within the inclusion labeled 1. The dependence on position $\mathbf{R}_1$ and orientation Ω_1 is summarized in the symbol 1.

The basic equations for the electric field $\mathbf{E}$ and the dielectric displacement $\mathbf{D}$ are Maxwell's electrostatic equations

$$\nabla\cdot\mathbf{D}=4\pi\rho_0, \quad \nabla\times\mathbf{E}=0, \tag{2.1}$$

where $\rho_0=\rho_0(\mathbf{r})$ is a fixed charge distribution, independent of the inclusions. Maxwell's equations (2.1) are assumed to be valid on the microscopic level for each fixed configuration $(1,\ldots,N)$ of inclusions. The dielectric displacement is given by

$$\mathbf{D}(1,\ldots,N;\mathbf{E}_0)=\epsilon_1\mathbf{E}(1,\ldots,N;\mathbf{E}_0)+4\pi\mathbf{P}(1,\ldots,N;\mathbf{E}_0), \tag{2.2}$$

where $\mathbf{P}(1,\ldots,N;\mathbf{E}_0)$ is the induced polarization, to be determined from the incident electric field on each of the inclusions. The applied field $\mathbf{E}_0(\mathbf{r})$ is assumed to be a solution of the equations

$$\nabla\cdot\epsilon_1\mathbf{E}_0=4\pi\rho_0,\quad \nabla\times\mathbf{E}_0=0. \tag{2.3}$$

The electric field $\mathbf{E}(1,\ldots,N;\mathbf{E}_0)$ is the sum of the applied field and the induced field,

$$\mathbf{E}(1,\ldots,N;\mathbf{E}_0)=\mathbf{E}_0+\mathsf{G}_0\cdot\mathbf{P}(1,\ldots,N;\mathbf{E}_0), \tag{2.4}$$

where G_0 is the Green's function for the electric field due to a given polarization in a uniform medium with a dielectric constant ϵ_1. The explicit form for G_0 acting on a given vector field $\mathbf{V}(\mathbf{r})$ is

$$[\mathsf{G}_0\cdot\mathbf{V}](\mathbf{r})=-\frac{4\pi}{3\epsilon_1}\mathbf{V}(\mathbf{r})+\int_\delta d\mathbf{r}' \times\frac{3(\mathbf{r}-\mathbf{r}')\cdot\mathbf{V}(\mathbf{r}')(\mathbf{r}-\mathbf{r}')-(\mathbf{r}-\mathbf{r}')^2\mathbf{V}(\mathbf{r}')}{\epsilon_1|\mathbf{r}-\mathbf{r}'|^5}, \tag{2.5}$$

where the subscript δ on the integral indicates that the integral is carried out with an infinitesimally small sphere centered at $\mathbf{r}$ excluded. The polarization $\mathbf{P}(1,\ldots,N;\mathbf{E}_0)$ is the sum of the polarizations induced in each of the spheres,

$$\mathbf{P}(1,\ldots,N;\mathbf{E}_0)=\sum_{j=1}^{N}\mathbf{P}(j;\mathbf{E}_j'(1,\ldots,N;\mathbf{E}_0)), \tag{2.6}$$

where $\mathbf{E}_j'(1,\ldots,N;\mathbf{E}_0)$ is the field incident on inclusion j, that is, the sum of the applied field $\mathbf{E}_0$ and the fields generated by the other inclusions,

$$\mathbf{E}_j'(1,\ldots,N;\mathbf{E}_0)=\mathbf{E}_0+\mathsf{G}_0\cdot\sum_{k\neq j}\mathbf{P}(k;\mathbf{E}_k'(1,\ldots,N;\mathbf{E}_0)). \tag{2.7}$$

Since the single-particle response $\mathbf{P}(1;\mathbf{E}_0)$ is assumed known, Eq. (2.7) for $j=1,\ldots,N$ provides a set of equations from which the incident fields $\{\mathbf{E}_j'(1,\ldots,N;\mathbf{E}_0)\}$ can, in principle, be found. Hence, for any configuration $(1,\ldots,N)$ and applied field $\mathbf{E}_0$ the induced polarization $\mathbf{P}(1,\ldots,N;\mathbf{E}_0)$ and electric field $\mathbf{E}(1,\ldots,N;\mathbf{E}_0)$ are, in principle, determined.

The macroscopic response of the system is obtained by a statistical averaging procedure.[20,21] We assume that the disorder of the system is described by a known probability distribution $W(1,\ldots,N)$. The distribution is assumed normalized to unity and symmetric in the labels $1,\ldots,N$. The average electric field is

$$\langle\mathbf{E}\rangle=\int\cdots\int d1\cdots dN\ W(1,\ldots,N)\mathbf{E}(1,\ldots,N;\mathbf{E}_0) \tag{2.8}$$

and the average polarization is

$$\langle\mathbf{P}\rangle=\int\cdots\int d1\cdots dN\ W(1,\ldots,N)\mathbf{P}(1,\ldots,N;\mathbf{E}_0). \tag{2.9}$$

These fields are related by the average of Eq. (2.2)

$$\langle\mathbf{D}\rangle=\epsilon_1\langle\mathbf{E}\rangle+4\pi\langle\mathbf{P}\rangle. \tag{2.10}$$

The averages satisfy Maxwell's equations

$$\nabla\cdot\langle\mathbf{D}\rangle=4\pi\rho_0,\quad \nabla\times\langle\mathbf{E}\rangle=0. \tag{2.11}$$

The problem is to find the constitutive equation relating the average polarization $\langle\mathbf{P}\rangle$ to the Maxwell field $\langle\mathbf{E}\rangle$. The relation will be nonlinear and nonlocal. We write it in the abbreviated form

$$\langle\mathbf{P}\rangle=\mathbf{X}(\langle\mathbf{E}\rangle). \tag{2.12}$$

In the following we derive a formally exact cluster expansion for the vector functional $\mathbf{X}(\langle\mathbf{E}\rangle)$. The terms of the cluster expansion are expressed in terms of the partial distribution functions corresponding to the probability distribution $W(1,\ldots,N)$.

The partial distribution function

$$n(1,\ldots,s)=\frac{N!}{(N-s)!}\int\cdots\int d(s+1)\cdots dN\ W(1,\ldots,N) \tag{2.13}$$

gives the probability of finding a configuration of s inclusions whatever the configuration of the remaining $N-s$ inclusions. The integrations in Eq. (2.13) are over positions $\{\mathbf{R}_j\}$ and orientational variables $\{\Omega_j\}$. We assume that the system in volume Ω on average is spatially uniform and possesses a well-defined thermodynamic limit $N\to\infty$, $\Omega\to\infty$ with uniform density $n(1)$ and translationally invariant partial distribution functions $n(1,\ldots,s)$.

The constitutive equation Eq. (2.12) is derived in the thermodynamic limit $N\to\infty$, $\Omega\to\infty$ at constant ratio $n=N/\Omega$. Because in this limit the system becomes translationally invariant, the equation has the property that the average polarization $\langle\mathbf{P}(\mathbf{r})\rangle$ at point $\mathbf{r}$ depends on the mean field $\langle\mathbf{E}(\mathbf{r}')\rangle$ at point $\mathbf{r}'$ only via the difference vector $\mathbf{r}-\mathbf{r}'$. Only points $\mathbf{r}'$ in the neighborhood of $\mathbf{r}$ contribute, and we shall show that the dependence on the difference $\mathbf{r}-\mathbf{r}'$ is short ranged. A uniform mean field $\langle\mathbf{E}\rangle$ gives rise to a particular value of the average polarization $\langle\mathbf{P}\rangle$. The dependence of $\langle\mathbf{P}\rangle$ on $\langle\mathbf{E}\rangle$ for uniform $\langle\mathbf{E}\rangle$ is the constitutive relation of prime interest. It is determined by the nonlinear response of the individual inclusions and by the microstructure of the suspension, as given by the partial distribution functions.

III. CLUSTER EXPANSION

It is evident from Eqs. (2.8) and (2.9) that both the average polarization $\langle\mathbf{P}(\mathbf{r})\rangle$ and the average electric field $\langle\mathbf{E}(\mathbf{r})\rangle$ are functionals of the applied field $\mathbf{E}_0(\mathbf{r}')$. It is known from Maxwell theory that for a finite macroscopic sample these relations are highly nonlocal. We shall show that a relation of the form Eq. (2.12), which is independent of the shape of the sample, can be established by eliminating the applied field $\mathbf{E}_0$ in favor of the average field $\langle\mathbf{E}\rangle$ and then taking the thermodynamic limit. We perform the elimination by the method of cluster expansion.[3]

The polarization $\mathbf{P}(1,\ldots,N;\mathbf{E}_0)$ is found on the microscopic level as the solution of the N-inclusion problem for the given configuration, placed in the applied field $\mathbf{E}_0(\mathbf{r}')$. The effect of adding a single inclusion is expressed conve-

niently in terms of cluster functions. These are defined successively as

$$\mathbf{P}(1;\mathbf{E}_0)=\mathbf{M}(1;\mathbf{E}_0),$$

$$\mathbf{P}(1,2;\mathbf{E}_0)=\mathbf{M}(1,2;\mathbf{E}_0)+\mathbf{M}(1;\mathbf{E}_0)+\mathbf{M}(2;\mathbf{E}_0),$$

$$\begin{aligned}\mathbf{P}(1,2,3;\mathbf{E}_0)=&\mathbf{M}(1,2,3;\mathbf{E}_0)+\mathbf{M}(1,2;\mathbf{E}_0)+\mathbf{M}(1,3;\mathbf{E}_0)\\&+\mathbf{M}(2,3;\mathbf{E}_0)+\mathbf{M}(1;\mathbf{E}_0)+\mathbf{M}(2;\mathbf{E}_0)\\&+\mathbf{M}(3;\mathbf{E}_0),\end{aligned}\tag{3.1}$$

etc. The general rule is

$$\mathbf{P}(\mathcal{N};\mathbf{E}_0)=\sum_{\mathcal{M}\subseteq\mathcal{N}}\mathbf{M}(\mathcal{M};\mathbf{E}_0),\tag{3.2}$$

where $\mathcal{N}$ is a set of inclusion labels and the sum is over all subsets of $\mathcal{N}$. The inverse of this rule is

$$\mathbf{M}(\mathcal{N};\mathbf{E}_0)=\sum_{\mathcal{M}\subseteq\mathcal{N}}(-1)^{N-M}\mathbf{P}(\mathcal{M};\mathbf{E}_0),\tag{3.3}$$

where N and M are, respectively, the number of labels in $\mathcal{N}$ and $\mathcal{M}$. Inserting Eq. (3.2) in Eq. (2.9), remembering that the number of subsets of s objects out of N objects is $N!/[(N-s)!s!]$, and using the definition Eq. (2.13) of the partial distribution functions, we obtain

$$\langle\mathbf{P}\rangle=\sum_{s=1}^{N}\frac{1}{s!}\int\cdots\int d1\cdots ds\; n(1,\ldots,s)\mathbf{M}(1,\ldots,s;\mathbf{E}_0).\tag{3.4}$$

From Eq. (2.4) we find for the average electric field

$$\begin{aligned}\langle\mathbf{E}\rangle=&\mathbf{E}_0+\mathsf{G}_0\cdot\sum_{s=1}^{N}\frac{1}{s!}\\&\times\int\cdots\int d1\cdots ds\; n(1,\ldots,s)\mathbf{M}(1,\ldots,s;\mathbf{E}_0).\end{aligned}\tag{3.5}$$

We obtain the constitutive equation (2.12) by formally inverting Eq. (3.5), substituting the resulting expression for $\mathbf{E}_0$ in terms of $\langle\mathbf{E}\rangle$ into Eq. (3.4), and taking the thermodynamic limit.

In order to invert Eq. (3.5) we perform a Taylor expansion of $\mathbf{M}(1,\ldots,s;\mathbf{E}_0)$ about $\langle\mathbf{E}\rangle$. Thus we introduce the difference field

$$\mathbf{Y}=\mathbf{E}_0-\langle\mathbf{E}\rangle\tag{3.6}$$

and find the expansion[22]

$$\mathbf{M}(1,\ldots,s;\mathbf{E}_0)=\mathbf{M}(1,\ldots,s;\langle\mathbf{E}\rangle)+\sum_{l=1}^{\infty}\mathsf{M}^{(l)}(1,\ldots,s;\langle\mathbf{E}\rangle):\mathbf{Y}^{(l)},\tag{3.7}$$

where $\mathsf{M}^{(l)}$ is the lth-order functional derivative divided by $l!$ and $\mathbf{Y}^{(l)}$ stands for the direct product of l vector fields $\mathbf{Y}$. The double dot : indicates $3l$-fold integration over spatial coordinates and $3l$-fold summation over vector indices. We write Eq. (3.5) in the form

$$\begin{aligned}\mathbf{Y}=&-\mathsf{G}_0\cdot\sum_{s=1}^{N}\frac{1}{s!}\int d1\cdots ds\; n(1,\ldots,s)\mathbf{M}(1,\ldots,s;\langle\mathbf{E}\rangle)\\&-\mathsf{G}_0\cdot\sum_{s=1}^{N}\frac{1}{s!}\int d1\cdots ds\; n(1,\ldots,s)\\&\times\sum_{l=1}^{\infty}\mathsf{M}^{(l)}(1,\ldots,s;\langle\mathbf{E}\rangle):\mathbf{Y}^{(l)}\end{aligned}\tag{3.8}$$

and solve this equation by iteration. This yields $\mathbf{Y}$ expressed formally in terms of $\langle\mathbf{E}\rangle$. The result is substituted into Eq. (3.7), and this yields $\mathbf{M}(1,\ldots,s;\mathbf{E}_0)$ expressed in terms of $\langle\mathbf{E}\rangle$. Substituting this into Eq. (3.4), we finally find the average polarization $\langle\mathbf{P}\rangle$ expressed in terms of $\langle\mathbf{E}\rangle$. In the thermodynamic limit this provides a formally exact expression for the constitutive equation (2.12). Practical results are derived by selection of terms involving particle correlation functions of low order, in the expectation that higher-order correlation functions make only small corrections.

In the iteration of Eq. (3.8) we use the fact that the lth-order derivative $\mathsf{M}^{(l)}$ is l linear, i.e., it is linear in each of its l legs. Consequently, the integration over particle coordinates and the summation over number of particles can be interchanged with the contraction over spatial coordinates and field components. The final expression for $\mathbf{X}(\langle\mathbf{E}\rangle)$ is a sum of many terms involving integrals over products of the partial distribution functions. The sum can be rearranged and ordered into classes of terms corresponding to the number of inclusion labels involved. This yields the cluster expansion

$$\mathbf{X}(\langle\mathbf{E}\rangle)=\sum_{s=1}^{\infty}\frac{1}{(s-1)!}\mathbf{X}_s(\langle\mathbf{E}\rangle),\tag{3.9}$$

where the subscript s indicates the number of inclusion labels.

In order to see the structure of terms in the cluster expansion (3.9), it is instructive to consider first the terms of low order. The first term of the cluster expansion is simply

$$\mathbf{X}_1(\langle\mathbf{E}\rangle)=\int d1\; n(1)\mathbf{M}(1;\langle\mathbf{E}\rangle).\tag{3.10}$$

It can be evaluated from the response of a single inclusion. The second term involves integration over the coordinates of two inclusions. It reads

$$\begin{aligned}\mathbf{X}_2(\langle\mathbf{E}\rangle)=&\tfrac{1}{2}\int d1\int d2[n(1,2)\mathbf{M}(1,2;\langle\mathbf{E}\rangle)\\&-2n(1)n(2)\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)].\end{aligned}\tag{3.11}$$

Its explicit calculation involves the solution of the two-inclusion response problem. In the second term we have used the symmetry in labels to simplify the expression. The third term in the cluster expansion reads explicitly

$$\mathbf{X}_3(\langle\mathbf{E}\rangle)=\tfrac{1}{3}\int\int\int d1\,d2\,d3\{n(1,2,3)\mathbf{M}(1,2,3;\langle\mathbf{E}\rangle)$$
$$-3n(1,2)n(3)\mathsf{M}^{(1)}(1,2;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)$$
$$-3n(1)n(2,3)\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2,3;\langle\mathbf{E}\rangle)$$
$$+6n(1)n(2)n(3)\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0$$
$$\times\mathsf{M}^{(1)}(2,\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)+6n(1)n(2)n(3)$$
$$\times\mathsf{M}^{(2)}(1;\langle\mathbf{E}\rangle):[\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)][\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)]\}. \tag{3.12}$$

To discuss the higher-order terms it is convenient to introduce a diagrammatic representation.

IV. DIAGRAMMATIC REPRESENTATION

Before presenting the diagrammatic representation we note that the cluster integrals can be slightly simplified. Since the inclusions are identical, we can single out label 1 and consider in each of the terms the polarization induced in that inclusion. Correspondingly, we define rooted cluster functions $\mathbf{M}(1;2,\ldots,s;\mathbf{E}_0)$, defined successively as

$$\theta(1)\mathbf{P}(1;\mathbf{E}_0)=\mathbf{M}(1;\mathbf{E}_0),$$

$$\theta(1)\mathbf{P}(1,2;\mathbf{E}_0)=\mathbf{M}(1;2;\mathbf{E}_0)+\mathbf{M}(1;\mathbf{E}_0),$$

FIG. 2. Rooted loaded trees T_2 with two labels.

$$\theta(1)\mathbf{P}(1,2,3;\mathbf{E}_0)=\mathbf{M}(1;2,3;\mathbf{E}_0)+\mathbf{M}(1;2;\mathbf{E}_0)+\mathbf{M}(1;3;\mathbf{E}_0)$$
$$+\mathbf{M}(1;\mathbf{E}_0), \tag{4.1}$$

etc., where $\theta(1)$ is the characteristic function of inclusion 1. The average polarization can be written as

$$\langle\mathbf{P}\rangle=\sum_{s=1}^{N}\frac{1}{(s-1)!}\int\cdots\int d1\cdots ds\; n(1,\ldots,s)$$
$$\times\mathbf{M}(1;2,\ldots,s;\mathbf{E}_0). \tag{4.2}$$

The average electric field is given by Eq. (3.5) as before. With the above definition the two-particle cluster term (3.11) can be rewritten as

$$\mathbf{X}_2(\langle\mathbf{E}\rangle)=\int\int d1\,d2[n(1,2)\mathbf{M}(1;2;\langle\mathbf{E}\rangle)-n(1)n(2)$$
$$\times\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)]. \tag{4.3}$$

The three-particle term (3.12) can be rewritten as

$$\mathbf{X}_3(\langle\mathbf{E}\rangle)=\int d1\,d2\,d3\{n(1,2,3)\mathbf{M}(1;2,3;\langle\mathbf{E}\rangle)-n(1,2)n(3)\mathsf{M}^{(1)}(1;2;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)$$
$$-n(1,3)n(2)\mathsf{M}^{(1)}(1;3;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)-n(1)n(2,3)\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2,3;\langle\mathbf{E}\rangle)$$
$$+n(1)n(2)n(3)\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathsf{M}^{(1)}(2;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)+n(1)n(2)n(3)$$
$$\times\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathsf{M}^{(1)}(3;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)+n(1)n(2)n(3)\mathsf{M}^{(2)}(1;\langle\mathbf{E}\rangle):[\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)]$$
$$\times[\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)]+n(1)n(2)n(3)\mathsf{M}^{(2)}(1;\langle\mathbf{E}\rangle):[\mathsf{G}_0\mathbf{M}(3;\langle\mathbf{E}\rangle)][\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)]\}. \tag{4.4}$$

The first term of the cluster expansion, given by Eq. (3.10), is associated with the diagram shown in Fig. 1. The second-order term in Eq. (4.3) is associated with the two diagrams shown in Fig. 2. Each box contains the labels involved and the line represents the factor G_0. The three-particle term in Eq. (4.4) is associated with the eight diagrams shown in Fig. 3.

It is evident from the above examples that the diagrams have the structure of rooted trees or arborescences.[23] We shall refer to the diagrams as loaded trees. The term $\mathbf{X}_s(\langle\mathbf{E}\rangle)$ is associated with a set of loaded trees of order s, each tree having a total of s labels in the boxes and at most $s-1$ branches. The location of a box, as counted from the left, will be called its generation. For example, the box on the right in the fifth diagram in Fig. 3 is of the third generation. At each box a number l of lines can issue to the right. This corresponds to a factor $\mathsf{M}^{(l)}$ and is called the valency of the box. Valency zero corresponds to a factor $\mathbf{M}$ and indicates the end of a branch. The symmetry number of a loaded tree equals the number of nontrivial permutations of labels over the boxes. If the symmetry number is taken into ac-

FIG. 1. Rooted loaded tree T_1 with one label.

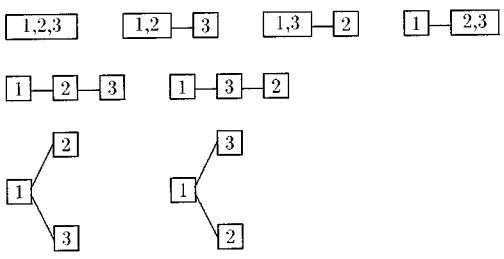


FIG. 3. Rooted loaded trees T_3 with three labels.

count, then a labeling rule can be adopted, for example, the labels can be ordered from left to right and from top to bottom.

Each of the terms in the integrand of the cluster integral $\mathbf{X}_s$ can be associated with a labeled loaded tree of s labels T_s. With each tree T_s we can associate a product of partial distribution functions $n(T_s)$ and a polarization $\mathbf{M}_s(T_s;\langle\mathbf{E}\rangle)$. For example, with the fourth diagram in Fig. 3 we associate the product

$$n\left(\boxed{1}\!-\!\boxed{2,3}\right) = n(1)\,n(2,3) \tag{4.5}$$

and the polarization

$$M\left(\boxed{1}\!-\!\boxed{2,3};\langle E\rangle\right) = \mathsf{M}^{(1)}\left(1;\langle E\rangle\right)\,\mathsf{G}_0\,M\left(2,3;\langle E\rangle\right). \tag{4.6}$$

With this notation the cluster integral of order s can be expressed as

$$\mathbf{X}_s(\langle\mathbf{E}\rangle)=\int d1\cdots\int ds\sum_{T_s}(-1)^{k-1}n(T_s)\mathbf{M}(T_s;\langle\mathbf{E}\rangle), \tag{4.7}$$

where the sum is over all labeled loaded trees of s labels and k indicates the number of boxes. We shall show that this can be rearranged to

$$\mathbf{X}_s(\langle\mathbf{E}\rangle)=\sum_{T_s}\mathbf{X}(T_s;\langle\mathbf{E}\rangle), \tag{4.8}$$

with the cluster integral $\mathbf{X}(T_s;\langle\mathbf{E}\rangle)$ corresponding to the loaded tree T_s. It is already evident from the two-particle cluster term given by Eq. (4.3) that we cannot simply interchange summation and integration in Eq. (4.7) since in the thermodynamic limit the separate integrals depend on the shape of the sample. In order to arrive at the form (4.8) with shape-independent integrals we must first rearrange the integrand.

V. REARRANGEMENT

In the preceding section we have shown that each term in the cluster expansion (3.9) is a cluster integral with an integrand that can be represented as a sum of loaded trees. In the linear theory[3] it was shown that the cluster integral of order s could be rearranged and expressed as a sum of integrals, each corresponding to an ordered partition of the s labels. It was shown that each term in this sum is by itself absolutely convergent. A similar rearrangement is possible in the nonlinear case. The cluster integral of order s can be rearranged and expressed as a sum of integrals, each of which is absolutely convergent.

As in the linear case, the two-particle cluster term in Eq. (4.3) can be rearranged as a sum of two cluster integrals

$$\begin{aligned}\mathbf{X}_2(\langle\mathbf{E}\rangle)=&\int d1\,d2\,n(1,2)[\mathbf{M}(1,2;\langle\mathbf{E}\rangle)\\&-\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle)]+\int d1\,d2[n(1,2)\\&-n(1)n(2)]\mathsf{M}^{(1)}(1;\langle\mathbf{E}\rangle)\mathsf{G}_0\mathbf{M}(2;\langle\mathbf{E}\rangle),\end{aligned} \tag{5.1}$$

each of which is absolutely convergent. For the first integral one sees this by considering large distances and using a multiple-scattering expansion of the polarization $\mathbf{M}(1;2;\langle\mathbf{E}\rangle)$. We discuss the multiple-scattering expansion further below. For the second integral the absolute convergence follows from the factorization $n(1,2)\approx n(1)n(2)$ at large distances.

The three-particle cluster term in Eq. (4.4) can be rearranged as a sum of eight terms

$$\mathbf{X}_3(\langle\mathbf{E}\rangle)=\int d1\,d2\,d3\sum_{j=1}^{8}I_j(1;2,3;\langle\mathbf{E}\rangle). \tag{5.2}$$

The first term reads

$$\begin{aligned}I_1(1;2,3;\langle\mathbf{E}\rangle)=&n(1,2,3)\{\mathbf{M}(1;2,3)-\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathbf{M}(2,3)\\&-\mathsf{M}^{(1)}(1;2)\mathsf{G}_0\mathbf{M}(3)-\mathsf{M}^{(1)}(1;3)\mathsf{G}_0\mathbf{M}(2)\\&+\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(2)\mathsf{G}_0\mathbf{M}(3)\\&+\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(3)\mathsf{G}_0\mathbf{M}(2)\\&+\mathsf{M}^{(2)}(1):[\mathsf{G}_0\mathbf{M}(2)][\mathsf{G}_0\mathbf{M}(3)]\\&+\mathsf{M}^{(2)}(1):[\mathsf{G}_0\mathbf{M}(3)][\mathsf{G}_0\mathbf{M}(2)]\},\end{aligned} \tag{5.3}$$

where for brevity we have omitted the argument $\langle\mathbf{E}\rangle$ on the right-hand side. The second term in Eq. (5.2) reads

$$\begin{aligned}I_2(1;2,3;\langle\mathbf{E}\rangle)=&[n(1,2,3)-n(1)n(2,3)][\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathbf{M}(2,3)\\&-\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(2)\mathsf{G}_0\mathbf{M}(3)\\&-\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(3)\mathsf{G}_0\mathbf{M}(2)].\end{aligned} \tag{5.4}$$

The third term reads

$$\begin{aligned}I_3(1;2,3;\langle\mathbf{E}\rangle)=&[n(1,2,3)-n(1,2)n(3)]\{\mathsf{M}^{(1)}(1;2)\mathsf{G}_0\\&\times\mathbf{M}^{(1)}(3)-\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(2)\mathsf{G}_0\mathbf{M}(3)\\&-\mathsf{M}^{(2)}(1):[\mathsf{G}_0\mathbf{M}(2)][\mathsf{G}_0\mathbf{M}(3)]\\&-\mathsf{M}^{(2)}(1):[\mathsf{G}_0\mathbf{M}(3)][\mathsf{G}_0\mathbf{M}(2)]\}.\end{aligned} \tag{5.5}$$

The fourth term is given by

$$I_4(1;2,3;\langle\mathbf{E}\rangle)=I_3(1;3,2;\langle\mathbf{E}\rangle). \tag{5.6}$$

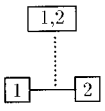


FIG. 4. Lattice of rooted loaded trees T_2 with two labels.

The fifth term reads

$$I_5(1;2,3;\langle\mathbf{E}\rangle)=[n(1,2,3)-n(1,2)n(3)-n(1)n(2,3)+n(1)n(2)n(3)]\mathsf{M}^{(1)}(1)\mathsf{G}_0\mathsf{M}^{(1)}(2)\times\mathsf{G}_0\mathbf{M}(3). \quad (5.7)$$

The sixth term is given by

$$I_6(1;2,3;\langle\mathbf{E}\rangle)=I_5(1;3,2;\langle\mathbf{E}\rangle). \quad (5.8)$$

The seventh term reads

$$I_7(1;2,3;\langle\mathbf{E}\rangle)=[n(1,2,3)-n(1,2)n(3)-n(1,3)n(2)+n(1)n(2)n(3)]\mathsf{M}^{(2)}(1):[\mathsf{G}_0\mathbf{M}(2)]\times[\mathsf{G}_0\mathbf{M}(3)] \quad (5.9)$$

and the eighth is given by

$$I_8(1;2,3;\langle\mathbf{E}\rangle)=I_7(1;3,2;\langle\mathbf{E}\rangle). \quad (5.10)$$

Interchanging summation and integration in Eq. (5.2) we find that $\mathbf{X}_3(\langle\mathbf{E}\rangle)$ can be written as a sum of eight integrals,

$$\mathbf{X}_3(\langle\mathbf{E}\rangle)=\sum_{j=1}^{8}\int d1\,d2\,d3\,I_j(1;2,3;\langle\mathbf{E}\rangle), \quad (5.11)$$

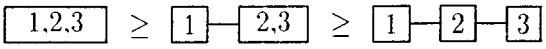
some of which are equal by symmetry. It may be seen by inspection that each of the eight integrals is absolutely convergent, either because of the distribution function factor or because of the polarization factor.

The above rearrangement can be generalized to the higher-order terms in the cluster expansion Eq. (3.9). The rearrangement leads to the form (4.8) with the cluster integral $\mathbf{X}(T_s;\langle\mathbf{E}\rangle)$ given by

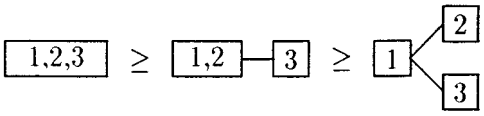
$$\mathbf{X}(T_s;\langle\mathbf{E}\rangle)=\int d1\cdots\int ds\; b(T_s)\mathbf{C}(T_s;\langle\mathbf{E}\rangle), \quad (5.12)$$

with so-called block distribution function $b(T_s)$ and chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$. The names are coined in correspondence with names for similar quantities in the linear theory.[3]

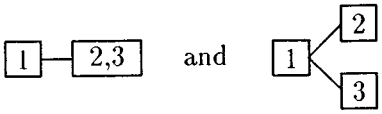
In order to define the block distribution $b(T_s)$ and chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$ we introduce a partial ordering of the loaded trees of s labels. We write $T_s\leqslant T_s'$ if the tree T_s' is either the same as the tree T_s or can be obtained from T_s by removing one or more lines, with the convention that upon removal of a line the box at the right end is merged with the one on its left end. For example, for the trees of three labels one has the ordering



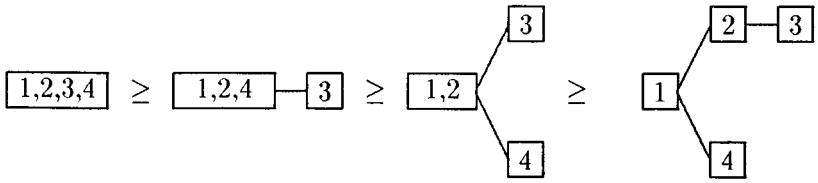
and also



but no ordering exists between



An example of ordered trees with four labels is



The block distribution function $b(T_s)$ is defined by

$$b(T_s)=\sum_{T_s'\geqslant T_s}(-1)^{k'-1}n(T_s'), \quad (5.13)$$

with the abbreviation

$$n(T_s')=n(B_1')\cdots n(B_{k'}'), \quad (5.14)$$

where B_j' denotes the labels in box j on the tree T_s', which has k' boxes. The chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$ is defined by

$$\mathbf{C}(T_s;\langle\mathbf{E}\rangle)=\sum_{T_s'\leqslant T_s}(-1)^{k-k'}\mathbf{M}(T_s';\langle\mathbf{E}\rangle), \quad (5.15)$$

where k is the number of boxes on tree T_s.

The proof of the identity (4.8) follows by substitution of the definitions (5.13) and (5.15) into Eq. (5.12). This yields

$$\begin{aligned}\sum_{T_s} b(T_s)\mathbf{C}(T_s;\langle\mathbf{E}\rangle)&=\sum_{T_s}\sum_{T_s'\geqslant T_s}(-1)^{k'-1}n(T_s')\\&\quad\times\sum_{T_s''\leqslant T_s}(-1)^{k-k''}\mathbf{M}(T_s'';\langle\mathbf{E}\rangle)\\&=\sum_{T_s'}\sum_{T_s''}(-1)^{k'-1}n(T_s')\mathbf{M}(T_s'';\langle\mathbf{E}\rangle)\\&\quad\times\sum_{T_s''\leqslant T_s\leqslant T_s'}(-1)^{k-k''}\\&=\sum_{T_s}(-1)^{k-1}n(T_s)\mathbf{M}(T_s;\langle\mathbf{E}\rangle).\end{aligned} \quad (5.16)$$

In the last line we have used the identity

$$\sum_{T_s''\leqslant T_s\leqslant T_s'}(-1)^{k-k''}=\delta_{T_s'',T_s'}, \quad (5.17)$$

which is proved below.

The collection of trees $\{T_s\}$ can be arranged in a lattice ordered according to the number of boxes, with the top row consisting of the single box with s labels, the second row consisting of trees with two boxes, etc. The bottom line consists of all rooted trees with s boxes, each containing a single label. We link every tree to those trees in the row below, from which it follows by removal of a line, as defined above, and indicate the link by a dotted line. Thus, for $s=2$ the lattice consists of two rows, as shown in Fig. 4. The lattice for $s=3$ is shown in Fig. 5. The ordering of trees corresponds to the order of rows for those trees that are connected by dotted lines running upward. For any two trees T_s'' and T_s' such that $T_s''\leqslant T_s'$ one has

$$\sum_{T_s''\leqslant T_s\leqslant T_s'}(-1)^{l''-l}=\begin{cases}0, & T_s''\neq T_s'\\ 1, & T_s''=T_s',\end{cases} \quad (5.18)$$

where the sum is over the trees T_s that can be obtained from T_s'' by removing lines and from which T_s' can be obtained by removing lines, and where l and l'' are, respectively, the row numbers in which T_s and T_s'' lie, the rows being counted from the bottom. The proof of Eq. (5.18) follows from the fact that the number of trees in the sum that are in the lth row from the bottom is $\binom{l''-l'}{l''-l}$, the number of ways one can select $l''-l$ of the $l''-l'$ lines that must be removed from T_s'' to get T_s'. The sum is therefore

$$\sum_{l=l'}^{l''}\binom{l''-l'}{l''-l}(-1)^{l''-l}=(1-1)^{l''-l'}=\begin{cases}0, & l''\neq l'\\ 1, & l''=l',\end{cases} \quad (5.19)$$

which is equivalent to Eq. (5.18). The latter is identical to Eq. (5.17) since the number of boxes on a tree T_s in row l is $k=s-l+1$.

A comparison of Eqs. (5.3)–(5.10) and the lattice for $s=3$, shown in Fig. 5, clarifies the rules of the game. Each of the integrands shown in Eqs. (5.3)–(5.10) corresponds to a particular tree on the lattice. The top tree corresponds to Eq. (5.3) and the remaining trees in the order from left to right and from top to bottom correspond to Eqs. (5.4)–(5.10), respectively. Label 1 has been selected and plays a special role.

VI. ABSOLUTE CONVERGENCE

In this section we discuss the absolute convergence of the cluster integrals $\{\mathbf{X}(T_s;\langle\mathbf{E}\rangle)\}$ occurring in Eq. (4.8). The discussion is similar to that in the linear case.[3] The integrand in Eq. (5.12) is the product of a block distribution function $b(T_s)$ and a chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$, each associated with the loaded tree T_s. To demonstrate absolute convergence of the integral we show that for widely separated configurations the integrand vanishes sufficiently rapidly, because of the vanishing either of $b(T_s)$ or of $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$.

We assume that the distribution function $W(1,\ldots,N)$ is such that the partial distribution functions $n(1,\ldots,s)$ have the product property: for a configuration with k widely separated groups, corresponding to a partition of the labels into k disjoint subsets $B_1, B_2,\ldots,B_k$, then

$$n(1,\ldots,s)\sim n(B_1)n(B_2)\cdots n(B_k). \quad (6.1)$$

If any line of the tree T_s is cut, then the s labels are separated into two groups: those attached to the part of the tree on the left side of the cut and those attached to the part on the right. We assert that the block distribution function $b(T_s)$ vanishes for any configuration in which the coordinates associated with the labels of the first group are widely separated from those associated with labels in the second group. To see this we note that the sum Eq. (5.13) defining $b(T_s)$ is over the trees in the lattice that can be obtained from T_s by removing lines. The trees in the sum can therefore be paired, the one having the line that is being cut, with the other in the row above that is obtained by removing the line. For the separated configuration the terms corresponding to each pair cancel since they have opposite signs and, on account of the product property (6.1), the same product of partial distribution functions appears in each. As an illustration of this result,

$$b\left(\begin{array}{c}\boxed{2}\\ \boxed{1}\!\!<\\ \boxed{3}\end{array}\right)=n(1,2,3)-n(1,2)n(3)-n(1,3)n(2)+n(1)n(2)n(3) \quad (6.2)$$

vanishes when 1 and 3 are near but far from 2; it does not vanish, however, when 2 and 3 are near but far from 1.

We now show that the chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$ vanishes sufficiently rapidly for those configurations in which coordinates corresponding to labels within one of the boxes $B_1,\ldots,B_k$ of the tree T_s are widely separated. To show this we study the multiple scattering expansion of the chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$.

The multiple-scattering expansion of the polarization $\mathbf{P}(1,\ldots,s;\mathbf{E}_0)$ of s inclusions placed in the field $\mathbf{E}_0(\mathbf{r})$ can be obtained by Taylor expansion about $\mathbf{E}_0$ of the argument $\mathbf{E}_j'$ in the separate terms $\mathbf{P}(j;\mathbf{E}_j'(1,\ldots,s;\mathbf{E}_0)$ in Eq. (2.6) and iteration of Eq. (2.7), specialized to $N=s$. Hence we obtain the multiple-scattering expansion of the polarization $\mathbf{M}(1;2,\ldots,s;\langle\mathbf{E}\rangle)$ of inclusion 1 in the presence of $s-1$ other inclusions, all placed in the field $\langle\mathbf{E}\rangle$ and with terms subtracted according to the cluster expansion Eq. (4.1). In the multiple-scattering expansion this polarization is expressed in terms of the single-particle polarizations $\{\mathbf{M}(j;\langle\mathbf{E}\rangle)\}$, their derivatives $\{\mathsf{M}^{(i)}(j;\langle\mathbf{E}\rangle)\}$ for $i=1,2,\ldots$, and the connecting Green's function G_0. It may be represented as a sum of rooted trees with label 1 at the root, a single label from $1,\ldots,s$ associated with each of the nodes, a factor $\mathsf{M}^{(i)}(j;\langle\mathbf{E}\rangle)$ corresponding to a node with label j and right-hand valency i, a factor $\mathbf{M}(j;\langle\mathbf{E}\rangle)$ corresponding to an end node with label j and with the conditions that the labels at each end of a line must differ and that each label must occur at least once. As an example, we show in Fig. 6 one of the rooted trees for $s=3$. Each of such rooted trees of s labels has an index t_s. The polarization $\mathbf{M}(1;2,\ldots,s;\langle\mathbf{E}\rangle)$ is given by the sum of polarizations corresponding to all different rooted trees of s labels,

$$\mathbf{M}(1;2,\ldots,s;\langle\mathbf{E}\rangle)=\sum_{t_s}\mathbf{M}(t_s;\langle\mathbf{E}\rangle). \tag{6.3}$$

The polarization $\mathbf{M}(T_s;\langle\mathbf{E}\rangle)$ corresponds to a subset of these diagrams, namely, those for which the labels are divided into the boxes $B_1,\ldots,B_k$ of the tree T_s and all allowed lines between labels within the boxes occur, but the different boxes are connected only by a single propagator, corresponding to a line of the tree T_s. A factor $(-1)^l$ provides a sign corresponding to the number l of lines in tree T_s.

A tree t_s is called reducible if it can be split into two branches of two distinct subsets of labels by the cutting of a single line. A tree t_s that is not reducible will be called irreducible. If the expression for $\mathbf{M}(T_s';\langle\mathbf{E}\rangle)$ is put into the definition Eq. (5.15) for the chain polarization $\mathbf{C}(T_s;\langle\mathbf{E}\rangle)$ there is a cancellation of many terms. All terms corresponding to trees $\{t_s\}$ that are reducible inside the boxes $\{B_j\}$ of the tree T_s cancel out. Only those trees $\{t_s\}$ remain that are reducible at the lines joining the boxes of the tree T_s. To demonstrate this result we note first that with a given reducible tree t_s occurring in $\mathbf{M}(T_s;\langle\mathbf{E}\rangle)$ we can associate a unique tree T_s'' by identifying the sets of labels in the irreducible parts of t_s with the boxes of the tree T_s''. The tree t_s will occur exactly once in each tree T_s' in the sum in Eq. (5.15) for which $T_s''\leqslant T_s'\leqslant T_s$. By the identity (5.18) these terms precisely cancel when the sum over T_s' is carried out.

We see therefore that for any configuration in which there is a wide separation of inclusions corresponding to labels within a box of the tree T_s, there must be at least two factors G_0 linking the separate inclusions. As a consequence, the chain polarization will vanish as the inverse sixth power of the separation, leading to absolute convergence. On the other hand, for configurations in which there are wide separations corresponding to the links between the boxes the chain polarization vanishes only as the inverse cube of the separation, but for exactly these configurations the corresponding block distribution function vanishes. Hence the product occurring in the integrand of Eq. (5.12) vanishes sufficiently rapidly for all configurations and the integral is absolutely convergent.

VII. DENSITY EXPANSION

In this section we relate the cluster expansion (3.9) to an expansion in powers of number density n and consider explicitly the term of lowest order in density. Each of the partial distribution functions $n(1,\ldots,s)$ can be expanded in powers of density. The lowest-order term is simply

$$n(1,\ldots,s)\approx n^s\prod_{j=1}^{s}\varphi(\Omega_j), \tag{7.1}$$

where $\varphi(\Omega_j)$ is the orientational distribution of inclusion j in the low-density limit. As a consequence, the term $\mathbf{X}_s$ in Eq. (3.9) carries at least a factor n^s. In a density expansion of $\mathbf{X}(\langle\mathbf{E}\rangle)$ at fixed $\langle\mathbf{E}\rangle$ only the single-particle term $s=1$ contributes to order n.

To lowest order in density the constitutive equation is therefore approximated by

$$\langle\mathbf{P}\rangle\approx\mathbf{X}_1(\langle\mathbf{E}\rangle)=n\int d\mathbf{R}_1 d\Omega_1\varphi(\Omega_1)\mathbf{M}(1;\langle\mathbf{E}\rangle). \tag{7.2}$$

As noted at the end of Sec. II it is of particular interest to consider this relation for uniform Maxwell field $\langle\mathbf{E}\rangle$. For a particular field point $\mathbf{r}$ the integration over position $\mathbf{R}_1$ yields a value equal to the integral of the polarization over the inclusion for fixed orientation Ω_1 and with center at a fixed position, say, the origin, when it is placed in the same uniform field $\langle\mathbf{E}\rangle$. This is just the dipole moment

$$\mathbf{p}_1(\Omega_1;\langle\mathbf{E}\rangle)=\int d\mathbf{r}\,\mathbf{P}(\mathbf{R}_1=\mathbf{0},\Omega_1;\mathbf{r};\langle\mathbf{E}\rangle). \tag{7.3}$$

We denote the average over orientations of the inclusion as

$$\boldsymbol{\mu}(\langle\mathbf{E}\rangle)=\int d\Omega_1\varphi(\Omega_1)\mathbf{p}_1(\Omega_1;\langle\mathbf{E}\rangle). \tag{7.4}$$

With this notation, the average polarization is, to first order in density,

$$\langle\mathbf{P}\rangle=n\boldsymbol{\mu}(\langle\mathbf{E}\rangle). \tag{7.5}$$

For example, for a spherical inclusion of radius a, centered at the origin, and made of a material for which the induced polarization in a uniform inner field $\mathbf{E}_i$ is

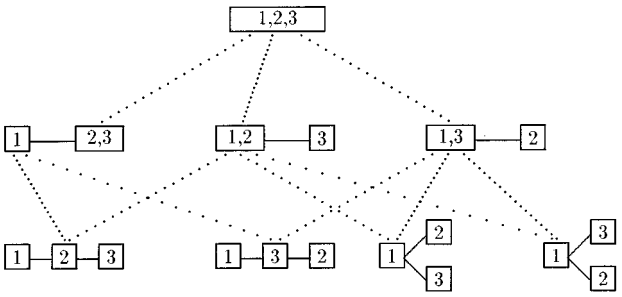


FIG. 5. Lattice of rooted loaded trees T_3 with three labels.

$$\mathbf{P}(\mathbf{r})=\begin{cases}\mathbf{g}(\mathbf{E}_i), & r<a\\ \mathbf{0}, & r>a,\end{cases} \tag{7.6}$$

the total induced dipole moment is

$$\mathbf{p}_1(\mathbf{E}_0)=\frac{4\pi}{3}a^3\mathbf{g}(\mathbf{E}_i). \tag{7.7}$$

The inner field $\mathbf{E}_i$ is related to the applied field $\mathbf{E}_0$ by

$$\mathbf{E}_i=\mathbf{E}_0-\frac{4\pi}{3\epsilon_1}\mathbf{g}(\mathbf{E}_i). \tag{7.8}$$

This can be solved for $\mathbf{E}_i$ as a function of $\mathbf{E}_0$,

$$\mathbf{E}_i=\mathbf{h}(\mathbf{E}_0). \tag{7.9}$$

Hence, in this case the function $\boldsymbol{\mu}(\mathbf{E}_0)$ to be used in Eq. (7.5) is

$$\boldsymbol{\mu}(\mathbf{E}_0)=\frac{4\pi}{3}a^3\mathbf{g}(\mathbf{h}(\mathbf{E}_0)). \tag{7.10}$$

An interesting example of a material with strongly nonlinear properties is CdS. An aqueous suspension of spherical particles of this material can show optical bistability.[24–26]

The next-order term in the density expansion of the constitutive relation involves the two-particle cluster term $\mathbf{X}_2$. This requires solution of the nonlinear response problem for a pair of inclusions placed in a uniform field.

VIII. NONLINEAR CLAUSIUS-MOSSOTTI RELATION

In this section we specialize to spherical inclusions of radius a and show that for this case one can derive a nonlinear Clausius-Mossotti relation $\langle\mathbf{P}\rangle=\mathbf{X}_{\rm NCM}(\langle\mathbf{E}\rangle)$ by restricting the volume of integration of the cluster integrals in Eq. (5.12) to the so-called virtual overlap volume and considering a uniform field $\langle\mathbf{E}\rangle$. In the linear case the same procedure leads to the Clausius-Mossotti formula for the effective dielectric constant.[27] The nonlinear Clausius-Mossotti relation (NCM) takes the form we have derived earlier on the basis of a Lorentz local field argument.[15]

The NCM relation contains only the single-particle response function $\boldsymbol{\mu}(\mathbf{E}_0)$, defined in Eq. (7.4), and the number density n. For spheres there are no orientational variables and the cluster integrals are over positions of centers only. In order to derive the NCM relation we limit the sum over trees in Eq. (4.8) to those in the bottom row of the lattice, in analogy to the linear case. For these trees we limit the integration over $3s$-dimensional configuration space in Eq. (5.12) to the region in which the inclusions overlap sequentially in successive generations. Thus, for the tree in the lower left-hand corner in Fig. 5, inclusion 2 must overlap with 1 and inclusion 3 must overlap with 2, while for the tree in the lower right-hand corner both inclusions 2 and 3 must overlap with 1, but not necessarily with each other. For each type of tree in the bottom line of the lattice there are $(s-1)!$ trees differing only by a permutation of the labels $2,\ldots,s$ over $s-1$ boxes. Their contributions to the sum in Eq. (4.8) differ only by a relabeling of the variables of integration and therefore are all the same. We can therefore write our approximation to the constitutive function in Eq. (3.9) as

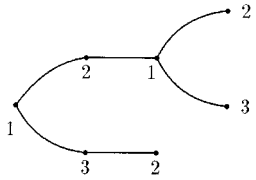


FIG. 6. Typical multiple-scattering diagram for three inclusions.

$$\mathbf{X}(\langle\mathbf{E}\rangle)\approx\mathbf{X}_{\rm ov}(\langle\mathbf{E}\rangle)=\sum_{s=1}^{\infty}\sum_{T_s^b}\mathbf{X}_{\rm ov}(T_s^b,\langle\mathbf{E}\rangle), \tag{8.1}$$

where the sum is over the trees with standard labeling in the bottom line of the lattice and the integration volume for each of these trees is restricted to the overlap volume, as defined above. In the overlap volume the block distribution function takes the simple form

$$b(T_s^b)=(-1)^{s-1}n^s \quad \text{(overlap)}. \tag{8.2}$$

The integral over the overlap volume for each tree T_s^b can be performed sequentially, starting with $\mathbf{R}_s$, corresponding to the label s in the lower right-hand corner of the labeled tree. We imagine this inclusion placed with its center at $\mathbf{R}_s$ in a uniform field $\langle\mathbf{E}\rangle$. The resulting induced field $\mathbf{E}_{\rm ind}(s;\langle\mathbf{E}\rangle)$ acts on the neighboring inclusion labeled i, connected to s by the lower right-hand line of the tree T_s^b. It was shown in Ref. 28, Eq. (3.27), that when this induced field is evaluated at a point $\mathbf{r}$ within a sphere of radius a centered at $\mathbf{R}_i$ and then integrated over all positions $\mathbf{R}_s$ such that the inclusion overlaps the sphere, one gets the result

$$\int_{|\mathbf{R}_s-\mathbf{R}_i|<2a}\mathbf{E}_{\rm ind}(s;\langle\mathbf{E}\rangle)d\mathbf{R}_s=-\frac{4\pi}{3\epsilon_1}\boldsymbol{\mu}(\langle\mathbf{E}\rangle),$$

$$0<|\mathbf{r}-\mathbf{R}_i|<a, \tag{8.3}$$

where $\boldsymbol{\mu}(\langle\mathbf{E}\rangle)$ is the dipole moment induced in sphere s.

The argument can be repeated for each of the remaining $s-2$ labels on the tree T_s^b and shows that each of the Green's functions gives a uniform field acting on the inclusion on the left end of the line. One can easily convince oneself that the sum in Eq. (8.1) corresponds to the Taylor expansion of the self-consistent equation

$$\mathbf{X}_{\mathrm{NCM}}(\langle\mathbf{E}\rangle)=n\boldsymbol{\mu}\left(\langle\mathbf{E}\rangle+\frac{4\pi}{3\epsilon_1}\,\mathbf{X}_{\mathrm{NCM}}(\langle\mathbf{E}\rangle)\right). \tag{8.4}$$

This is the nonlinear Clausius-Mossotti relation, which can be found alternatively from a Lorentz local-field argument.[15] Note that in Eq. (8.4) the field $\langle\mathbf{E}\rangle$ is assumed to be uniform. We have investigated the consequences of Eq. (8.4) for the absorption line shape in a fluid of two-level atoms with intensity-dependent polarizability.[15]

In the case of uniform spheres with nonlinear dielectric constant $\epsilon_2(E_i)$ the induced polarization for uniform inner field $\mathbf{E}_i$ can be expressed as

$$\mathbf{g}(\mathbf{E}_i)=\frac{\epsilon_2(E_i)-\epsilon_1}{4\pi}\,\mathbf{E}_i\,. \tag{8.5}$$

If we replace the applied field $\mathbf{E}_0$ in Eq. (7.8) by the Lorentz local field

$$\mathbf{F}_L=\langle\mathbf{E}\rangle+\frac{4\pi}{3\epsilon_1}\,\langle\mathbf{P}\rangle, \tag{8.6}$$

then this relation becomes

$$\mathbf{E}_i=\frac{3\epsilon_1}{\epsilon_2(E_i)+2\epsilon_1}\left(\langle\mathbf{E}\rangle+\frac{4\pi}{3\epsilon_1}\,\langle\mathbf{P}\rangle\right). \tag{8.7}$$

From Eqs. (7.7) and (8.5) we find for the average polarization

$$\langle\mathbf{P}\rangle=\phi\,\frac{\epsilon_2(E_i)-\epsilon_1}{4\pi}\,\mathbf{E}_i\,, \tag{8.8}$$

where $\phi=(4\pi/3)na^3$ is the volume fraction. Substituting Eq. (8.7) and solving for $\langle\mathbf{P}\rangle$ we obtain

$$\langle\mathbf{P}\rangle=\frac{3\epsilon_1}{4\pi}\,\phi\,\frac{\epsilon_2(E_i)-\epsilon_1}{\epsilon_2(E_i)+2\epsilon_1-\phi(\epsilon_2(E_i)-\epsilon_1)}\,\langle\mathbf{E}\rangle. \tag{8.9}$$

From Eqs. (8.8) and (8.9) we find that the inner field $\mathbf{E}_i$ is related to the average field $\langle\mathbf{E}\rangle$ by

$$\langle\mathbf{E}\rangle=\frac{1}{3\epsilon_1}\,[\,\epsilon_2(E_i)+2\epsilon_1-\phi(\epsilon_2(E_i)-\epsilon_1)]\mathbf{E}_i\,. \tag{8.10}$$

Substituting Eq. (8.9) into Eq. (2.10) and defining the effective dielectric constant by $\langle\mathbf{D}\rangle=\epsilon_e(\langle\mathbf{E}\rangle)\langle\mathbf{E}\rangle$, we find

$$\epsilon_e(\langle\mathbf{E}\rangle)=\epsilon_1+3\phi\epsilon_1\,\frac{\epsilon_2(E_i)-\epsilon_1}{\epsilon_2(E_i)+2\epsilon_1-\phi[\,\epsilon_2(E_i)-\epsilon_1]}, \tag{8.11}$$

where E_i must be expressed in terms of $\langle\mathbf{E}\rangle$ via Eq. (8.10). This expression for the effective dielectric constant was derived by Levy and Bergman.[29] It may be regarded as a generalization of the Maxwell-Garnett formula to the nonlinear case. It is equivalent to the nonlinear Clausius-Mossotti relation (8.4) for the case of uniform spheres. The latter relation is more general since it requires only the nonlinear dipolar polarizability.

IX. DISCUSSION

We have shown that the method of cluster expansion yields a macroscopic constitutive equation of the form (2.12), relating the average polarization $\langle\mathbf{P}\rangle$ to the Maxwell field $\langle\mathbf{E}\rangle$ in a system of nonlinear dielectric inclusions immersed in a linear dielectric medium. The vector functional $\langle\mathbf{P}\rangle=\mathbf{X}(\langle\mathbf{E}\rangle)$ is given by a sum of cluster integrals, as shown in Eqs. (3.9), (4.8), and (5.12). In the calculation of the macroscopic response the Maxwell field $\langle\mathbf{E}\rangle$ may be assumed to be uniform. The constitutive equation yields the corresponding value $\langle\mathbf{P}\rangle$ of the uniform average polarization. The equation involves the microstructure of the suspension via the particle distribution functions.

The expression derived for the constitutive equation is formally exact, but explicit evaluation requires approximations since the calculation of cluster integrals is limited to the simplest ones. For a suspension of spherical inclusions a particular class of integrals gives rise to a nonlinear Clausius-Mossotti relation involving only the number density and the nonlinear single-particle dipolar response to an applied uniform field. The formalism shows how correlation corrections to this mean-field-type result can, in principle, be calculated. In practice, the calculation of correction terms cannot go beyond the pair and triplet correlation functions. It is expected that higher-order correlation functions provide only small corrections.

We have developed the formalism for a system of nonlinear dielectric inclusions immersed in a linear dielectric medium, but clearly the theory applies to many other systems with similar structure. The problem of electrical or thermal conductivity is mathematically identical to the dielectric one. The problem of an elastic system of nonlinear elastic inclusions imbedded in a linear matrix is very similar. We have used the dipole character of the Green's function in the discussion of absolute convergence, but the formal rearrangement holds independent of the nature of the propagator. In particular, we can apply the formalism to the calculation of local-field effects in nonlinear optics.

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