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A CLASS OF MOLECULAR  
CORRELATION FUNCTIONS  
RELATED TO  
URSELL FUNCTIONS

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### Synopsis

We study a class of intermolecular correlation functions  $\mathcal{Y}_{[p]}$  appearing in refractive index theory. An explicit expression for  $\mathcal{Y}_{[p]}$  in terms of Ursell functions and a recurrence relation in terms of distribution functions are derived. The function  $\mathcal{Y}_{[p]}$  is shown to be invariant under permutations of the variables belonging to the dihedral group  $D_p$ . The results are applied to a problem of refractive index theory.

## Introduction

Intermolecular positional correlation forms the core of a description of fluid structure (see e.g. FRISCH and LEBOWITZ 1964, FISHER 1964, RICE and GRAY 1965, COLE 1967, EGELSTAFF 1967, and, for experimental data, FRISCH and SALSBERG 1968). The response of a molecular fluid to light is largely<sup>1</sup> determined by the response of an isolated molecule and by the equilibrium structure of the unperturbed fluid. It can therefore be described in terms of molecular correlation. Molecular refractive index theory results in a perturbation series for the refractive index  $m$ , which can be interpreted as describing a series of elementary scattering processes (YVON 1937, MAZUR 1958, BULLOUGH 1968, BULLOUGH, e.a. 1968, to be referred to as I, HYNNE 1970, to be referred to as II). A general term of such series involving  $p$  molecules, contains a  $(p-1)$ -fold integral having a particular  $p$ -body correlation function<sup>2</sup> as a weight factor. This correlation function gauges the contribution to the refractive index of a multiple scattering process with  $p$  scattering events from  $p$  molecules in given configuration. Clearly, the character of the many-body response (as condensed in  $m$ ) depends decisively on the set of correlation functions.

In this paper we consider correlation functions  $\mathcal{Y}_{[p]}$  that appear as weight factors in a theory of the refractive index of a molecular fluid formulated in terms of a 'screened' intermolecular interaction (II). Although entirely microscopic<sup>3</sup>, the screened theory has interesting macroscopic consequences: from the theory we have derived (HYNNE and BULLOUGH 1972, to be referred to as III) a generalized form of a dispersion relation, previously obtained by ONSAGER (1936) and BÖTTCHER (1942) by purely macroscopic

<sup>1</sup> Namely in the approximations of a quasistatic linear response theory and the polarization diagram approximation (I).

<sup>2</sup> We use the term 'correlation function' to denote an arbitrary combination of distribution functions (compare e.g. HILL 1958). We deviate from the terminology in our previous papers on refractive index theory which did not distinguish distribution functions from other correlation functions.

<sup>3</sup> The screened theory is initially completely equivalent to the fundamental unscreened theory (BULLOUGH 1968, I, II) but the 'bulk approximation' (see II) is required to reach the final, translationally invariant form.

arguments. We have also obtained (HYNNE 1974) an expression for absorption lines, at variance with simple two-body results, but agreeing with linewidths from coupled oscillator theory (HOLTSMARK 1925). The physical significance of these results shows that the screened formulation is physically very natural and motivates a study of the  $\mathcal{Y}$  functions. A more concrete incentive is the necessity of knowing the asymptotic behaviour of the  $\mathcal{Y}$  functions for a proof of convergence in the refractive index theory.

Correlation of  $p$  molecules can be expressed by the  $p$ -body (reduced) molecular distribution function, which gives the probability density of configurations of any subset of  $p$  molecules. (See e.g. HILL 1958, FRISCH and LEBOWITZ 1964; compare also section 2 of this paper). The  $p$ -body correlation function

$$\mathcal{Y}_{[p]} = \mathcal{Y}_{123 \dots p} = \mathcal{Y}_p(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_p) \quad (1.1)$$

considered here is a function of the  $p$  points in space  $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_p$ , and can be expressed as a combination of distribution functions of orders  $q \leq p$ . Although the set of distribution functions is perhaps the most natural choice other sets of functions, notably the set of Ursell functions,<sup>4</sup> may serve equally well as basis for a description of intermolecular correlation. It is the purpose of this paper to characterize the set of  $\mathcal{Y}$  functions in relation to the two fundamental sets of functions, the set of distribution functions and the set of Ursell functions.

In the following section we introduce generalized correlation functions and define  $\mathcal{Y}$  functions by an equation emerging from the refractive index theory (II). The most important part of the paper is a derivation in section 3 of an explicit expression (2.12) for the  $\mathcal{Y}$  functions in terms of generalized Ursell functions and a recurrence relation (2.11) in terms of generalized distribution functions. Section 4 contains a discussion of some properties of  $\mathcal{Y}$  functions, and section 5 an application of the result (2.12) to the original physical problem. The short section 6 summarizes the results.

<sup>4</sup> The Ursell functions can be defined without reference to distribution functions. For this and for a more general discussion of Ursell functions see in particular PERCUS 1964; see also the brief review in section 2 below. Notice, however, that there exists a different usage of the term 'Ursell function'; see e.g. FISHER 1964 and UHLENBECK and FORD 1962 and compare the original paper by URSELL (1927).



## 2. Definition of $\mathcal{G}$ functions

Rather than using ordinary distribution functions we shall work in terms of generalized distribution functions

$$\mathcal{G}_{[p]} = \mathcal{G}_{123 \dots p} = \langle \varrho(\mathbf{x}_1) \varrho(\mathbf{x}_2) \varrho(\mathbf{x}_3) \dots \varrho(\mathbf{x}_p) \rangle_{\text{av}} \quad (2.1)$$

which are averages of products of the 'instantaneous' density of molecules

$$\varrho(\mathbf{x}) = \sum_j \delta(\mathbf{x} - \mathbf{x}_j^{\text{in}}), \quad (2.2)$$

taken at different points. The instantaneous density  $\varrho(\mathbf{x})$  depends on the configuration of molecules<sup>5</sup> (specified by the positions  $\mathbf{x}_j$ ) of a member of the grand canonical ensemble. The system is homogeneous, and the average density  $n = \langle \varrho(\mathbf{x}) \rangle_{\text{av}}$  is independent of  $\mathbf{x}$ . In equation (2.1) and below we use subscript indices to denote position variables.

The  $\mathcal{G}$  functions generalize the ordinary distribution functions of statistical mechanics (see e.g. HILL, 1956) to include self-correlations, and the first few functions are (see e.g. LEBOWITZ and PERCUS 1963;  $\mathcal{G}_{1234}$  is exhibited in HYNNE 1974, p. 452)

$$\left. \begin{aligned} \mathcal{G}_1 &= n \\ \mathcal{G}_{12} &= n^2 g_{12} + n \delta_{12} \\ \mathcal{G}_{123} &= n^3 g_{123} + n^2 (\delta_{12} g_{23} + \delta_{23} g_{31} + \delta_{31} g_{12}) + n \delta_{12} \delta_{23} \end{aligned} \right\} \quad (2.3)$$

In equation (2.3)  $n^p g_{[p]}$  is the ordinary  $p$ -body distribution function and  $\delta_{ij} = \delta(\mathbf{x}_i - \mathbf{x}_j)$  denotes a delta function representing a self-correlation.

Although ordinary correlation functions are perhaps appropriate for most applications, generalized functions are in many ways simpler than ordinary ones. In many-body optics it is possible to exploit the simplicity of the generalized functions to great advantage by formally expressing radiation reaction in terms of self-correlations (I). This definition is made initially in the (more fundamental) 'unscreened theory' (I), but it is carried over, with new significance, into the screened theory. (See II and, in particular, III). The  $\mathcal{G}$  functions therefore emerge from the screened theory with all self-correlations included, and it is natural to express them in terms of the generalized distribution functions.

<sup>5</sup> The refractive index theory (I, II) applies only to optically isotropic molecules for which orientational correlation is irrelevant.

The function  $\mathcal{Y}_{[p]}$  is the average value of the instantaneous (configurational dependent) function  $\mathcal{Y}_{[p]}^{\text{in}}$ , recursively defined by the relation

$$\left. \begin{aligned} \mathcal{Y}_1^{\text{in}} &= \varrho_1 = \varrho(\mathbf{x}_1) \\ \mathcal{Y}_{123\dots p}^{\text{in}} &= \mathcal{Y}_{123\dots p-1}^{\text{in}} \varrho_p - \sum_{q=1}^{p-1} \mathcal{Y}_{123\dots q}^{\text{in}} \mathcal{Y}_{q+1\dots p}, \end{aligned} \right\} \quad (2.4)$$

which emerges from an integral equation in the refraction index theory (equation (2.6) of III).

We easily find the first few  $\mathcal{Y}$  functions directly from the definition (2.4):

$$\left. \begin{aligned} \mathcal{Y}_1 &= \mathcal{G}_1 \\ \mathcal{Y}_{12} &= \mathcal{G}_{12} - \mathcal{G}_1 \mathcal{G}_2 \\ \mathcal{Y}_{123} &= \mathcal{G}_{123} - \mathcal{G}_{12} \mathcal{G}_3 - \mathcal{G}_{23} \mathcal{G}_1 - \mathcal{G}_{31} \mathcal{G}_2 + 2 \mathcal{G}_1 \mathcal{G}_2 \mathcal{G}_3 \end{aligned} \right\} \quad (2.5)$$

It is remarkable that these  $\mathcal{Y}$  functions are identical with the corresponding generalized Ursell functions, which can be defined as (I, STELL 1964, LEBOWITZ and PERCUS 1963)

$$\mathcal{G}_{[p]} = \sum_{\pi \in \mathcal{P}_p} \prod_{Q \in \pi} \mathcal{U}_Q. \quad (2.6)$$

In equation (2.6) the sum is taken over the collection  $\mathcal{P}_p$  of all partitions of the set of indices  $[p] = (1, 2, 3, \dots, p)$ .<sup>6</sup>

The generalized Ursell functions may be obtained from a simpler recurrence relation, derivable from equation (2.6) (compare PERCUS 1964):

$$\mathcal{G}_{[p]} = \sum_Q \mathcal{U}_Q \mathcal{G}_{[p]-Q}, \quad 1 \in Q \quad (2.7)$$

in which the sum is taken over all subsets  $Q$  of  $[p]$  containing 1, and  $[p]-Q$  denotes a set difference with ordered elements (compare footnote 6 and below). The  $p$ -body Ursell function<sup>7</sup> can be characterized (PERCUS 1964) as the part of the correlation between  $p$  particles not contained in lower order functions. This characterization is natural in view of the definition (2.6), and it manifests itself in the asymptotic properties of the Ursell functions. Let the variables of  $\mathcal{U}_{[p]}$  be partitioned into two sets with indices  $Q$  and  $R = [p] - Q$  and let  $d_{QR}$  denote the minimum distance between the two sets:

<sup>6</sup> Below we shall take sets of indices like  $[p]$  and  $Q$  to denote ordered sets. Here, the ordering is immaterial because both  $\mathcal{G}_{[p]}$  and  $\mathcal{U}_{[p]}$  are symmetric in all their variables.

<sup>7</sup> Here and below 'Ursell functions' and 'distribution functions' denote generalized functions unless the contrary is expressly stated.

$$d_{QR} = \min | \mathbf{x}_i - \mathbf{x}_j |, \quad i \in Q, j \in R. \tag{2.8}$$

For any such partition the Ursell function  $\mathcal{U}_{[p]}$  satisfies

$$\mathcal{U}_{[p]} \rightarrow 0 \quad \text{for} \quad d_{QR} \rightarrow \infty. \tag{2.9}$$

This is the cluster property of the Ursell function (compare UHLENBECK and FORD 1962), which follows (compare KAHN and UHLENBECK 1938) from equation (2.6) and the factorization of distribution functions

$$\mathcal{G}_{[p]} \rightarrow \mathcal{G}_Q \mathcal{G}_R \quad \text{for} \quad d_{QR} \rightarrow \infty.$$

The asymptotic behaviour (2.9) makes the Ursell functions very suitable for discussion of convergence of integrals, a property we exploit in section 5.

However, direct evaluation shows that

$$\mathcal{U}_{1234} = \mathcal{U}_{1234} + \mathcal{U}_{13} \mathcal{U}_{24}; \tag{2.10}$$

so despite the striking coincidence at the lowest orders, the class of  $\mathcal{U}$  functions differs from the class of Ursell functions. Nevertheless, the results (2.5) and (2.10) suggest that the two classes of functions are simply related.

Whereas it is relatively easy to obtain expressions for lower order  $\mathcal{U}$  functions directly from (2.4), several features of the defining relation (2.4) complicate the derivation of a general expression for  $\mathcal{U}_{[p]}$ , whether in terms of distribution functions or in terms of Ursell functions: Equation (2.4) is a non-linear many-terms mixed recurrence relation in the instantaneous functions  $\mathcal{Y}^{\text{in}}$  involving the averaging operation in addition to arithmetic operations.

In the next section we shall solve this problem by deriving the following two relations

$$\mathcal{G}_{[p]} = \sum_{\sigma \in \mathcal{G}_p} \prod_{s \in \sigma} \mathcal{Y}_s \tag{2.11}$$

$$\mathcal{U}_{[p]} = \sum_{\gamma \in \mathcal{C}_p} \prod_{c \in \gamma} \mathcal{U}_c \tag{2.12}$$

which independently determine  $\mathcal{U}_{[p]}$ : equation (2.11) is a pure recurrence relation for  $\mathcal{U}_{[p]}$  in terms of distribution functions whereas equation (2.12) is an explicit expression for  $\mathcal{U}_{[p]}$  in terms of Ursell-functions.<sup>8</sup> The sums in equations (2.11) and (2.12) are taken over certain sets of partitions of the index set  $[p] = (1, 2, 3, \dots, p)$  defined in the following section. Indeed, the

<sup>8</sup> The result (2.12) has been quoted in II: here we present the derivation of the result.



core of the derivation involves essentially just manipulations with partitions of index sets, and it would be a futile notational complication to formulate the derivation in terms of the functions. We therefore base the derivation on two lemmas on ‘ordered partitions’ which we derive in the following section. Since this arrangement may obscure the motivation for the various steps of the derivation, we start with a brief outline of the argument.

### 3. Derivation of Equations (2.11) and (2.12)

To derive (2.11) we first obtain an expression for a product of functions  $g(\mathbf{x})$  (compare equation (2.1)) which upon averaging yields equation (2.11). The structure of the terms of the sum in equation (2.11) can be ascertained by scrutinizing equation (2.4). Here, we prove the result by induction. For this proof we use equation (2.4) and a lemma showing how the set  $\mathcal{S}_{p+1}$  of partitions of  $[p+1]$  can be generated from the set  $\mathcal{S}_p$  of partitions of  $[p]$ . From equation (2.11) we obtain (2.12) by comparison of equations (2.6) and (2.11) using another lemma which states that any partition of  $[p]$  can be uniquely decomposed into a certain subpartition of a partition belonging to  $\mathcal{S}_p$ . We first derive the lemmas.

We consider partitions of the set

$$[p] = (1, 2, 3, \dots, p) \quad (3.1)$$

of the first  $p$  positive integers. The relevant partitions are all characterized with reference to the numerical order of the integers.<sup>9</sup> We shall also need to consider ordered subsets of  $[p]$  as well as partitions of such subsets. We therefore take  $[p]$  to denote the naturally ordered set, and we shall understand that any set of integers (whether it is element of a partition or not) is ordered according to magnitude unless the contrary is stated. By an ordered partition of an ordered set we simply mean a partition in which the elements are ordered within each set of the partition, whereas the sets of the partition are not ordered among themselves. (Nevertheless, the ordering induces a relation among the sets, which we exploit below).

It is very helpful to represent partitions by diagrams. Let the elements  $1, 2, 3, \dots, p$  of the basic index set  $[p]$  be represented by consecutive vertices of a regular polygon of  $p$  sides. A partition of  $[p]$  is then represented by a collection of polygons (which may include points and lines as degenerate

<sup>9</sup> The ordering arises from a chronological ordering of scattering events in the refractive index theory (II).



cases), each having the representative points of a set of the partition as vertices. The sides of a set-polygon connect vertices corresponding to cyclically consecutive elements of a set. Figure 1 c exemplifies the diagram representation by showing the representation of the partition

$$\{ (1, 4, 7), (2, 8), (3), (5, 6) \} \tag{3.2}$$

of the set [8].

From any partition of [p] containing a set Q with more than one element we obtain a particular subpartition by dividing Q into a non-empty, proper,

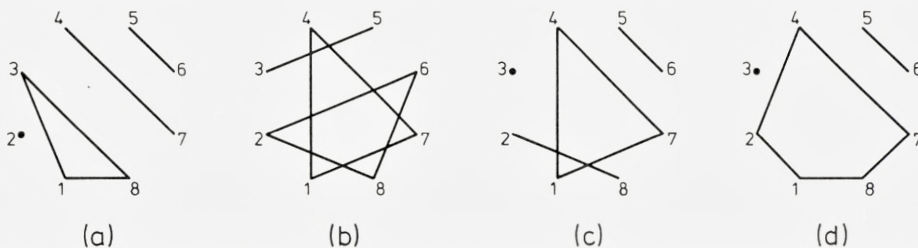


Figure 1. Diagrammatic representations of partitions exemplifying the various types of partitions:

- (a) The *s*-partition (3.3)
- (b) The *c*-partition (3.5)
- (c) The composite partition (3.2)
- (d) The basis (3.4) of the composite partition (c).

The composite partition (c) is neither an *s*-partition nor a *c*-partition; but it can be obtained from the *s*-partition (d) which is its basis by replacing the sets of (d) by definite *c*-partitions of these. This representation of the composite partition (3.2) as a subpartition of its basis is the *sc*-decomposition of the partition.

ordered subset of *consecutive* elements from *Q* and the ordered subset of the remaining elements from *Q*. We call this special subpartitioning an *s*-process (where *s* stands for ‘sequence’). We define an *s*-partition of [p] as any partition that can be obtained from [p] by repeated use of *s*-processes. By definition, [p] is itself an *s*-partition.<sup>10</sup> The diagram representation permits an especially simple characterization: A partition is an *s*-partition if and only if it is represented by a diagram in which sides of different polygons do not intersect. This is a direct consequence of the definition of *s*-partitions. Figure 1 a illustrates the property for the *s*-partition

$$\{ (1, 3, 8), (2), (4, 7), (5, 6) \}. \tag{3.3}$$

The diagram representation shows that we may replace the term ‘consecutive’ by ‘cyclically consecutive’ in the definition of the *s*-process.

<sup>10</sup> We shall not distinguish between the one-set partition  $\{[p]\}$  and the set [p] itself.

We denote by  $\mathcal{S}_p$  the collection of all  $s$ -partitions  $\sigma_p$  of  $[p]$ , and by  $\mathcal{S}_p^0$  the subset of  $\mathcal{S}_p$  consisting of the partitions  $\sigma_p^0$  in which the integers 1 and  $p$  belong to the same set. We obtain a mapping  $f_p$  from  $\mathcal{S}_p$  into the set  $\mathcal{S}_{p+1}$  of all partitions of  $[p+1]$  by defining the image  $f_p(\sigma_p)$  of a partition  $\sigma_p \in \mathcal{S}_p$  as the partition obtained from  $\sigma_p$  by adjoining  $p+1$  to the set in  $\sigma_p$  containing the integer 1. Since 1 and  $p+1$  are cyclic neighbours in  $[p+1]$ , and since  $\sigma_p \in \mathcal{S}_p$ ,  $f_p(\sigma_p)$  belongs to  $\mathcal{S}_{p+1}$  and hence to  $\mathcal{S}_{p+1}^0$ . Conversely, for each  $\sigma_{p+1}^0 \in \mathcal{S}_{p+1}^0$  there is a unique original element under  $f_p$  obtained simply by removing the integer  $p+1$  from  $\sigma_{p+1}^0$ . Thus,  $f_p$  establishes a one-to-one correspondence between  $\mathcal{S}_p$  and  $\mathcal{S}_{p+1}^0$ .

We now find a prescription for generating the whole collection  $\mathcal{S}_{p+1}$  from  $\mathcal{S}_{p+1}^0$  and hence (by  $f_p$ ) from  $\mathcal{S}_p$ . We obtain  $\mathcal{S}_{p+1}$  as the collection of the partitions in  $\mathcal{S}_{p+1}^0$  and the partitions obtained from each of these partitions by employing one  $s$ -process in all possible different ways giving partitions in which 1 and  $p+1$  belong to different sets. All the partitions obtained this way belong to  $\mathcal{S}_{p+1}$  by construction, and each element  $\sigma_{p+1}$  of  $\mathcal{S}_{p+1}$  is generated exactly once. If  $\sigma_{p+1} \in \mathcal{S}_{p+1}^0$ , this is obvious. If  $\sigma_{p+1} \notin \mathcal{S}_{p+1}^0$ , it arises precisely once from the unique partition obtained from  $\sigma_{p+1}$  by uniting the sets containing the elements 1 and  $p+1$ : The resulting partition is indeed contained in  $\mathcal{S}_{p+1}^0$  since 1 and  $p+1$  are cyclic neighbours in  $[p+1]$ . We refer to the rule for obtaining  $\mathcal{S}_{p+1}$  from  $\mathcal{S}_p$  as lemma 1.

Consider diagrams of partitions as two-dimensional point sets. We say that two sets of an ordered partition are connected if the diagram of the partition contains a continuous curve joining points of the polygons that represent the two sets.<sup>11</sup>

Clearly, connectivity is an equivalence relation and hence gives rise to a classification of the sets of a partition. From an arbitrary partition  $\pi$  we obtain another partition  $\sigma_\pi$  which we call the basis of  $\pi$ , by replacing each connectivity class by the union of all sets in the class. The basis of a partition has a diagram in which no polygon-sides intersect: it is an  $s$ -partition. For example, the basis of the partition (3.2) (exhibited in figure 1 c) is

$$\{(1, 2, 4, 7, 8), (3), (5, 6)\} \quad (3.4)$$

which is an  $s$ -partition as figure 1 d clearly shows. An  $s$ -partition is its own basis.

A partition in which all sets are connected is said to be connected and

<sup>11</sup> 'Connectivity' is not used in the graph-theoretical sense: the diagrams are not graphs in the narrow sense of this term (compare e.g. BERGE 1962).



is called a  $c$ -partition. Compare the diagram in figure 1b which represents the  $c$ -partition,

$$\{(1, 4, 7), (2, 6, 8), (3, 5)\} \tag{3.5}$$

of the set [8]. The set of all  $c$ -partitions of  $[p]$  is denoted  $\mathcal{C}_p$ . The basis of a  $c$ -partition of  $[p]$  is  $[p]$  itself (compare footnote 10).

Any partition determines its basis uniquely and can be recovered from this by a unique, partitioning of the sets of the basis into connected partitions. Therefore, any partition can be uniquely decomposed into a  $c$ -subpartition of an  $s$ -partition. We refer to this result as lemma 2. It shows that  $c$ -partitions are in a sense complementary to  $s$ -partitions.

The sets  $\mathcal{S}_p$  and  $\mathcal{C}_p$  appearing in equation (2.11) and (2.12) are now well defined, and we procede to prove these relations. Assume<sup>12</sup>

$$\varrho_1 \varrho_2 \varrho_3 \dots \varrho_p = \sum_{\sigma \in \mathcal{S}_p} \mathcal{Y}_{S_1}^{\text{in}} \prod_{j>1} \mathcal{Y}_{S_j} \tag{3.6}$$

where the sum is taken over all partitions  $\sigma = \{S_1, S_2, \dots\} \in \mathcal{S}_p$ , and  $S_1$  is the set containing the integer 1. Multiply both sides of equation (3.6) by  $\varrho_{p+1}$  and eliminate all products  $\mathcal{Y}_{S_1}^{\text{in}} \varrho_{p+1}$  by equation (2.4). By employing lemma 1 we then find that the resulting expression has the form (3.6) with  $p$  replaced by  $p + 1$ , and the validity of equation (3.6) follows by induction. From equation (3.6) we obtain the recurrence relation (2.11) by taking the average value.

Consider now equation (2.6). By lemma 2 we can write the sum over  $\mathcal{P}_p$  in this equation as the sum over  $\mathcal{S}_p$  of the sum over all  $c$ -subpartitions: The existence of the  $sc$ -decomposition of an arbitrary partition guarantees that all terms of (2.6) are included in the double sum, and the uniqueness of the decomposition ensures that each term is included only once. All terms of (2.6) having a given basis  $\sigma \in \mathcal{S}_p$  factorize alike, corresponding to the sets  $S$  of  $\sigma$ . We can therefore rewrite equation (2.6)

$$\mathcal{G}_{[p]} = \sum_{\sigma \in \mathcal{S}_p} \prod_{S \in \sigma} \sum_{\gamma \in \mathcal{C}(S)} \prod_{C \in \gamma} \mathcal{U}_C \tag{3.7}$$

in which  $\mathcal{C}(S)$  denotes the collection of all connected partitions of the ordered set  $S$ .

To prove the expression (2.12) equate the right hand sides of equations (2.11) and (3.7) and assume equation (2.12) to be valid for all orders smaller than  $p$ . All terms in the sums over  $\mathcal{S}_p$  except those corresponding to  $\sigma = [p]$  then cancel<sup>10</sup> leaving the expression (2.12) at order  $p$ , and the general validity of equation (2.12) follows by induction.

<sup>12</sup> We simplify the notation when no confusion can arise.



#### 4. Discussion of Results

The derivation of equation (2.12) in the preceding section reveals that the two equations, (2.11) and (2.12), are in a sense complementary with respect to equation (2.6). The  $\mathcal{Y}$  functions may therefore be naturally characterized as being intermediate between the distribution functions and the Ursell functions. Both equations have a form comparable to that of equation (2.6), but in equation (2.11) the  $\mathcal{Y}$  functions appear similar to Ursell functions, whereas in equation (2.12) they appear similar to distribution functions.

Equation (2.12) is an explicit expression for the  $\mathcal{Y}$  functions. It shows that these are sums of products of Ursell functions. To illustrate the structure of the  $\mathcal{Y}$  functions we have displayed these up to order six, in figure 2, using a diagram notation related to the one used for partitions: A diagram with dashed lines represents a product of Ursell functions, and a polygon covering a set of vertices corresponding to an index set  $Q$  indicates the presence of a factor  $\mathcal{U}_Q$ . The terms of the sum for  $\mathcal{Y}_{[p]}$  appear in classes within which the terms only differ by cyclic permutations or by complete reversal followed by cyclic permutations of the indices. (Compare the discussion of symmetry below). For clarity and to save space we therefore represent the terms of a class by just one diagram with unnumbered vertices, and indicate the number of terms in a class by a coefficient to the diagram. For example, there are six terms in two classes at order five, namely

$$\left. \begin{aligned} \mathcal{Y}_{12345} &= \mathcal{U}_{12345} + \mathcal{U}_{135} \mathcal{U}_{24} + \mathcal{U}_{124} \mathcal{U}_{35} \\ &+ \mathcal{U}_{235} \mathcal{U}_{14} + \mathcal{U}_{134} \mathcal{U}_{25} + \mathcal{U}_{245} \mathcal{U}_{13}. \end{aligned} \right\} \quad (4.1)$$

Equation (2.11) gives the  $\mathcal{Y}$ -functions in terms of distribution functions only implicitly. A simpler recurrence relation is readily obtained from equation (2.11):

$$\mathcal{G}_{[p]} = \sum_Q \mathcal{Y}_Q \prod_j \mathcal{G}_{Q_j}, \quad 1 \in Q. \quad (4.2)$$

Here the sum is taken over all subsets  $Q$  of  $[p]$  containing 1, and  $\{Q, Q_1, Q_2, \dots\}$  is the smallest<sup>13</sup> partition of  $[p]$  in which each set  $Q_j$  consists of a single chain of consecutive integers. Evidently, the partition is determined uniquely by  $Q$ .

Equation (4.2) is directly comparable to equation (2.7). The only difference of form is that the single function  $\mathcal{G}_{[p]-Q}$  in the equation with Ursell

<sup>13</sup> That is, the partition with the least number of sets.

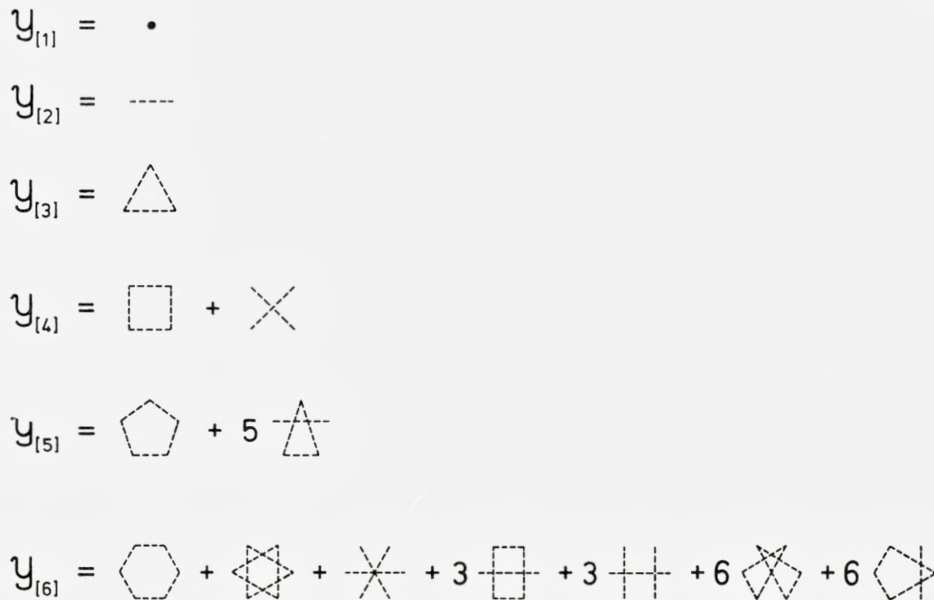


Figure 2. Diagrammatic representations of the first six  $\mathcal{Y}$  functions.

functions is replaced by a product of  $\mathcal{G}$  functions covering the set  $[p] - Q$  in the equation with  $\mathcal{Y}$  functions.

It is plain from equation (4.2) that the explicit expression for  $\mathcal{Y}_{[p]}$  in terms of distribution functions must have the form

$$\mathcal{Y}_{[p]} = \sum_{\sigma \in \mathcal{S}_p} c_{\sigma} \prod_{s \in \sigma} \mathcal{G}_s \tag{4.3}$$

The coefficients  $c_{\sigma}$  can be obtained from equation (4.2). This is easy for partitions with few sets. In particular, the coefficient  $c_{\zeta}$  to the constant term  $\mathcal{G}_1 \mathcal{G}_2 \dots \mathcal{G}_p = n^p$  of  $\mathcal{Y}_{[p]}$  (corresponding to  $\zeta = \{(1), (2), \dots, (p)\}$ ) is found to be  $c_{\zeta} = (-1)^{p-1} (p)_{p-1} / p!$ , which (apart from sign) is known as a Catalan number (SLOANE 1973). The constant terms of the  $\mathcal{Y}$  functions are of special interest in the refractive index theory (II) where they give rise to contributions which produce the 'cavity field factor' of the dispersion relation (see section 2 of III). But the general coefficient  $c_{\sigma}$  depends on the detailed structure of the partition  $\sigma$  in a rather complicated way,<sup>14</sup> and this fact detracts from the usefulness of the explicit form (4.3). The simple

<sup>14</sup> In the corresponding expression for the Ursell functions, the coefficients are  $(-1)^{q-1} (q-1)!$ , determined solely by the number  $q$  of sets in the corresponding partition.

expression (2.12) in terms of Ursell functions is the natural representation of  $\mathcal{Y}_{[p]}$ .

Both distribution functions and Ursell functions are symmetric in all variables, i.e.  $\mathcal{G}_{[p]}$  and  $\mathcal{U}_{[p]}$  are invariant under all permutations of  $[p]$ . In contrast, for  $p > 3$   $\mathcal{Y}_{[p]}$  is only invariant under permutations belonging to the dihedral group  $D_p$ , a proper subgroup of order  $2p$  of the symmetric group of degree  $p$  (and order  $p!$ ). The group  $D_p$  consists of all cyclic permutations of  $[p]$  and of these followed by complete reversal of order (which e.g. takes  $(1, 2, \dots, p-1, p)$  into  $(p, p-1, \dots, 2, 1)$ ). The elements in  $D_p$  are precisely the permutations that carry the polygon representing  $[p]$  into itself (except for the numbering). It is clear from the explicit form (2.12) that  $\mathcal{Y}_{[p]}$  is invariant under permutations from  $D_p$ : These map the set of connected partitions onto itself (except for ordering) and hence just cause a rearrangement of the terms in the sum on the right hand side of equation (2.12). (The Ursell functions are symmetric in all variables). On the other hand, there can be no further symmetry: For any permutation  $P \notin D_p$  of  $[p]$  there exists at least one pair  $(i, j)$  of not cyclically consecutive integers which is mapped by  $P$  into consecutive integers. Therefore,  $P$  maps the  $c$ -partition  $\{(i, j), [p] - (i, j)\}$  into an  $s$ -partition, and consequently, there exists at least one term in the sum on the right hand side of equation (2.12) which transforms under  $P$  into a term not contained in the original sum (and not cancelled by other terms).

A consequence of the incomplete symmetry of  $\mathcal{Y}_{[p]}$  is that the asymptotic behaviour of  $\mathcal{Y}_{[p]}$  depends on the limit considered. Let the variables of  $\mathcal{Y}_{[p]}$  be divided into two sets as discussed above equation (2.8), define  $d_{QR}$  by equation (2.8), and define

$$d_Q = \max |\mathbf{x}_i - \mathbf{x}_j|, \quad i, j \in Q. \quad (4.4)$$

Equations (2.9) and (2.12) then show that

$$\mathcal{Y}_{[p]} \rightarrow 0 \quad \text{for} \quad d_{QR} \rightarrow \infty, \quad d_Q, d_R < \infty, \quad (4.5)$$

if and only if<sup>15</sup>  $Q$  consists of cyclically consecutive integers of  $[p]$ . In particular,  $\mathcal{Y}_{[p]} \rightarrow 0$ , when the distance from one point to all the other points goes to infinity. These asymptotic properties of  $\mathcal{Y}$  functions are important in refractive index theory as we shall see in the following section.

In closing this section we note a straightforward extension of the results.

<sup>15</sup> The 'only if' part of the statement disregards possible accidental zeros for special configurations within the two sets of points.



The  $\mathcal{Y}$  functions are generalized correlation functions in the sense that they include all self-correlations. By simply omitting these self-correlations we obtain a corresponding set of 'ordinary' functions which evidently satisfies equations analogous to (2.11), (2.12) with the  $\mathcal{G}$  and  $\mathcal{U}$  functions replaced by ordinary distribution functions and Ursell functions. Obviously, the ordinary functions also share the symmetry and the asymptotic behaviour (4.5) with the  $\mathcal{Y}$  functions.

### 5. $\mathcal{Y}$ functions in Refractive Index Theory

We now analyse a problem of convergence arising in refractive index theory, in which the special structure of the  $\mathcal{Y}$  functions plays a peculiar role.

In microscopic refractive index theory (e.g. YVON 1937, BULLOUGH 1967, I) the macroscopic response of a many-body system to an external electromagnetic field is naturally described in terms of elementary scattering processes taking place in vacuum. In this theory, the response related to bulk properties is mixed at all orders in multiple scattering with irrelevant surface effects associated with molecular description of reflection and diffraction (I). Mathematically, the surface effect appears through integrals over a finite region, which diverge when taken over all space.

We have systematically eliminated the surface effect to all orders in multiple scattering and obtained a translationally invariant theory, the screened theory (II), by a reformulation of the theory in which the elementary scattering processes take place in the medium (compare BULLOUGH 1965, 1967). This elimination involves extension of integrations to all space, a procedure that demands a proof of convergence. It is this problem we consider here.

A typical integral to be analysed (from the term at order  $p$  in multiple scattering) is

$$\iint \dots \int \tilde{\mathbf{F}}_{12} \cdot \tilde{\mathbf{F}}_{23} \dots \tilde{\mathbf{F}}_{(p-1)p} \exp(im \mathbf{k}_0 \cdot (\mathbf{x}_p - \mathbf{x}_1)) \mathcal{Y}_{123 \dots p} d\mathbf{x}_2 d\mathbf{x}_3 \dots d\mathbf{x}_p \quad (5.1)$$

in which  $\mathbf{k}_0$  is a fixed vector of length  $k_0$ , and the refractive index  $m$  is taken to be real.<sup>16</sup> The tensor  $\tilde{\mathbf{F}}_{jk} = \tilde{\mathbf{F}}(\mathbf{x}_j, \mathbf{x}_k; \omega)$  is given by

<sup>16</sup> The choice  $\text{Im}(m) = 0$  is consistent with translational invariance, but means neglect of external scattering. This is a logically necessary but unphysical feature of a translationally invariant theory. But the final equation (of which (5.1) is a part) admits of no purely real solution for  $m$  (compare especially HYNNE 1974). Thus, the translationally invariant form of the screened theory contains a logical inconsistency (compare BULLOUGH 1965, 1967). We shall not discuss this question further here, however.

$$\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) = (\nabla\nabla + m^2 k_0^2 \mathbf{U}) \left( \frac{\exp(imk_0 r)}{m^2 r} \right), \quad r = |\mathbf{x} - \mathbf{x}'| \quad (5.2)$$

where  $\mathbf{U}$  is the unit tensor. It describes the propagation of radiation from a dipole in a medium of refractive index  $m$ . It has the asymptotic form

$$\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) \sim k_0^2 (\mathbf{U} - \hat{\mathbf{r}}\hat{\mathbf{r}}) \frac{\exp(imk_0 r)}{r}, \quad k_0 r \gg 1, \quad (5.3)$$

where  $\hat{\mathbf{r}} = (\mathbf{x} - \mathbf{x}')/r$ .

For  $m$  real,  $\tilde{\mathbf{F}}$  is long range, and the convergence of the multiple integral (5.1) is ensured neither by the  $\tilde{\mathbf{F}}$  tensors alone nor by the  $\mathcal{Y}$  functions alone. (Compare the discussion of the asymptotic behaviour of the  $\mathcal{Y}$  functions in the preceding section). It is through the special *combination* of Ursell functions and  $\tilde{\mathbf{F}}$  tensors the integrals converge. As we shall see, the convergence is only just secured, however.

Express  $\mathcal{Y}_{[p]}$  by equation (2.12) as a sum of products of Ursell functions, and consider a typical term. The structure of such a term is best visualized by the diagram for the product of Ursell functions in which the  $\tilde{\mathbf{F}}$  tensors are indicated by heavy lines; a coincidence of a dashed and a heavy line is indicated by adding a cross to the heavy line (compare figure 3 a). Because of the short range of the Ursell functions, we can integrate first over the relative coordinates of each cluster (set of particles covered by one Ursell function) with one particle of the cluster held fixed. Hereby we are left with integrations over relative positions of clusters. We can assume that the  $\tilde{\mathbf{F}}$  tensors that connect particles in different clusters can be replaced by  $\tilde{\mathbf{F}}$  tensors connecting the fixed particles of the clusters. (This approximation is good when the clusters are far apart, and certainly proper for discussion of convergence). The crucial point now is, that every cluster is connected with

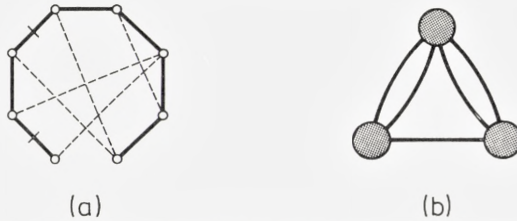


Figure 3. (a) Diagram representing an integral of the type shown in equation (5.1) for  $p = 8$  with  $\mathcal{Y}_{[8]}$  replaced by a typical term  $\mathcal{U}_{126} \mathcal{U}_{348} \mathcal{U}_{57}$  of its expansion (2.12). (b) A schematic representation of the same term exposing its structure of clusters (represented by shaded circles in (b) and by dashed polygons in (a)) connected by 'external'  $\tilde{\mathbf{F}}$  tensors (represented by heavy lines).



every other cluster by at least three independent chains of  $\tilde{\mathbf{F}}$  tensors. This fact is illustrated in figure 3 b for the term shown in figure 3 a. Here, clusters are indicated by large shaded circles, and  $\tilde{\mathbf{F}}$  tensors going between clusters are shown whilst  $\tilde{\mathbf{F}}$  tensors going inside a cluster are omitted. Any two of the three clusters in figure 3 b are connected by precisely three independent chains of  $\tilde{\mathbf{F}}$  tensors. (This exemplifies the 'worst case': in the term corresponding to the partition exhibited in figure 1 b, e.g., which also has three clusters, there are four independent chains between any pair).

An immediate consequence of this structure of multiply connected sets of clusters is that the integral over all positions of any one cluster with all the remaining clusters fixed in arbitrary configuration, converges. This almost proves the convergence of the multiple integral (5.1). The remaining step of a complete and rigorous proof is complicated by the fact that the individual integrals are not in general absolute convergent. This means that the process of integration over all space must be specified, for example as a limit of integration over a finite region; it is then still necessary to specify the passage to that limit. Such a proof is outside the scope of this paper.

As conclusion we may say that the result (2.12) forms an excellent basis for analysis of convergence of the multiple integral (5.1). This analysis strongly suggests that the multiple integral does converge although the convergence is shown to be conditional and extremely slow. Certainly, the transformation to the translationally invariant screened theory has eliminated all the manifestly divergent integrals that appear in the unscreened theory when the integrations are extended to all space.

## 6. Summary of Results

The  $p$ -body correlation function

$$\mathcal{Y}_{[p]} = \mathcal{Y}_{123 \dots p} = \mathcal{Y}_p(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_p) \quad (6.1)$$

is a function of  $p$  variables (points in space). It is symmetric in the variables corresponding to the dihedral permutation group  $D_p$ , i.e. it is invariant under cyclic permutations of the variables as well as under complete reversal of the order of the variables. It is a generalized correlation function in the sense that it includes all self-correlations, but all results can be reinterpreted in terms of ordinary functions.

The set of  $\mathcal{Y}$  functions is related to the set of generalized distribution functions on the one hand, and to the set of generalized Ursell functions on the other hand, by the pair of equations (2.11), (2.12), the main result of



this paper. This pair of equations shows that the  $\mathcal{Y}$  functions can be said to be intermediate between distribution functions and Ursell functions. Each of the two equations independently determine the  $\mathcal{Y}$  functions: equation (2.11) is a recurrence relation for the  $\mathcal{Y}$  functions in terms of generalized distribution functions, and (2.12) is an explicit expression in terms of generalized Ursell functions. The two equations involve sums over either of two distinct sets of partitions of the index set  $[p]$  that marks the variables of the functions. These partitions are defined in section 3, and the derivation of equation (2.11) and (2.12) is based on an analysis of 'ordered partitions' resulting in a theorem (lemma 2, stated below equation (3.5)) on decomposition of partitions. The  $\mathcal{Y}$  functions of orders up to six are displayed in figure 2 in a diagram notation explained in section 4. The first three  $\mathcal{Y}$  functions are identical to the corresponding Ursell functions.

The explicit expression (2.12) is utilized to prove (with qualifications) that characteristic asymptotic properties of the  $\mathcal{Y}$  functions just secure convergence of integrals appearing in refractive index theory.

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