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Renormalized Cluster Expansion for Multiple Scattering in Disordered Systems

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We study wave propagation in a disordered system of scatterers and derive a renormalized cluster expansion for the optical potential or self-energy of the average wave. We show that in the problem of multiple scattering a repetitive structure of Ornstein–Zernike type may be detected. We derive exact expressions for two elementary constituents of the renormalized scattering series, called the reaction field operator and the short-range connector. These expressions involve sums of integrals of a product of a chain correlation function and a nodal connector. We expect that approximate calculation of the reaction field operator and the short-range connector allows one to find a good approximation to the self-energy, even for high density of scatterers. The theory applies to a wide variety of systems.

KEY WORDS: Cluster expansion; multiple scattering; disordered systems; optical potential; self-energy.

1. INTRODUCTION

In this article we deal with the theory of linear transport in a disordered system of scatterers with a fixed geometry.(1,2) We derive an exact renormalized cluster expansion for the transport operator or coefficient characterizing the propagation of the average wave. The theory may be formulated in quantum mechanics as well as for classical continuum or lattice systems.(3,4) In quantum mechanics the desired transport quantity is the optical potential or self-energy. In classical electromagnetic wave propagation it is the refractive index, and in electrostatics it is the effective dielectric constant. Other examples to which the theory applies are the

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effective viscosity of fluid suspensions, the effective rate constant in diffusion-controlled reactions, etc.

We develop the theory on the basis of the cluster expansion for the effective dielectric constant of a suspension of dielectric spheres, derived some years ago by Felderhof *et al.*(5) This article built on earlier work by Finkel'berg,(6,7) Batchelor,(8) and Jeffrey.(9,10) The cluster expansion was applied to the problem of effective viscosity by Schmitz(11) and to the problem of quantum mechanical wave propagation and to the rate coefficient of diffusion-controlled reactions by Mattern and Felderhof.(12,13) We show here that the cluster expansion may be resummed effectively. In graph–theoretic language, we perform a renormalization or topological reduction.(14)

The renormalization procedure we propose is closely related to that presented by Wertheim(15) for a system of polarizable point dipoles in the theory of nonpolar dielectrics. By an analysis of the many-body scattering sequences Wertheim detected a repetitive structure which allows a formulation in terms of equations of the Ornstein–Zernike type. We show here that his analysis may be generalized. Apart from dropping the assumption of point scatterers, we also introduce important new features.

Our final result allows us to evaluate the self-energy in a relatively simple way. The self-energy is expressed via equations of Ornstein–Zernike type in terms of elementary constituent operators which may be evaluated by averaging scattering operators defined from the s-body scattering problem over the s-body positional correlation functions, which are assumed known. It may reasonably be expected that the two- and three-body contributions to the elementary constituents already provide a good approximation. The renormalization structure of the theory suggests that the resulting values of the self-energy are accurate even at high density of the scattering system.

Exactly the same formalism applies to the calculation of material properties in related systems. Thus, we may evaluate the effective dielectric constant in a liquid or suspension of polarizable particles, the effective viscosity of suspensions, the rate of diffusion-controlled reactions in a disordered system of static sinks, the short-time diffusion coefficient of a suspension of Brownian particles, the effective diffusion coefficient in a disordered system of static impurities, etc. As a first application of the theory we consider in a following article the theory of nonpolar dielectrics.

In the following we present our theory in purely algebraic terms. The reader may find it convenient to develop a graph-theoretic language and illustrate the equations with the aid of diagrams. We have preferred a concise algebraic formulation above a graphical presentation because the latter would require an excessive amount of explanation.

2. FORMULATION OF THE PROBLEM

We consider an m-component vector wave propagating in a disordered static array of scatterers. Our aim is to determine the effective scattering properties of the medium for the average wave. The time-independent linear wave equation for a particular configuration of scatterers reads

$$\mathscr{L}_0 \psi(1,..., N; \mathbf{r}) - V(1,..., N)\, \psi(1,..., N; \mathbf{r}) = s(\mathbf{r}) \tag{2.1}$$

where $\mathscr{L}_0$ is the wave operator for the uniform medium, and $V(1,..., N)$ is the potential operator, which depends on the configuration of scatterers. An example of the wave operator is $\mathscr{L}_0 = E - H_0$, where E is the energy and H_0 the Hamilton operator for a free particle. Finally, $s(\mathbf{r})$ in (2.1) is a source term, which has been included for mathematical convenience. We assume that the scattering potential consists of a sum of identical one-body terms

$$V(1,..., N) = \sum_{j=1}^{N} V(j) \tag{2.2}$$

The label j in $V(j)$ indicates the parametric dependence on the position of the scattering center $\mathbf{R}_j$ and possibly orientational variables Ω_j.

We assume that the disorder of the system is described by a known probability distribution $W(1,..., N)$. The distribution is assumed normalized to unity and symmetric in the labels $1,..., N$. The partial distribution functions

$$n(1,..., s) = \frac{N!}{(N-s)!} \int \cdots \int d(s+1) \cdots dN\, W(1,..., N) \tag{2.3}$$

give the probability of finding a configuration of s scatterers whatever the configuration of the remaining $N-s$ scatterers. The integrations in (2.3) 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 distribution functions $n(1,..., s)$.

Let

$$\psi_0(\mathbf{r}) = \int G_0(\mathbf{r} - \mathbf{r}') \cdot s(\mathbf{r}')\, d\mathbf{r}' \tag{2.4}$$

be the solution in the absence of scatterers, where $G_0(\mathbf{r} - \mathbf{r}')$ is the free-space Green's function corresponding to outgoing waves. Defining the N-body T-matrix by

$$V(1,..., N)\, \psi(1,..., N) = T(1,..., N)\, \psi_0 \tag{2.5}$$

one obtains for the self-energy operator of the average wave, defined by $\langle V\psi\rangle = X\langle\psi\rangle$,

$$X = \langle T\rangle(I + G_0\langle T\rangle)^{-1} \tag{2.6}$$

where the average is over the probability distribution $W(1,\ldots,N)$. The self-energy $\chi(\mathbf{q})$ is defined in the thermodynamic limit by

$$\lim_{\substack{N\to\infty\\ \Omega\to\infty}} (\mathbf{q}\,|X|\,\mathbf{q}') = 8\pi^3\chi(\mathbf{q})\,\delta(\mathbf{q}-\mathbf{q}') \tag{2.7}$$

where we employ the notation

$$(\mathbf{q}\,|A|\,\mathbf{q}') = \int [\exp(-i\mathbf{q}\cdot\mathbf{r})]\,A(\mathbf{r},\mathbf{r}')[\exp(i\mathbf{q}\cdot\mathbf{r}')]\,d\mathbf{r}\,d\mathbf{r}' \tag{2.8}$$

The self-energy may be used to evaluate the average Green's function, defined by $\langle\psi\rangle = G_{\mathrm{av}}s$,

$$G_{\mathrm{av}}(\mathbf{q}) = [\omega(\mathbf{q}) - \chi(\mathbf{q})]^{-1} \tag{2.9}$$

where $\omega(\mathbf{q})$ is defined by

$$(\mathbf{q}\,|\mathscr{L}_0|\,\mathbf{q}') = 8\pi^3\omega(\mathbf{q})\,\delta(\mathbf{q}-\mathbf{q}') \tag{2.10}$$

The self-energy $\chi(\mathbf{q})$ is the key quantity to be calculated. Both $\omega(\mathbf{q})$ and $\chi(\mathbf{q})$ are tensors of rank m.

3. CLUSTER EXPANSION

The formal solution of the wave equation (2.1) may be written in the form

$$\psi(1,\ldots,N) = K(1,\ldots,N)\,\psi_0 \tag{3.1}$$

where $K(1,\ldots,N)$ is a linear operator depending on the particle configuration. The average wave function is given by

$$\langle\psi\rangle = \int d1\cdots dN\, W(1,\ldots,N)\,K(1,\ldots,N)\,\psi_0 \tag{3.2}$$

We may express this in terms of a sum of integrals over the partial distribution functions by introducing cluster operators L as follows

$$\begin{aligned} K(\varnothing) &= L(\varnothing) = I \\ K(1) &= L(1) + L(\varnothing) \\ K(1,2) &= L(1,2) + L(1) + L(2) + L(\varnothing) \end{aligned} \tag{3.3}$$

Here $\varnothing$ denotes the empty set, so $K(\varnothing)$ is the identity I. The general rule is

$$K(\mathcal{N}) = \sum_{\mathcal{M} \subset \mathcal{N}} L(\mathcal{M}) \tag{3.4}$$

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

$$L(\mathcal{N}) = \sum_{\mathcal{M} \subset \mathcal{N}} (-1)^{N-M} K(\mathcal{M}) \tag{3.5}$$

where N and M are, respectively, the number of labels in $\mathcal{N}$ and $\mathcal{M}$. Inserting (3.4) in (3.2), remembering that the number of subsets of s objects out of N objects is $[N!/(N-s)!\,s!]$, and using the definition (2.3) of the partial distribution functions, we obtain

$$\langle\psi\rangle = \sum_{s=0}^{\infty} \frac{1}{s!} \int d1 \cdots ds\, n(1,\dots,s)\, L(1,\dots,s)\, \psi_0 \tag{3.6}$$

For a finite number N of scatterers, the partial distribution function $n(1,\dots,s)$ vanishes for $s > N$. Similarly, we define cluster operators M as follows:

$$\begin{aligned} 0 &= M(\varnothing) \\ V(1)\, K(1) &= M(1) \\ V(1,2)\, K(1,2) &= M(1,2) + M(1) + M(2) \\ V(1,2,3)\, K(1,2,3) &= M(1,2,3) + M(1,2) + M(1,3) + M(2,3) \\ &\quad + M(1) + M(2) + M(3) \\ &\;\;\vdots \end{aligned} \tag{3.7}$$

In analogy to (3.5), we have the general rule

$$M(\mathcal{N}) = \sum_{\mathcal{M} \subset \mathcal{N}} (-1)^{N-M} V(\mathcal{M})\, K(\mathcal{M}) \tag{3.8}$$

We note that $L(\mathcal{N})=G_0M(\mathcal{N})$, except when $\mathcal{N}$ is the empty set. In the same manner as (3.6), we obtain the average

$$\langle V\psi\rangle=\sum_{s=0}^{\infty}\frac{1}{s!}\int d1\cdots ds\, n(1,\dots,s)\, M(1,\dots,s)\,\psi_0 \tag{3.9}$$

We introduce the short-hand notation

$$(n, M)=\sum_{s=0}^{\infty}\frac{1}{s!}\int d1\cdots ds\, n(1,\dots,s)\, M(1,\dots,s) \tag{3.10}$$

From (2.5) and (3.9) we find that the average T-matrix is given by

$$\langle T\rangle=(n, M) \tag{3.11}$$

Similarly, we find from (3.6)

$$I+G_0\langle T\rangle=(n, L) \tag{3.12}$$

The self-energy operator defined by (2.6) may therefore be written

$$X=(n, M)(n, L)^{-1} \tag{3.13}$$

Writing the inverse as a geometric series and ordering according to the number of scatterers involved in each term, we find that the self-energy operator may be cast in the form of a cluster expansion$^{(5)}$

$$X=\sum_{s=1}^{\infty}X_s \tag{3.14}$$

where

$$X_s=\int\cdots\int d1\cdots ds$$

$$\times\sum_{(B)}(-1)^{k-1}\sigma(B)\, n(B_1)\, M(B_1)\, n(B_2)\, L(B_2)\cdots n(B_k)\, L(B_k) \tag{3.15}$$

Here the sum in the integrand is over all partitions of the labels $1,\dots,s$ into disjoint subsets, with the first s_1 labels appearing in the first subset, the next s_2 labels in the second subset, etc. Within the sum, $k=k(B)$ is the number of subsets in the partition (B), and B_1 is the first subset, B_2 the second,..., and B_k the kth. Furthermore,

$$\sigma(B)=1\Big/\prod_{j=1}^{k}s_j! \tag{3.16}$$

is the symmetry number of the partition. We represent a partition into k disjoint (i.e., with no label in common) subsets by $(B) = (B_1 \mid B_2 \mid \cdots \mid B_k)$ with slashes indicating the partitioning.

So far our results are exact for any finite number N of scatterers. In order to justify a statistical treatment we must envisage the thermodynamic limit $N \to \infty$, $\Omega \to \infty$ at constant $n = N/\Omega$. One expects that in this limit the self-energy operator X exists and becomes translational invariant, i.e., the kernel $X(\mathbf{r}, \mathbf{r}')$ in the limit depends only on the difference $\mathbf{r} - \mathbf{r}'$. The existence of the thermodynamic limit independent of the shape of the sample will be made plausible in the sequel. The existence has been proven for nonoverlapping scatterers of finite range in electrostatics(5) and in the case of the Schrödinger equation for a scalar particle.(12) We stress that the thermodynamic limit exists only for the ratio in (3.13), but not for the two operators in (3.11) and (3.12) separately. This is particularly clear in electrostatics, where the sample shape dependence of (3.11) and (3.12) is easily shown on macroscopic grounds from Maxwell theory.

4. MULTIPLE SCATTERING EXPANSION

Physically the decomposition of the many-body potential into a sum of one-body potentials according to (2.2) will occur because the scatterers are spatially separated and do not overlap. Correspondingly, the many-body scattering operators may be analyzed in terms of a multiple scattering expansion. To derive this expansion, we start from the identity

$$V(1,..., N)\, \psi(1,..., N) = \sum_{j=1}^{N} V(j)\, K(1,..., N)\, \psi_0 \tag{4.1}$$

which follows from (2.2) and (3.1). Combining this with

$$K(1,..., N)\, \psi_0 = \psi_0 + G_0 V(1,..., N)\, \psi(1,..., N) \tag{4.2}$$

which follows from (2.1), (3.1), and the definition of the Green's function, we find the integral equation

$$K(\mathcal{N}) = I + G_0 \sum_{j \in \mathcal{N}} V(j)\, K(\mathcal{N}) \tag{4.3}$$

Solving this equation by iteration and collecting terms corresponding to repeated interactions with the same scatterer, we obtain(5)

$$K(\mathcal{N}) = I + \sum_{l=1}^{\infty} \sum_{[j]}' \prod_{i=1}^{l} G_0 M(j_i) \tag{4.4}$$

where the second sum is over all sequences $[j]$ of l labels (counting repetitions) selected from the set $\mathcal{N}$ with the condition, indicated by the prime, that no label be repeated in succession. For example, if $\mathcal{N}$ consists of the two labels 1 and 2, then, indicating the terms in (4.3) by the corresponding sequences,

$$K(1,2) = I + ([1] + [2]) + ([12] + [21]) + ([121] + [212]) + \cdots \tag{4.5}$$

The multiple scattering expansion (4.4) is also called the binary collision expansion(16,17) or the single-site expansion.(1)

To get the multiple scattering expansion of the operator L, we put the expansion (4.4) of K in the expression (3.5), which gives(5)

$$L(\mathcal{N}) = \sum_{l=N}^{\infty} \sum_{[j]}'' \prod_{i=1}^{l} G_0 M(j_i) \tag{4.6}$$

where the second sum is over all sequences $[j]$ of l labels selected from the set $\mathcal{N}$ with the conditions, indicated by the double prime, that no label be repeated in succession and that every label in $\mathcal{N}$ occur at least once in the sequence. For a proof of this identity we refer to Ref. 5. In analogy to (4.6), the multiple scattering expansion of the cluster operator M defined in (3.8) reads

$$M(\mathcal{N}) = \sum_{l=N}^{\infty} \sum_{[j]}'' M(j_1) \prod_{i=2}^{l} G_0 M(j_i) \tag{4.7}$$

In the following it will be useful to define related operators for which the first and last scatterers in any sequence are specified. We denote such an operator by

$$M_{ij}(\mathcal{N}) = \theta(i)\, M(\mathcal{N})\, \theta(j) \tag{4.8}$$

where $\theta(i)$ and $\theta(j)$ have the effect of specifying that the first scatterer is i and the last one is j. The scattering operator $M_{ij}(\mathbf{r}, \mathbf{r}'; \mathcal{N})$ is localized in the sense that it vanishes unless the field variable $\mathbf{r}$ is located inside the range of scatterer i and $\mathbf{r}'$ is located inside the range of scatterer j. When summing over i and j

$$M(\mathcal{N}) = \sum_{ij=1}^{N} M_{ij}(\mathcal{N}) \tag{4.9}$$

and the operator M is localized correspondingly.

We may further simplify the analysis by decomposing the cluster operators L and M into a sum of terms corresponding to different permutations of the labels. Thus, we define

$$\bar{L}(\mathcal{N})=\sum_{l=N}^{\infty}\sum_{[j]}{}^{'''}\prod_{i=1}^{l}G_0M(j_i) \tag{4.10}$$

where the second sum is over all sequences $[j]$ of l labels selected from the set $\mathcal{N}$ with the conditions, indicated by the triple prime, that no label be repeated in succession, that every label in $\mathcal{N}$ occur at least once in the sequence, and that a label j can only occur for the first time in the sequence if the preceding labels have appeared already. Thus, the operator $\bar{L}(123)$ is given by

$$\bar{L}(123)=([123])+([1213]+[1231]+[1232])+\cdots \tag{4.11}$$

The corresponding expression for $L(123)$ has 3! as many terms. Similarly, we define $\bar{M}(\mathcal{N})$ by

$$\bar{M}(\mathcal{N})=\sum_{l=N}^{\infty}\sum_{[j]}{}^{'''}M(j_1)\prod_{i=2}^{l}G_0M(j_i) \tag{4.12}$$

The cluster integral X_s given by (3.15) now simplifies to

$$X_s=\int\cdots\int d1\cdots ds$$

$$\times\sum_{(B)}(-1)^{k-1}n(B_1)\,\bar{M}(B_1)\,n(B_2)\,\bar{L}(B_2)\cdots n(B_k)\,\bar{L}(B_k) \tag{4.13}$$

where again the sum is over all partitions (B) of the labels 1,..., s into k disjoint subsets with the first s_1 labels appearing in the first subset, the next s_2 labels in the second subset, etc. The first three cluster integrals read explicitly

$$X_1=\int d1\,n(1)\,\bar{M}(1)$$

$$X_2=\int d1\,d2[n(12)\,\bar{M}(12)-n(1)\,n(2)\,\bar{M}(1)\,\bar{L}(2)]$$

$$X_3=\int d1\,d2\,d3[n(123)\,\bar{M}(123)-n(12)\,n(3)\,\bar{M}(12)\,\bar{L}(3)$$

$$-n(1)\,n(23)\,\bar{M}(1)\,\bar{L}(23)+n(1)\,n(2)\,n(3)\,\bar{M}(1)\,\bar{L}(2)\,\bar{L}(3)] \tag{4.14}$$

In principle the cluster expansion (3.14) with the cluster integrals (4.13) may be used for explicit calculation. However, it turns out that it is advantageous to perform a rearrangement of terms based on a nodal analysis of the multiple scattering expansion.

5. NODAL ANALYSIS

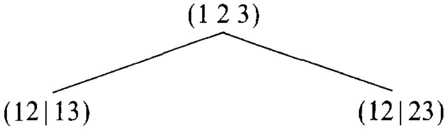
The multiple scattering expansion allows an analysis of the various scattering sequences and a classification according to complexity. We return to the average in (3.9), which may now be written in the form

$$\langle V\psi\rangle = \sum_{s=1}^{\infty} \int d1 \cdots ds\, n(1,..., s)\, \bar{M}(1,..., s)\, \psi_0 \tag{5.1}$$

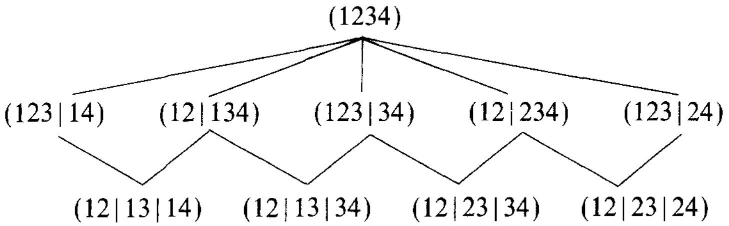
The operator $\bar{M}(\mathcal{N})$ may be decomposed into a sum of contributions corresponding to a partition of the set of labels into connected subsets as follows:

$$\bar{M}(\mathcal{N}) = \sum_{C} D(C) \tag{5.2}$$

where $C \equiv (C_1 \mid C_2 \mid \cdots \mid C_k)$ is a partition of the ordered set of labels into subsets of at least two elements such that each subset has precisely one label in common with the preceding subset. To classify the partitions it is convenient to arrange them into a lattice of rows. The first (top) row contains the partition into one subset, i.e., the set of labels itself; the second row contains the partitions into two subsets, etc. In the lattice each partition is associated with those partitions in the row above that are obtained by merging adjoining subsets, i.e., by removing a slash and one of the two common labels. Thus, for $s = 2$, the lattice consists of a single row (12) and for $s = 3$ the lattice is



while for $s = 4$



This arrangement results in a partial ordering of the partitions (denoted by $\leqslant$) with $(C) \leqslant (C')$ if the partition (C') is either the same as the partition (C) or can be obtained from (C) by removing one or more slashes.

We now classify the scattering sequences according to their nodal points. A label j is a nodal point of a scattering sequence $[12...]$ if at that point the label j may be replaced by $j \mid j$ such that all labels to the left of the slash have only the label j in common with those on the right. A label j may occur more than once as a nodal point in a scattering sequence. After identifying all nodal points and indicating them by slashes in the above manner, the scattering sequence $[12 \cdots j_1 \mid j_1 \cdots j_2 \mid \cdots]$ may be associated uniquely with the corresponding partition $(C_1 \mid C_2 \mid \cdots \mid C_k)$. The chain operator $D(C)$ is the sum of all those scattering sequences in $\bar{M}(\mathcal{N})$, as defined in (4.10), that have nodal points associated with the partition $C \equiv (C_1 \mid C_2 \mid \cdots \mid C_k)$. Conversely, since $\bar{M}(\mathcal{N})$ is the complete sum of scattering sequences satisfying the conditions listed following (4.8), it is given by (5.2).

It will be convenient to have an expression for the chain operator $D(C)$. We write

$$\begin{aligned} &D_{1l}(C_1 \mid C_2 \mid \cdots \mid C_k) \\ &\quad = M(1)\, N_{1j_1}(C_1)\, M(j_1)\, N_{j_1 j_2}(C_2)\, M(j_2) \cdots N_{j_{k-1} l}(C_k)\, M(l) \end{aligned} \tag{5.3}$$

where j_i is the label of a nodal point and l is any label from the last subset C_k. Furthermore, the nodal connector $N(C_i)$ is irreducible in the sense that it cannot be further decomposed by the identification of a nodal point. The complete chain operator $D(C)$ is obtained by summing over the labels l from C_k,

$$D(C) = \sum_{l \in C_k} D_{1l}(C_1 \mid C_2 \mid \cdots \mid C_k) \tag{5.4}$$

By definition the first label in all scattering sequences contributing to $D(C)$ is 1.

6. ORNSTEIN–ZERNIKE STRUCTURE

In this section we show that the definition of nodal points allows one to detect a repetitive structure of the Ornstein–Zernike type. It follows from (5.2) and (5.3) that $\bar{M}(\mathcal{N})$ may be decomposed as

$$\bar{M}(\mathcal{N}) = \bar{M}_{11}(\mathcal{N}) + \bar{M}_{1d}(\mathcal{N}) \tag{6.1}$$

where $\bar{M}_{11}(\mathcal{N})$ is the sum of all chain operators for which 1 is both the first and the last scatterer, and $\bar{M}_{1d}(\mathscr{N})$ is the sum of terms for which the last scatterer differs from 1. Explicitly,

$$\begin{aligned} \bar{M}_{11}(\mathscr{N}) &= \sum_{C} D_{11}(C) \\ \bar{M}_{1d}(\mathscr{N}) &= \sum_{C} \sum_{\substack{l \in C_k \\ l \neq 1}} D_{1l}(C) \end{aligned} \tag{6.2}$$

In the case of $D_{11}(C)$ the label 1 must occur in every subset. Corresponding to (6.1), we write (5.1)

$$\langle V\psi \rangle = \left[\int d1\, n(1)\, B(1) + \int d1\, d2\, n(1)\, n(2)\, A(1, 2) \right] \psi_0 \tag{6.3}$$

where the *bridge operator* $B(1)$ is defined by

$$B(1) = M(1) + \sum_{s=2}^{\infty} \int d2 \cdots ds\, [n(1,..., s)/n(1)]\, \bar{M}_{11}(1,..., s) \tag{6.4}$$

This operator includes all scattering sequences in which 1 is the first and last scatterer. Only 1 can occur as a nodal point in these sequences. In the second term in (6.3) the label 2 is used in a generic manner and indicates any label different from 1. The operator $A(1, 2)$, defined by (6.3), is given by an expression analogous to (6.4) involving the operator $\bar{M}_{1d}(\mathscr{N})$.

The bridge operator $B(1)$ describes the effect of a single scatterer renormalized by its environment. This suggests that we decompose the operator $A(1, 2)$ as

$$A(1, 2) = B(1)\, H(1, 2)\, B(2) \tag{6.5}$$

which defines the pair connector $H(1, 2)$. The latter describes propagation via other renormalized scatterers. This is expressed by the Ornstein–Zernike type equation

$$H(1, 2) = C(1, 2) + \int d3\, n(3)\, C(1, 3)\, B(3)\, H(3, 2) \tag{6.6}$$

which defines the *direct connector* $C(1, 2)$.

One of the contributions to the direct connector $C(1, 2)$ will be provided by direct propagation between the two scatterers as given by the vacuum Green's function G_0. We subtract this contribution and define the *short-range connector* $S(1, 2)$ by

$$C(1, 2) = G_0 + S(1, 2) \tag{6.7}$$

The corresponding *pair connector* $F(1,2)$ is given by the Ornstein–Zernike equation

$$F(1,2)=S(1,2)+\int d3\, n(3)\, S(1,3)\, B(3)\, F(3,2) \tag{6.8}$$

Substituting the above equations in (6.3) and comparing with the solution found from the average equations

$$\langle V\psi\rangle = X(1-G_0X)^{-1}\,\psi_0 \tag{6.9}$$

we see that the self-energy operator X is given by

$$X=\int d1\, n(1)\, B(1)+\int d1\, d2\, n(1)\, n(2)\, B(1)\, F(1,2)\, B(2) \tag{6.10}$$

Thus, it is sufficient to study the pair connector $F(1,2)$, which in turn is given by the short-range connector $S(1,2)$.

The reader may be convinced of the validity of (6.10) by writing (6.9) as a geometric series, substituting (6.10), and employing the integral equation (6.8) in iterated form. A comparison with (6.3) with use of (6.5) and the iterated form of (6.6) with (6.7) then demonstrates the validity of (6.10).

In (6.3)–(6.6) we have adopted notation employed by Wertheim$^{(15)}$ in the theory of nonpolar dielectrics. However, our definition (6.7) of the short-range connector $S(1,2)$ differs from Wertheim's.

We note that the equations developed in this section are valid for the finite system. In the final equation (6.10) the thermodynamic limit may be taken. Both the bridge operator $B(1)$ and the pair connector $F(1,2)$ are expected to have a well-defined thermodynamic limit independent of sample shape.

7. REACTION FIELD OPERATOR

In this section we express the bridge operator $B(1)$ defined in (6.4) in terms of the chain operators $D(C)$ given by (5.3) and correlation functions describing the statistical distribution of scatterers. In (6.4) the kernel $\bar{M}_{11}(\mathcal{N})$ is given by (6.2) with the operators

$$\begin{aligned} &D_{11}(C_1\,|\,C_2\,|\cdots|\,C_k)\\ &\quad = M(1)\, N_{11}(C_1)\, M(1)\, N_{11}(C_2)\, M(1)\cdots N_{11}(C_k)\, M(1) \end{aligned} \tag{7.1}$$

The label 1 must occur in every subset. The normalized s-particle distribution functions $g(1,..., s)$ are defined by

$$g(1,..., s) = n(1,..., s) \Big/ \prod_{j=1}^{s} n(j) \tag{7.2}$$

and the corresponding correlation functions $h(1,..., t)$ by

$$g(1,..., s) = \prod_{t=2}^{s} \prod_{Q_t} [1 + h(Q_t)] \tag{7.3}$$

where Q_t is a subset of t labels from $1,..., s$ and the double product is over all subsets with at least two labels. For example, for $s = 2$

$$g(1, 2) = 1 + h(1, 2) \tag{7.4}$$

and for $s = 3$

$$g(1, 2, 3) = [1 + h(12)][1 + h(13)][1 + h(23)][1 + h(123)] \tag{7.5}$$

It is clear that, when the expansion (7.3) is substituted in (6.4) with $\bar{M}_{11}(1,..., s)$ expanded into chain operators, different groups of labels of each partition may or may not be connected by correlation functions. If there is no correlation between any of the labels, different from 1, to the left of a factor $M(1)$ and those, different from 1, to the right, then the corresponding integral in (6.4) factorizes. Hence we recognize a repetitive structure and may write

$$B(1) = M(1)[1 - S(1)\, M(1)]^{-1} \tag{7.6}$$

where the operator $S(1)$ may be expressed as a sum of integrals over a product of correlation functions h and a nodal operator $N_{11}(C)$ defined by

$$N_{11}(C) = N_{11}(C_1)\, M(1)\, N_{11}(C_2)\, M(1) \cdots N_{11}(C_k) \tag{7.7}$$

so that $D_{11}(C) = M(1)\, N_{11}(C)\, M(1)$. We call $S(1)$ the *reaction field operator.* We decompose $S(1)$ according to the number of labels involved and write

$$S(1) = \sum_{s=2}^{\infty} S_s(1) \tag{7.8}$$

with

$$S_s(1) = \sum_{C} \int d2 \cdots ds\, n(2) \cdots n(s)\, k(C)\, N_{11}(C) \tag{7.9}$$

where $k(C)$ is a correlation function corresponding to the partition C of s labels. We find the correlation functions $k(C)$ by substituting (7.8) in (7.6) and comparing with (6.4).

The term $M(1)\,N_{11}(C_1)\,M(1)$ in (6.4) can be obtained only from $M(1)\,S(1)\,M(1)$ in (7.6) and yields the relation

$$k(C_1)=g(C_1) \tag{7.10}$$

The term $M(1)\,N_{11}(C_1)\,M(1)\,N_{11}(C_2)\,M(1)$ follows from

$$M(1)\,S(1)\,M(1)+M(1)\,S(1)\,M(1)\,S(1)\,M(1)$$

and yields

$$k(C_1\,|\,C_2)+k(C_1)\,k(C_2)=g(C_1,\,C_2) \tag{7.11}$$

where $(C_1,\,C_2)$ indicates that the sets have been joined. Combining (7.10) and (7.11), we can write

$$k(C_1\,|\,C_2)=k(C_1,\,C_2)-k(C_1)\,k(C_2) \tag{7.12}$$

This relation may be generalized. As an example, we consider three subsets. Then we obtain as above

$$\begin{aligned}&k(C_1\,|\,C_2\,|\,C_3)+k(C_1)\,k(C_2\,|\,C_3)\\&+\;k(C_1\,|\,C_2)\,k(C_3)+k(C_1)\,k(C_2)\,k(C_3)=g(C_1,\,C_2,\,C_3)\end{aligned} \tag{7.13}$$

On the other hand, considering the union of C_2 and C_3, we also have

$$k(C_1\,|\,C_2,\,C_3)+k(C_1)\,k(C_2,\,C_3)=g(C_1,\,C_2,\,C_3) \tag{7.14}$$

Subtracting the latter two identities and using (7.12), we find

$$k(C_1\,|\,C_2\,|\,C_3)=k(C_1\,|\,C_2,\,C_3)-k(C_1\,|\,C_2)\,k(C_3) \tag{7.15}$$

By induction we prove the general rule

$$\begin{aligned}k(C_1\,|\cdots|\,C_j\,|\,C_{j+1}\,|\cdots|\,C_k)=k(C_1\,|\cdots|\,C_j,\,C_{j+1}\,|\cdots|\,C_k)\\-k(C_1\,|\cdots|\,C_j)\,k(C_{j+1}\,|\cdots|\,C_k)\end{aligned} \tag{7.16}$$

This identity suggests that we call $k(C)$ a *chain correlation function.* We may regard (7.16) as a recurrence relation, which together with (7.10) allows one to construct the chain correlation functions of all orders. The general expression in terms of the g-functions may be formulated with the aid of the lattice of partitions introduced in Section 5. It is given by

$$k(C)=\sum_{(C')\geqslant(C)}(-1)^{k'-1}g(C'_1)\,g(C'_2)\cdots g(C'_{k'}) \tag{7.17}$$

where the sum is over the given partition together with those partitions in all the rows above that can be obtained from it by removing slashes, and $k' = k(C')$ is the row number of C'. The relation (7.17) is easily proven by induction with use of (7.16) specialized to the case where $k = j + 1$, as in (7.15). We remark that the block distribution functions defined in I have the same structure (7.17) and hence satisfy an identity analogous to (7.16).

To conclude this section, we note that the partitions (C) occurring in (7.9) are special, in that every subset contains the label 1. However, the relations for the chain correlation functions $k(C)$ developed above are valid more generally.

8. SHORT-RANGE CONNECTOR

In this section we show that the short-range connector $S(1, 2)$ introduced in Section 6 may also be expressed as a sum of integrals over a product of a chain correlation function and a nodal connector.

The operator $A(1, d)$ defined in (6.3) is given by

$$A(1, d) = \sum_{s=2}^{\infty} \int d2 \cdots ds [n(1,\ldots, s)/n(1)\, n(d)]\, \bar{M}_{1d}(1,\ldots, s) \tag{8.1}$$

According to (5.2) and (5.3), the operator $\bar{M}_{1d}(1,\ldots, s)$ may be expressed as a sum of products of single-particle scattering operators and nodal connectors. We consider first the simple two-particle contribution to (8.1). It is given by

$$A_2(1, 2) = g(1, 2)\, M(1)\, N_{12}(1, 2)\, M(2) \tag{8.2}$$

We write this in the form

$$A_2(1, 2) = M(1)[G_0 + S_2(1, 2)]\, M(2) \tag{8.3}$$

with

$$S_2(1, 2) = g(1, 2)[N_{12}(1, 2) - G_0] + h(1, 2)\, G_0 \tag{8.4}$$

Here the separation into two terms has the advantage that both are relatively short range. The combination $N_{12}(1, 2) - G_0$ connects the two scatterers by at least three Green's functions, as may be seen from the multiple scattering expansion.

The nodal connector $N_{jj'}(C_i)$ has a contribution G_0 whenever the two labels j and j' of the nodal point differ. If the first nodal point and all the labels preceding it differ from the second nodal point and all the labels following it, and if these two sets of labels are uncorrelated, then the propagator G_0 is an articulation line serving as the only link between two distinct parts of the scattering sequence. We take care of this weak link by the term G_0 in (6.7). The remaining contribution to the direct connector $C(1, 2)$ is the short-range connector $S(1, 2)$.

By substitution of (6.6) and (6.7) into (6.5) and iteration it is clear that $A(1, 2)$ is a sum of contributions given by chains of bridge operators connected either by the propagator G_0 or by the short-range connector $S(1, 2)$. Thus, each chain is an alternation of G-pieces, consisting of bridge operators connected by propagators G_0, and S-pieces, consisting of bridge operators connected by short-range connectors $S(1, 2)$. Consider a particular S-piece between two G-pieces. The sum of all possible S-pieces at this location is precisely the pair connector $F(1, 2)$ given by (6.8). By definition of the articulation line, this involves an average over labels not correlated with any other labels of the chain. It follows from (3.14), (4.11), and (6.10) that

$$\begin{aligned} B(1)\,F(1, d)\,B(d) = \sum_{s=2}^{\infty} \sum_{l=2}^{s} \int d2 \cdots ds\, \delta(d-l) \\ \times \sum_{(B)} (-1)^{k-1} [n(B)/n(1)\,n(l)]\, \bar{M}_{1l}(B) \qquad (8.5) \end{aligned}$$

where $\delta(d-l)$ is the Dirac delta function $\delta(\mathbf{R}_d - \mathbf{R})\,\delta(\Omega_d - \Omega_l)$ and

$$\bar{M}(B) \equiv \bar{M}(B_1 \mid B_2 \mid \cdots \mid B_k) = \bar{M}(B_1)\,G_0 \bar{M}(B_2)\,G_0 \cdots G_0 \bar{M}(B_k) \qquad (8.6)$$

This expression contains precisely those subtractions necessary to eliminate all articulation lines. We may therefore rewrite the expression as

$$\begin{aligned} B(1)\,F(1, d)\,B(d) = \sum_{s=2}^{\infty} \sum_{l=2}^{s} \int d2 \cdots ds\, \delta(d-l) \\ \times \sum_{(B)} \{[n(B)/n(1)\,n(l)]\, \bar{M}_{1l}(B)\}_{\mathrm{irr}} \qquad (8.7) \end{aligned}$$

where the subscript irr indicates that the expression in curly brackets is to be made irreducible by the appropriate subtractions. By the same arguments as given following (6.4), we find for the short-range connector

$$S(1, d) = \sum_{s=2}^{\infty} S_s(1, d) \qquad (8.8)$$

with $S_2(1, d)$ given by (8.4), and for $s \geqslant 3$

$$\begin{aligned} S_s(1, d) = \sum_{C} \sum_{l=2}^{s} \int d2 \cdots ds \\ \times \delta(d-l) [n(2) \cdots n(s)/n(l)]\, k(C)\, N_{1l}(C) \qquad (8.9) \end{aligned}$$

Here the chain correlation function $k(C)$ is given by (7.17) and the nodal connector by $D_{1d}(C)=M(1)\,N_{1d}(C)\,M(d)$ with $D_{1d}(C)$ given by (5.3). The expression (8.8) with (8.9) for the short-range connector is exact and valid for any finite system of scatterers.

9. DISCUSSION

In Section 6 we derived the expression (6.10) for the self-energy operator X by recognizing that the response of the system to an incident wave ψ_0 may be analyzed in terms of Ornstein–Zernike type equations. In the preceding two sections we derived expressions for the reaction field operator $S(1)$, which determines the bridge operator $B(1)$ via (7.6), and for the short-range connector $S(1, 2)$, which determines the pair connector $F(1, 2)$ via (6.8). The expressions are valid for the finite system, but at this stage we may take the thermodynamic limit.

In the thermodynamic limit the density $n(1)$ will become independent of the position $\mathbf{R}_1$ of scatterer 1. The bridge operator $B(1)$ and the reaction field operator $S(1)$ will depend only on the differences $\mathbf{r}-\mathbf{R}_1$ and $\mathbf{r}'-\mathbf{R}_1$. Similarly, the short-range connector $S(1, 2)$ and the pair connector $F(1, 2)$ will depend only on the differences $\mathbf{r}-\mathbf{R}_1$ and $\mathbf{r}'-\mathbf{R}_2$ and the difference in positions $\mathbf{R}=\mathbf{R}_2-\mathbf{R}_1$. The self-energy $\chi(\mathbf{q})$, defined in (2.7), becomes

$$\chi(\mathbf{q})=\int d\Omega_1\, n(\Omega_1)(\mathbf{q}\,|\,B(1)\,|\,\mathbf{q})|_{\mathbf{R}_1-0}$$

$$+\int d\Omega_1\, d\Omega_2\, d\mathbf{R}\; n(\Omega_1)\, n(\Omega_2)(\mathbf{q}\,|\,B(1)\,F(1,2)\,B(2)\,|\,\mathbf{q})|_{\mathbf{R}_1=0} \tag{9.1}$$

where Ω_1 and Ω_2 are orientational variables and the matrix element has been defined in (2.8). If the scatterers are spherical, then there is no dependence on orientational variables and (9.1) simplifies to

$$\chi(\mathbf{q})=n(\mathbf{q}\,|\,B(1)\,|\,\mathbf{q})+n^2\int d\mathbf{R}(\mathbf{q}\,|\,B(1)\,F(1,2)\,B(2)\,|\,\mathbf{q}) \tag{9.2}$$

where n is the average number density and the center of sphere 1 is taken to be at the origin. Here $B(1)$ is given by (7.6) and (7.8), and $F(1, 2)$ is given by (6.8) and (8.8).

So far our equations are exact. In explicit calculations we are forced to make approximations that may, however, be made at the level of the elementary constituents, i.e., the reaction field operator $S(1)$ given by (7.8) and (7.9), and the short-range connector $S(1, 2)$ given by (8.8) and (8.9). It may be expected that approximations to these operators, based on the solution of the one-body, two-body, or, at most, the three-body scattering problem will yield good results for the self-energy $\chi(\mathbf{q})$. The rationale for this expectation is that the Ornstein–Zernike structure of the theory automatically accounts for repetitions of elementary events. A similar situation prevails in the theory of gases, where the Boltzmann equation and its Enskog correction, which are based on the same principle, have been eminently successful.(18)

For future use in approximation schemes it will be worthwhile to have the explicit expressions for the two- and three-body contributions to the operators $S(1)$ and $S(1, 2)$. From (7.8) and (7.9) we find for the two-body contribution to $S(1)$

$$S_2(1) = \int d2\, n(2)\, k(1, 2)\, N_{11}(1, 2) \tag{9.3}$$

and for the three-body contribution

$$\begin{aligned} S_3(1) = \int & d2\, d3\, n(2)\, n(3) \\ & \times [k(1, 2, 3)\, N_{11}(1, 2, 3) + k(1, 2 \mid 1, 3)\, N_{11}(1, 2 \mid 1, 3)] \end{aligned} \tag{9.4}$$

We have used that the nodal connector $N_{11}(12 \mid 23)$ vanishes identically, since the label 1 does not occur in the last group. The two-body contribution to $S(1, 2)$ is given by (8.4), which we repeat here,

$$S_2(1, 2) = g(1, 2)[N_{12}(1, 2) - G_0] + h(1, 2)\, G_0 \tag{9.5}$$

The three-body contribution follows from (8.9) and reads explicitly

$$\begin{aligned} S_3(1, 2) = \int d3\, n(3)[& k(1, 2, 3)\, N_{12}(1, 2, 3) + k(1, 2 \mid 2, 3)\, N_{12}(1, 2 \mid 2, 3) \\ & + k(1, 2, 3)\, N_{12}(1, 3, 2) + k(1, 3 \mid 1, 2)\, N_{12}(1, 3 \mid 1, 2) \\ & + k(1, 3 \mid 2, 3)\, N_{12}(1, 3 \mid 3, 2)] \end{aligned} \tag{9.6}$$

In the last three terms we have renamed the labels of the nodal connectors. In the nodal connectors the order of the labels is important. Note in particular that $N_{12}(1, 3, 2)$ differs from $N_{12}(1, 2, 3)$. We recall that a nodal connector with one or more slashes may be written as a product. For example,

$$N_{12}(1, 2 \mid 2, 3) = N_{12}(1, 2)\, M(2)\, N_{22}(2, 3) \tag{9.7}$$

Equation (6.10) for the self-energy operator has appeared in the literature.(19) The two contributions were called the diagonal and offdiagonal parts of the self-energy operator. A detailed analysis of approximations based on this equation has been given by Watabe and Yonezawa.(19) For example, the so-called quasicrystalline approximation(1,2) (QCA) corresponds to putting $S(1) \approx 0$ and $S(1, 2) \approx h(1, 2)\, G_0$.

A comparison of the cluster expansion (3.14) with (4.14) shows that approximations to the reaction field operator $S(1)$ and the short-range conector $S(1, 2)$ are to be preferred to approximations obtained directly from the cluster expansion, for example, by keeping only the first few terms. The advantage of the present scheme is that exact resummations are performed and approximations are made at a late stage.

The nature and quality of the approximations will depend on the particular problem. Nonetheless, the generality of our scheme provides a unifying viewpoint and allows a comparison of a wide variety of systems. As a first application of the theory, we shall consider in a subsequent article the theory of nonpolar dielectrics.

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