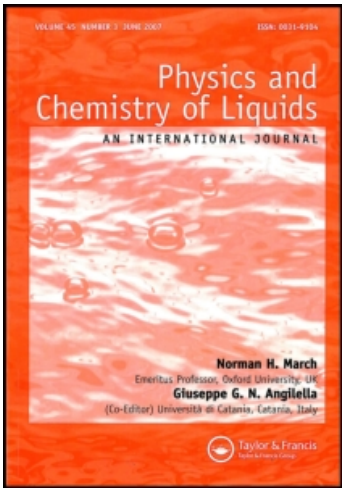

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Graph Theoretic Techniques in the Theory of Classical Fluids

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Review Article

Graph Theoretic Techniques in the Theory of Classical Fluids

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The mathematical ideas underlying the graph theoretic approach to the equilibrium theory of classical fluids are treated from an elementary point of view. The emphasis is placed on modern developments based on the techniques of functional differentiation and topological reduction. The aim is to provide the non-expert reader with a mathematical guide to recent papers which employ graph theoretic methods, particularly to those dealing with perturbation theory.

1 INTRODUCTION

It has long been well-known that graph theoretic methods can profitably be used in the analysis of many important problems in statistical mechanics, the classic work along these lines being that of Mayer[1] and Yvon.[2] In recent years, however, there has been a renewed and growing interest in graphical methods, arising in large part from the recognition of the value of perturbation theory in treating the equilibrium properties of fluids. Not all the original work on perturbation theory made use of graphical techniques, but in nearly all cases the results, and those of other theoretical approaches, can be expressed very concisely in graphical terms, thereby allowing a unified discussion of a wide variety of theoretical methods.

This more recent work has rested heavily on a number of fundamental papers, notably those of Morita and Hiroike,[3] de Dominicis[4] and Stell,[5] in which systematic use is made of two techniques which are relatively unfamiliar to many with less than specialist knowledge of the field, those of

functional differentiation and *topological reduction.* Most quantities in statistical mechanics are functionals of one sort or another. For example, the radial distribution function $g(r)$ in a monatomic liquid is a functional of the pair potential $v(r)$, since the value of $g(r)$ for any particular value of r is determined by the value of $v(r)$ for all r. We are then led naturally to the concept of functional differentiation if we wish to calculate the variation in $g(r)$ resulting from a small variation in $v(r)$, a situation with obvious relevance to perturbation calculations. Topological reduction is simply a general name for a process of resuming a series of graphs in order to simplify the graphical prescription for a quantity of interest. The key step in any such operation is invariably a classification of the relevant graphs on the basis of their topological structure.

The present article is devoted to mathematical aspects of the principles and application of these methods. Our aim is to leave the non-specialist reader in a position to tackle the much more technical accounts to be found in the original papers, particularly those on perturbation theory,[6–14] and in recent review articles such as those of Wortis[15] and Stell,[16,17] and at the same time to fill in the missing mathematical steps in the many excellent reviews of applications which already exist.[18–25] The main effort is directed towards giving simplified but rigorous proofs of the fundamental lemmas and to discussing how and when the lemmas can be applied. We hope thereby to provide a mathematical guide to the now extensive literature on the subject. To allow a coherent presentation we phrase our arguments in large part in the language of the theory of permutation groups, but the results we borrow are all very elementary and can be found in standard undergraduate texts such as that of Hall.[26]

Section 2 is largely concerned with basic definitions. Unfortunately the subject is one which is bedevilled by differences in terminology, not only amongst different authors but also between different papers by the same author. We have tried not to add too much to this confusion, adopting for the most part the terms used by Morita and Hiroike[3] and by Stell.[5] We also discuss (in Section 2.5) a number of problems which arise in the process of topological reduction, but which have largely been ignored in the literature. Section 3 is concerned with the development of a number of simple group theoretic arguments; these are used in Section 4 and Section 5, where the method of functional differentiation is formulated in terms of graph theoretic operations. Section 6 is devoted to the proof and use of lemmas on topological reduction. Applications are discussed at various points in the text, but though they are all of some practical importance they are chosen primarily to illustrate how the mathematical difficulties which arise are typically overcome. We therefore limit ourselves to the simple case of a one-component system of monatomic particles interacting via a pair potential $v(1, 2)$. (For con-

venience we shall frequently use the notation $i \equiv \mathbf{r}_i$.) The starting point in the discussion of the thermodynamic and structural properties of such a system is the grand partition function, which we write in the form

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \cdots \int d1 \ldots dN z^*(1) \ldots z^*(N) \prod_{i<j}^{N} [1 + f(i,j)] \quad (1.1)$$

where

$$f(i,j) = \exp[-\beta v(i,j)] - 1 \quad (1.2)$$

is the Mayer f-function and $z^*(i) = z \exp[-\beta\phi(i)]$, where z is the activity and $\phi(i)$ is the potential at a point i due to an external field. The generalization to inhomogeneous systems is retained because it creates few complications and means the result can be applied, for example, in the discussion of surface phenomena.

2 SOME GRAPH THEORETIC CONCEPTS

2.1 Elementary definitions: free and labelled graphs

Graphs are used in classical statistical mechanics as a shorthand means of representing definite integrals in which the variables of integration are the coordinates 1, 2, 3, ..., specifying the position of particles within the system of interest. Consider, for example, the function

$$F(\mathbf{r}) = \int \cdots \int d1 \ldots d6 \gamma(\mathbf{r})\gamma(1)\gamma(2)\gamma(3)\gamma(4)\gamma(5)\gamma(6) B(\mathbf{r},1)B(\mathbf{r},2) \times B(1,2)B(1,3)B(2,3)B(3,4)B(3,5)B(3,6)\xi_3(1,2,3) \quad (2.1)$$

where $\gamma(\mathbf{r})$, $B(\mathbf{r}, \mathbf{r}')$ and $\xi_3(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ are respectively, one, two and three point functions of the particle coordinates and the integration extends over the whole volume of the system. The function $F(\mathbf{r})$ can be represented in the graphical form shown in Figure 1, the algebraic interpretation of any such graph being made with the help of the well-known rules which we recall

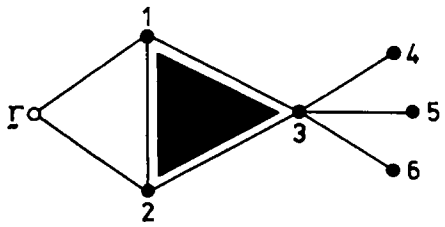

FIGURE 1 The graphical representation of the function $F(\mathbf{r})$, Eq. (2.1).

below. Mathematically the right-hand side of (2.1) and the graph pictured in Figure 1 are to be regarded as equivalent representations of the same object.

Figure 1 is an example of a *labelled graph*, which in the general case is made up of a certain number of *circles*, each labelled with the particle coordinate to which it corresponds and with each of which is associated a one-point function; *bonds* linking pairs of circles and associated with two-point functions; and $(s-1)$-dimensional *faces* $(s > 2)$ linking groups of s circles and associated with s-point functions. A *linear graph* is a graph composed only of circles and bonds. A bond may be regarded as a one-dimensional face, but the special importance of two-point functions makes it more convenient to treat bonds as separate entities. Bonds and faces are said to be *incident* with the circles which they link. Circles are classified either as *root points* or as *field points*. Root points are represented by white circles and correspond to coordinates which are not integrated over. Field points correspond to variables of integration and in the most common case, when the associated one-point functions are all the same, are represented by black circles. Other choices for the one-point functions correspond to different *colourings* of the field points. We shall return to the question of coloured graphs in Section 6, but elsewhere it will be assumed that the field points are all black. If the functions associated with the bonds (or faces) are not all identical, the bonds (or faces) are said to be of different *species*.

A graph containing white circles is called a *rooted graph*. An integral represented by a rooted graph is both a function of the coordinates of the white circles and a functional of the functions associated with the circles, bonds and faces. In the conventional terminology the example shown in Figure 1 is a singly-rooted graph composed of one white γ-circle, six black γ-circles, eight B-bonds and one ξ_3-face. If the function associated with a circle is identically unity, the circle in question is called a black or white 1-*circle*.

We shall use the term *simple graph* to denote a graph in which no set of circles is linked by more than one bond or face, and no bond or face is incident more than once with the same circle. This definition excludes graphs which are either *bond-composite* or *face-composite*, or which contain *loops*.

The field points of a graph correspond to dummy variables of integration. Relabelling the field points may therefore change the appearance of the integrand but the value of the integral will be unchanged. To that extent the way in which the field points are labelled is without significance and the labels may conveniently be omitted altogether. A graph in which the field points are unlabelled is called a *free graph*. The one-to-one correspondence with a certain definite integral remains. However, whereas the *value* of a labelled graph is simply the integral which the graph represents, the definition of the value of a free graph brings in a combinatorial factor related to its

topological structure. This apparently small distinction is of great importance, the power of the graphical method in specific cases being largely determined by the ease with which expressions involving free graphs can be manipulated; we shall return to this question (in Section 2.3) after first discussing what is meant by the *connectivity* of a graph.

2.2 Connectivity

Two circles in a graph are said to be *adjacent* if they are linked by a bond or share a common face. A sequence of adjacent circles forms a *path*. Then a graph is *connected* if there exists at least one path between each pair of circles. If a graph is *disconnected*, it is composed of two or more connected *components*, and if two circles lie in different components there is no path between them.

Removal of a circle from a connected graph may cause the graph to become disconnected. In that case the circle in question is called a *connecting circle*. Removal of a circle means, pictorially, that the circle and all bonds and faces incident with it are erased. For example, when the arrowed circle in Figure 2(a) is removed, the graph becomes disconnected. By extension, a *connecting subset* is a group of circles such that upon its removal the graph becomes disconnected. The *order* of a connecting subset is the number of circles of which it is composed.

In the case of rooted graphs there are two particularly important classes of connecting circles. Removal of an *articulation circle* causes the graph to separate into two or more pieces, at least one of which contains no white circle. Thus the connecting circle shown in Figure 2(a) is in fact an articulation circle. In the same way, *articulation subsets* are a special case of connecting subsets. The most important such subset is an articulation pair, of which an example is shown in Figure 2(b). Any articulation circle in a graph with more

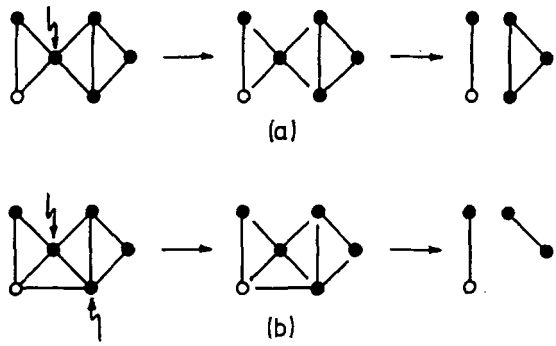

FIGURE 2 The effect of removing (a) an articulation circle and (b) an articulation pair.

than three circles forms an articulation pair with at least one other circle in that graph. A graph which is free of articulation circles is called 1-*irreducible*; a graph which is free of articulation pairs is called 2-*irreducible*. Thus 2-irreducibility implies 1-irreducibility, but not vice versa. The *multiplicity* of an articulation circle is the number of pieces into which the graph separates when the circle is removed. By convention a circle which is not an articulation circle is allotted a multiplicity of one.

A *nodal circle* is a connecting circle in a graph containing two or more white circles such that all paths between two particular white circles pass through it. On removal of the nodal circle the graph separates into two or more pieces, the two white circles in question appearing in different pieces. Obviously if two white circles are linked by a bond there can be no associated nodal circle. An articulation circle may simultaneously be a nodal circle if it is of multiplicity three or more.

A graph may be either *simply* or *multiply* connected. Since the question of the multiple connectivity of graphs with faces raises certain difficulties, we shall confine our definitions to the case of linear graphs. Two paths between a given pair of circles are said to be *independent* if they have no intermediate circle in common. If there exist (at least) n independent paths between each pair of circles the graph is said to be (at least) *n-tuply connected*. Thus in Figure 3, graph (a) is simply connected, graph (b) is triply connected and graph (c) is a disconnected graph with two components, each of which is doubly connected. According to a well-known result is graph theory known as Menger's theorem,[28] a graph lacking a connecting subset of order smaller than s must be at least s-tuply connected. In particular, a graph without connecting circles must be at least doubly connected. This is less straightforward to prove than might appear at first sight, though the converse statement is easily verified.

In passing it is worth pointing out that many of the most important graph theoretic manipulations in the theory of fluids are concerned with the progressive elimination of classes of weakly connected graphs.

2.3 Topological equivalence and the value of a free graph

Let Γ be a free graph with m black circles and let $\tilde{\Gamma}$ be an arbitrarily labelled version. The value of the labelled graph is left unaltered by application of any element of the group consisting of the $m!$ possible permutations of the labels on the black circles, since the integrals associated with different labellings differ, at most, only in the variables of integration. However, there is a subgroup of permutations which also leave the integrand unchanged or, alternatively, give rise to graphs characterized by the same set of *connections*. Two such graphs are said to be *topologically equivalent* and the subgroup of

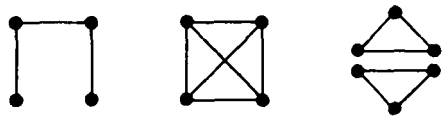

FIGURE 3 Graphs with different degrees of connectivity (see text).

permutations which transform an arbitrarily labelled graph into another which is topologically equivalent is called the *graph group* of Γ. The *symmetry number* of a simple graph is equal to the order of the graph group, but for composite graphs the symmetry number is obtained by multiplying the order of the graph group by a factor $n!$ for every pair of circles linked by n bonds of a given species and every set of s circles linked by n $(s-1)$-dimensional faces of a given species.

Two graphs which are labelled versions of the same free graph but are characterized by different sets of connections are called *topologically inequivalent*. Since the graph group is a subgroup of the symmetric group of degree m, it follows from Lagrange's theorem on the order of a group and its subgroups that

$$m! = \{\text{the order of the graph group}\} \times \{\text{the number of ways of labelling } \Gamma \text{ which yield topologically inequivalent graphs}\} \tag{2.2}$$

Returning to the example shown in Figure 1, we see that topologically equivalent graphs are obtained by combining any interchange of labels 1 and 2 with any permutation of 4, 5 and 6. Thus the graph group is of order 12 and from (2.2) it follows that a total of 60 topologically inequivalent graphs can be generated by permuting the labels on the black circles. It is also convenient to introduce the notion of *complete inequivalence*: two labelled graphs are said to be completely inequivalent if they are labelled versions of two different or *topologically distinct* free graphs. In such a case there is no permutation of the labels which will transform one graph into the other. Note that we use the words "equivalent" and "inequivalent" to describe labelled graphs, reserving the term "distinct" for the characterization of free graphs. Where we use the word "graph" without further qualification, we have in mind the case of free graphs, though in much of the discussion the distinction between free and labelled graphs is irrelevant.

We are now in a position to give the definition of the value of a free graph. Adopting the convention that when either the symbol representing a graph or the word "graph" appears in an equation, the result must be interpreted in

terms of the value of that graph, the value of a free graph Γ with m black circles is given by

$$\Gamma = (1/m!)\{\text{the sum of all topologically inequivalent labelled versions of } \Gamma\}$$
$$= \tilde{\Gamma}/|\Gamma| \tag{2.3}$$

where $\tilde{\Gamma}$ is *any* labelled version of Γ and $|\Gamma|$ is its symmetry number. Thus in the example already introduced, (Eq. (2.1) and Figure 1), we see that $\tilde{\Gamma} = F(\mathbf{r})$ and $\Gamma = \frac{1}{12}F(\mathbf{r})$.

We now introduce the concept of a *star product.*[5] Let Γ_1 be a connected graph with n_1 white 1-circles and let Γ_2 be a connected and possibly identical graph with n_2 white 1-circles. Now consider the n_3 white circles with labels common to both graphs. Then the star product $\Gamma_1 * \Gamma_2$ is the graph obtained by linking together Γ_1 and Γ_2 in such a way that the white circles carrying identical labels coincide. The star product contains $n_1 + n_2 - n_3$ white circles and Γ_1 and Γ_2 are said to be *connected in parallel* at the n_3 white circles. If the white circles of Γ_1 and Γ_2 have no label in common, or if one or both is without any white circles, $\Gamma_1 * \Gamma_2$ is a disconnected graph having Γ_1 and Γ_2 as its components. The definitions are easily extended. For example, if two graphs are connected in parallel at white γ-circles, the corresponding circles in the star product become γ^2-circles; if there is a bond (or face) linking two (or more) of the white circles, the two (or more) corresponding circles in the star product will be linked by a double bond (or face), and so on. It is important to note that in general the symmetry number of a star product is not the product of the symmetry numbers of the constituent graphs. Some simple examples of the formation of star products are shown in Figure 4.

Star irreducible graphs are connected graphs which cannot be expressed as the star product of two connected graphs except when one of the two is a graph consisting of a single white circle. Other graphs are called *reducible.* The class of star irreducible graphs excludes all graphs containing white connecting subsets, and all graphs in which two white circles are linked by a bond or a set of s white circles is linked by an $(s-1)$-dimensional face, with the exception of graphs consisting only of white circles connected by a single bond or face. On the other hand it obviously includes all connected graphs consisting only of black circles and bonds. Some examples of star irreducible and reducible graphs are shown in Figure 5. It is convenient to exclude graphs consisting of a single white circle from the class of star irreducible graphs. In that case a product of two star irreducible graphs can be uniquely decomposed into its constituent parts. This is not true of reducible graphs, as can be seen from the example in Figure 4(b). However, any reducible graph

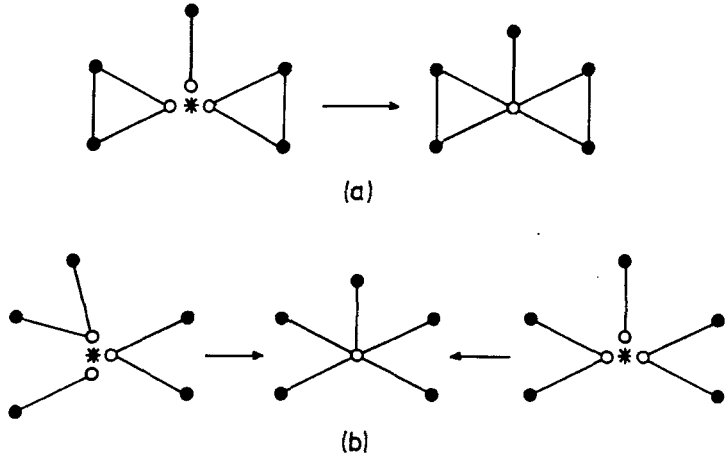

FIGURE 4 The formation of star products from (a) graphs which are all star irreducible and (b) graphs of which some are reducible.

can be uniquely written as a product of *factors* which are star irreducible. If two graphs have no factors in common, the symmetry number (and hence the value) of their star product is equal to the product of their symmetry numbers (or values). It should be clear that star irreducible graphs play a role analagous to that of prime numbers in ordinary number theory.

2.4 Lemma I: the exponentiation theorem

Given the definition of a star irreducible graph, we can proceed immediately to the statement of an important result which we shall refer to as the "exponentiation" theorem.

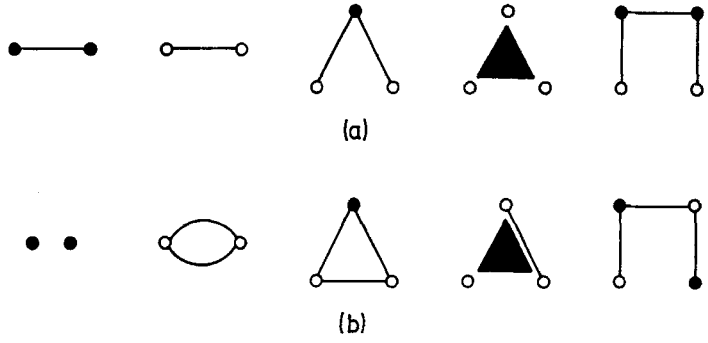

FIGURE 5 Examples of graphs which are (a) star irreducible and (b) reducible.

Lemma 1 Let G be a set of topologically distinct, star irreducible graphs, and let H be the set consisting of all graphs in G and all possible star products of graphs in G. Then

$$\{\text{the sum of all graphs in } H\} = \exp\{\text{the sum of all graphs in } G\} - 1 \quad (2.4)$$

The proof is straight forward and has been given many times. In its present form the lemma is a combination of Lemmas 3 and 4 of Morita and Hiroike.[3] The proof relies on the fact that the symmetry number of a graph Γ in H obtained as the star product of a graph Γ_1 taken n_1 times, a graph Γ_2 taken n_2 times, ..., and a graph Γ_s taken n_s times, where the Γ_i ($i = 1, \ldots, s$) are graphs in G, is

$$|\Gamma| = \left(\prod_{i=1}^{s} n_i!\right)\left(\prod_{i=1}^{s} |\Gamma_i|^{n_i}\right) \quad (2.5)$$

This is true only for star irreducible graphs.

In practice the exponentiation theorem is usually applied in reverse, that is to say by taking the logarithm of a suitably chosen sum of graphs, thereby eliminating graphs which are reducible. For example, the z^*-circle, f-bond expansion of the grand partition function (1.1) is given by

$$\Xi = 1 + \{\text{the sum of all topologically distinct, simple graphs consisting of one or more black } z^*\text{-circles and } f\text{-bonds}\} \quad (2.6)$$

which begins in the manner shown in Figure 6(a). From the exponentiation theorem it follows immediately that

$$\log \Xi = \{\text{the sum of all topologically distinct, simple, connected graphs consisting of black } z^*\text{-circles and } f\text{-bonds}\} \quad (2.7)$$

which starts as shown in Figure 6(b). Here the effect of taking the logarithm is to eliminate all graphs which are not connected; in a similar way the lemma

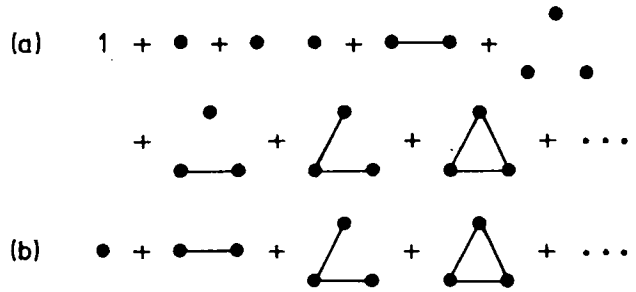

FIGURE 6 The first few graphs in the z^*-circle, f-bond expansion of (a) Ξ and (b) $\log \Xi$.

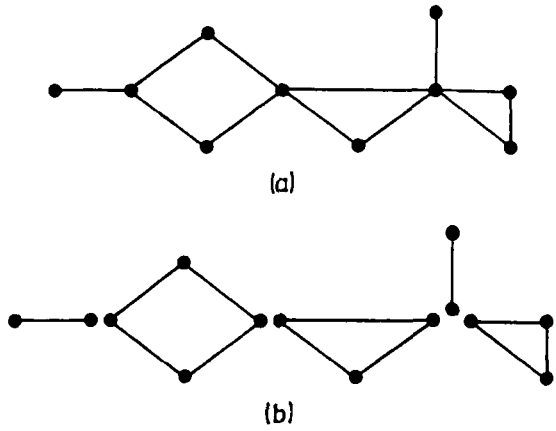

FIGURE 7 An example of (a) a graph and (b) its 1-irreducible maximal subgraphs.

can be used to eliminate graphs with white articulation circles from a collection of singly-rooted graphs.

2.5 Subgraphs and maximal subgraphs

A *subgraph* of a graph Γ is any graph which can be obtained from Γ by removal of circles, deletion of bonds and deletion of faces, or any combination of these operations. The union $\Gamma_1 \cup \Gamma_2$ of two subgraphs of a graph Γ is the graph obtained by linking together Γ_1 and Γ_2 in such a way that the circles, bonds and faces which are common to both are merged. The union of two subgraphs is itself a subgraph of Γ.

A subgraph is *maximal* with respect to a given property if it is not embedded in any other subgraph with the same property. Maximal subgraphs are not necessarily unique and "maximal" must not be interpreted in the sense of "largest". As a trivial example, the maximal connected subgraphs of a disconnected graph are simply the components of the graph, whereas the maximal connected subgraph of a connected graph is the graph itself and is consequently unique.

Classes of maximal subgraphs which are of particular importance are those which are connected and either 1-irreducible or 2-irreducible. Consider the graph shown in Figure 7(a). This has five maximal 1-irreducible subgraphs, which are pictured in 7(b). In general, if μ_i is the multiplicity of circle i (which is the same as the number of maximal 1-irreducible subgraphs in which i appears), and if there are n circles, the number $n(1)$ of 1-irreducible subgraphs is given by the relation[4]

$$n - \mu + n(1) = 1 \tag{2.8}$$

where $\mu = \sum_{i=1}^{n} \mu_i$. (Remember that a circle which is not an articulation circle has a multiplicity of one.) In the example illustrated in Figure 7 there are three articulation circles, with multiplicities of two, two and three. Thus $\mu = 14$, in agreement with (2.8). A similar but more complicated relation exists between the number of 2-irreducible subgraphs and the number of articulation pairs. Expressions of this type have been used by de Dominicis[4] to obtain relations between physically significant quantities. We shall discuss the work of de Dominicis again in Section 6.4.

We now draw together a number of results having a bearing on the question of the uniqueness or otherwise of the maximal 1-irreducible and 2-irreducible subgraphs of a given graph. These have a variety of important applications, as we shall see in the discussion of topological reduction in Section 6.

Lemma II.1 Two maximal 1-irreducible subgraphs of a graph Γ have at most one circle in common.

Proof If Γ_1 and Γ_2 are 1-irreducible subgraphs of Γ with more than one circle in common, then $\Gamma_1 \cup \Gamma_2$ is also 1-irreducible and neither Γ_1 nor Γ_2 can be maximal. If Γ_1 and Γ_2 have only one circle in common, that circle is an articulation circle of $\Gamma_1 \cup \Gamma_2$, and Γ_1 and Γ_2 could each be maximal.

Corollary If σ is a subset of the circles of Γ consisting of at least two elements and if there exist 1-irreducible subgraphs of Γ which contain σ, then there is a unique maximal such subgraph.

Lemma II.2 If Γ is a graph with one white circle, and if the white circle is not an articulation circle, any maximal 1-irreducible subgraph which contains the white circle contains all the black circles adjacent to it.

Proof (See Figure 8(a).) Let Γ_1 be a subgraph of Γ which is 1-irreducible and contains the white circle, x say; let y be a black circle which is adjacent to x but not in Γ_1; and let z be a black circle in Γ_1. Since x is not an articulation circle, there exists a path connecting y and z which does not contain x. Let Γ_2 be the subgraph consisting of the circles of that path, the bonds and faces linking adjacent circles in the path and any other circles incident with such faces. Then $\Gamma_1 \cup \Gamma_2$ is a subgraph of Γ which is 1-irreducible. Hence Γ_1 is not maximal.

Corollary Let Γ be a graph with one white circle such that the white circle is not an articulation circle. If there exist 1-irreducible subgraphs of Γ which contain the white circle, then there is a unique maximal such subgraph.

Proof From the lemma it follows that any such maximal 1-irreducible subgraph must contain not only the white circle but also all black circles ad-

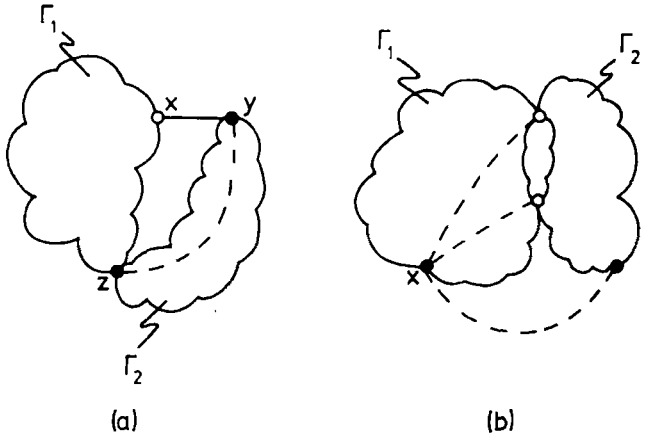

FIGURE 8 Illustrating the proof of (a) Lemma II.2 and (b) Lemma II.4. The curly lines symbolize subgraphs and the dashed lines represent paths.

jacent to it. Hence, by the corollary to Lemma II.1, there exists exactly one such subgraph.

Lemma II.3 Maximal 2-irreducible subgraphs of a graph Γ have at most two circles in common.

Proof As in Lemma II.1. If two 2-irreducible subgraphs Γ_1 and Γ_2 have exactly two circles in common, these circles form an articulation pair in $\Gamma_1 \cup \Gamma_2$.

Corollary If σ is a subset of the circles of Γ consisting of at least three elements, and if there exist 2-irreducible subgraphs of Γ which contain σ, then there is a unique maximal such subgraph.

Lemma II.4 Let Γ be a 1-irreducible graph with two white circles. If the white circles are non-adjacent and do not form an articulation pair, and if there exist 2-irreducible subgraphs of Γ containing both white circles, then there is a unique maximal such subgraph.

Proof (See Figure 8(b).) Let Γ contain two such maximal subgraphs, Γ_1 and Γ_2 say. Clearly Γ_1 and Γ_2 have only the white circles in common; otherwise, by Lemma II.3, they are not maximal. Both Γ_1 and Γ_2 must also contain one or more black circles, since the white circles are not linked by a bond. Note that a given circle of Γ is not a part of any maximal 2-irreducible subgraph if, and only if, the removal of some pair of circles of that subgraph causes the circle in question to become disconnected from the subgraph.

Consider a black circle, x say, of Γ_1. Since the white circles do not form an articulation pair, x must be connected to the black circles of Γ_2 by at least one path which does not contain a white circle. Clearly x is also connected to the white circles by paths which lie entirely within Γ_1. But there is no pair of circles in Γ_2 the removal of which will disconnect x from Γ_2. Thus Γ_2 is not maximal and nor, by a similar argument, is Γ_1.

3 SYMMETRY NUMBERS, ORBITS AND STABILIZERS

Let Γ be a simple graph having m black circles and an otherwise arbitrary structure. Then the graph group of Γ partitions the graph into t *orbits* of lengths $n_1, \ldots, n_t$, with $\sum_{i=1}^{t} n_i = m$. An orbit is made up of the black circles associated with any set of labels which is mapped onto itself by every element of the graph group. In the example shown in Figure 1 there are three orbits: $\{1, 2\}$, $\{3\}$ and $\{4, 5, 6\}$. The *stabilizer* of any black circle of Γ is the subset of all elements in the graph group which leave the label attached to that circle invariant. In the same example, the stabilizer of circle 1 (or 2) is the set of all permutations of the labels 4, 5 and 6, the stabilizer of 3 is the graph group itself, and so on. The stabilizer of any circle is a subgroup of the graph group and the stabilizers of all circles within a given orbit are isomorphic. From a fundamental result in the theory of permutation groups (Hall,[26] p. 56) it follows that

$$\{\text{the order of the graph group}\} = \{\text{the order of the stabilizer of any black circle}\} \times \{\text{the length of the orbit in which that circle appears}\} \quad (3.1)$$

The number of topologically distinct graphs which can be obtained by whitening a black circle of Γ is equal to the number of orbits. This result is implicit in the definition of an orbit.

Whitening any of the black circles of the graph cannot lead to an increase in the symmetry number and will usually cause it to decrease. Let $\Gamma^{(i)}$ be a graph obtained from Γ by whitening one (any) black circle in orbit i. Then the graph group of $\Gamma^{(i)}$ is isomorphic to the stabilizer of any circle in orbit i of Γ. From (3.1) we see that the symmetry number of $\Gamma^{(i)}$ is

$$|\Gamma^{(i)}| = |\Gamma|/n_i \quad (3.2)$$

Thus the symmetry number is reduced if orbit i contains more than one circle.

The black circles of $\Gamma^{(i)}$ are similarly partitioned into orbits. If the length of orbit i' is $n_{i'}$ and there are t' orbits, then $\sum_{i'=1}^{t'} n_{i'} = (m - 1)$. Each orbit of

$\Gamma^{(i)}$ must lie within an orbit of Γ, but there may be no complete orbit which is common to both graphs. If $\Gamma^{(i,i')}$ is the graph obtained by whitening a black circle in orbit i' of $\Gamma^{(i)}$, the graph group of $\Gamma^{(i,i')}$ is the stabilizer of one circle in orbit i' of $\Gamma^{(i)}$. Thus

$$|\Gamma^{(i,i')}| = |\Gamma^{(i)}|/n_{i'} = |\Gamma|/n_i n_{i'} \tag{3.3}$$

and

$$|\Gamma^{(i,i',i'')}| = |\Gamma^{(i,i')}|/n_{i''} = |\Gamma^{(i)}|/n_{i'} n_{i''} = |\Gamma|/n_i n_{i'} n_{i''} \tag{3.4}$$

where $\Gamma^{(i,i',i'')}$ is a graph obtained by whitening a black circle in orbit i'' (of length $n_{i''}$) of $\Gamma^{(i,i')}$. This procedure can be extended until all black circles except one have been whitened.

The black circles in a given orbit of $\Gamma^{(i)}$ must all be joined to the whitened circle by a bond of the same species, except when none are so joined. The set of topologically distinct graphs which can be obtained from $\Gamma^{(i)}$ by removing a bond incident with the white circle and whitening the circle at the other end is therefore given by

$$\{\Gamma^{(i)} \text{ with a black circle in orbit } i' \text{ whitened and the bond joining this circle to the original white circle removed, where } i' \text{ ranges over all orbits in which the circles are connected to the original white circles by a bond}\} \tag{3.5}$$

It follows that the set of all topologically distinct graphs obtainable from Γ by removing a bond, whitening the circles at each end and labelling them 1 and 2 can be found by attaching the label 1 to the white circle of $\Gamma^{(i)}$, labelling the new white circle 2 and repeating the procedure for all orbits i of Γ, i.e.

$$\{\Gamma^{(i)} \text{ with its white circle labelled 1, a circle of orbit } i' \text{ whitened and labelled 2 and the bond joining 1 and 2 removed, where } i \text{ ranges over all orbits and } i' \text{ is subject to the same restriction as in (3.5)}\} \tag{3.6}$$

Use of the prescription (3.6) ensures that graphs for which the two white circles originate in the same orbit of Γ are counted once, whereas graphs where the circles originate in different orbits are counted twice. This takes proper account of the fact that in graphs of the first type the order of the labelling of the white circles is irrelevant, but in the second case the interchange of labels generates a graph which is topologically distinct from the original one.

It is instructive to look finally at the way in which the orbits of a star product are related to those of its constituent graphs. Suppose that a star product, Γ say, is formed solely from star irreducible graphs taken from a set

$\{\Gamma_i\}$. If a particular black circle in Γ_i lies in an orbit of length t_i, its orbit in Γ will be of length $n_i t_i$, where n_i is the number of times that Γ_i is taken in forming the star product. This is the origin of the factor $n_i!$ in Eq. (2.5). If, on the other hand, some of the constituent graphs are reducible, the lengths of the orbits may increase by much larger factors, as in the simple example shown in Figure 4(b). Thus Eq. (2.5) gives only a lower bound on the symmetry number of a star product formed from reducible graphs, with the result that the exponentiation theorem cannot be applied to such graphs.

4 GRAPHICAL INTERPRETATION OF FUNCTIONAL DIFFERENTIATION

Let Γ be a simple graph composed of m black γ-circles, B-bonds and ξ_s-faces. As before we shall use the symbol $\tilde{\Gamma}$ to denote a labelled version of Γ and as a specific example we shall consider the graph shown in Figure 1 with the white circle removed. The corresponding integral is a functional of γ, B and ξ_3 and we may properly speak of the functional derivatives of the integral with respect to γ, B and ξ_3. However, it is equally legitimate and more convenient to speak of the functional derivatives of $\tilde{\Gamma}$, since the labelled graph and the integral are mathematically equivalent.

4.1 Differentiation with respect to a one-point function

If $\mathscr{F}$ is a functional of a function $f(\mathbf{r})$, and if $\delta\mathscr{F}$ is the variation in $\mathscr{F}$ arising from a small variation $\delta f(\mathbf{r})$ in $f(\mathbf{r})$, then the functional derivative $\delta\mathscr{F}/\delta f(\mathbf{r})$ is defined by the relation

$$\delta\mathscr{F} = \int \delta f(\mathbf{r}) \frac{\delta\mathscr{F}}{\delta f(\mathbf{r})} d\mathbf{r} \tag{4.1}$$

The functional $\mathscr{F}$ may be represented by a labelled graph, $\tilde{\Gamma}$ say, with circles which are all black. Symbolically

$$\tilde{\Gamma} = \int \cdots \int d1 \ldots dm Q(1, \ldots, m)\gamma(1), \ldots, \gamma(m) \tag{4.2}$$

where $Q(1, \ldots, m)$ expresses the functional dependence on the functions associated with the bonds and faces of Γ. In the example quoted in the introduction to this section the function $Q(1, \ldots, m)$ is given explicitly by

$$Q(1, \ldots, 6) = B(1, 2)B(1, 3)B(2, 3)B(3, 4)B(3, 5)B(3, 6)\xi_3(1, 2, 3) \tag{4.3}$$

Now consider a small variation in the function γ. The corresponding variation in the value of $\tilde{\Gamma}$ is given by

$$\tilde{\Gamma} + \delta\tilde{\Gamma} = \int \cdots \int d1 \ldots dmQ(1, \ldots, m) \prod_{i=1}^{m} [\gamma(i) + \delta\gamma(i)] \tag{4.4}$$

Expansion of the product shows that to first order in $\delta\gamma$

$$\tilde{\Gamma} + \delta\tilde{\Gamma} = \tilde{\Gamma} + \sum_{k=1}^{m} \int \cdots \int d1 \ldots dmQ(1, \ldots, m) \frac{\delta\gamma(k)}{\gamma(k)} \prod_{i=1}^{m} \gamma(i) \tag{4.5}$$

Interchanging the labels 1 and k in the kth integral gives

$$\delta\tilde{\Gamma} = \sum_{k=1}^{m} \int \cdots \int d1 \ldots dmQ(k, 2, \ldots, 1, \ldots, m) \frac{\delta\gamma(1)}{\gamma(1)} \prod_{i=1}^{m} \gamma(i) \tag{4.6}$$

and comparison with (4.1) shows that

$$\frac{\delta\tilde{\Gamma}}{\delta\gamma(1)} = \sum_{k=1}^{m} \int \cdots \int d2 \ldots dmQ(k, 2, \ldots, 1, \ldots, m)\gamma(2) \ldots \gamma(m) \tag{4.7}$$

Each of the m integrals in (4.7) may be represented by a graph with $(m - 1)$ labelled black circles and a white 1-circle labelled 1. In other words

$$\frac{\delta\tilde{\Gamma}}{\delta\gamma(1)} = \{\text{the sum of all labelled graphs obtained by replacing one black } \gamma\text{-circle of } \Gamma \text{ by a white 1-circle labelled 1 and labelling the remaining circles in any one way}\} \tag{4.8}$$

4.2 Differentiation with respect to a two-point function

The analogue of (4.1) for the case when the variation in $\mathscr{F}$ is brought about by a variation $\delta f(\mathbf{r}, \mathbf{r}')$ in a two-point function is

$$\delta\mathscr{F} = \iint f(\mathbf{r}, \mathbf{r}') \frac{\delta\mathscr{F}}{\delta f(\mathbf{r}, \mathbf{r}')} d\mathbf{r}d\mathbf{r}' \tag{4.9}$$

Equation (4.9) serves as the definition of the functional derivative $\delta\mathscr{F}/\delta f(\mathbf{r}, \mathbf{r}')$. However, there is now an added complication. In all cases of interest the functional $\mathscr{F}$ and the function f are symmetric with respect to the interchange of the variables $\mathbf{r}$ and $\mathbf{r}'$; the functional derivative must therefore possess the same symmetry.

We first write the integral $\tilde{\Gamma}$ in the form

$$\tilde{\Gamma} = \int \cdots \int d1 \ldots dm R(1, \ldots, m) \prod_{(i,j)}' B(i, j) \tag{4.10}$$

where the restricted product is taken over all unordered pairs (i, j) drawn from the set $\{1, \ldots, m\}$ for which a $B(i, j)$-bond exists. The function $R(1, \ldots, m)$ represents the structure of the graph apart from the B-bonds. In the example given earlier

$$R(1, \ldots, 6) = \gamma(1)\gamma(2)\gamma(3)\gamma(4)\gamma(5)\gamma(6)\xi_3(1, 2, 3) \tag{4.11}$$

We now proceed as in Section 4.1. The equation corresponding to (4.5) is

$$\tilde{\Gamma} + \delta\tilde{\Gamma} = \tilde{\Gamma} + \sum_{(k,l)}' \int \cdots \int d1, \ldots, dm R(1, \ldots, m) \frac{\delta B(k, l)}{B(k, l)} \prod_{(i,j)}' B(i, j) \tag{4.12}$$

If in a particular integral we make the interchanges $1 \Leftrightarrow k$ and $2 \Leftrightarrow l$, the value of the integral is unaltered. The same is also true if we make the interchanges $1 \Leftrightarrow l$ and $2 \Leftrightarrow k$. We may therefore rewrite (4.12) as

$$\delta\tilde{\Gamma} = \frac{1}{2} \sum_{(k,l)}' \int \cdots \int d1 \ldots dm \Big\{ R(k, l, \ldots, 1, \ldots, 2, \ldots, m) \frac{\delta B(1, 2)}{B(1, 2)} + R(l, k, \ldots, 2, \ldots, 1, \ldots, m) \frac{\delta B(2, 1)}{B(2, 1)} \Big\} \prod_{(i,j)}' B(i, j) \tag{4.13}$$

Since we assume that $B(1, 2) = B(2, 1)$ and $\delta B(1, 2) = \delta B(2, 1)$, comparison with (4.9) shows that the functional derivative is given in properly symmetrized form by

$$\frac{\delta\tilde{\Gamma}}{B(1, 2)} = \frac{1}{2} \sum_{(k,l)}' \int \cdots \int d2 \ldots dm \{ R(k, l, \ldots, 1, \ldots, 2, \ldots, m) + R(l, k, \ldots, 2, \ldots, 1, \ldots, m) \} \prod_{(i,j)}' B(i, j) \tag{4.14}$$

The graphical representation of (4.14) is

$$\frac{\delta\tilde{\Gamma}}{\delta B(1, 2)} = \tfrac{1}{2}\{\text{the sum of all labelled graphs obtained in pairs by i) removing a } B\text{-bond of } \Gamma\text{, replacing the black circles at each end by white 1-circles labelled 1 and 2 and labelling the remaining circles in any one way, and ii) taking the previous graph and interchanging labels 1 and 2}\} \tag{4.15}$$

4.3 Differentiation with respect to an s-point function

The general method of proceeding should now be clear. We therefore quote the result for ξ_s without proof:

$$\frac{\delta\tilde{\Gamma}}{\delta\xi_s(1,\ldots,s)} = (1/s!)\{\text{the sum of all labelled graphs obtained in groups of } s! \text{ by i) removing an } \xi_s\text{-face of } \Gamma\text{, replacing the black circles at each vertex by white 1-circles labelled } 1,\ldots,s \text{ in a specific order and labelling the remaining circles in any one way, and ii) taking the previous graph and making all non-trivial permutations of the labels } 1,\ldots,s\} \tag{4.16}$$

As before, the factor $1/s!$ arises from the need to maintain the symmetry of the functional derivative.

5 THREE LEMMAS ON FUNCTIONAL DIFFERENTIATION

The results expressed by Eqs. (4.8), (4.15) and (4.16) are of interest insofar as they provide a straightforward interpretation of the process of functional differentiation with respect to a function of one or more variables. However, as we have already remarked, the power of the graphical method is largely related to the ease with which relations involving free graphs can be manipulated. The extension of (4.8), (4.15) and (4.16) to the case of free graphs requires the proper weighting of the topologically distinct graphs which arise when the labels of the black circles are removed. This creates certain combinatorial problems which can be overcome with the help of the ideas introduced in Section 3.

5.1 Differentiation with respect to a one-point function

Lemma III Let Γ be a simple graph composed of black γ-circles, bonds and faces. Then

$$\frac{\delta\Gamma}{\delta\gamma(1)} = \{\text{the sum of all topologically distinct graphs obtained by replacing one black } \gamma\text{-circle of } \Gamma \text{ by a white 1-circle labelled } 1\} \tag{5.1}$$

Proof By combining the definition (2.3) with the rule (4.8) and multiplying (4.8) through by $\gamma(1)$ we find that

$$\gamma(1)\frac{\delta\Gamma}{\delta\gamma(1)} = \frac{1}{|\Gamma|}(\tilde{\Gamma}_{\gamma_1} + \cdots + \tilde{\Gamma}_{\gamma_m}) \tag{5.2}$$

where m is the number of black circles of Γ and the graphs $\tilde{\Gamma}_{\gamma_1}, \ldots, \tilde{\Gamma}_{\gamma_m}$ are obtained from Γ by choosing each black circle in turn, whitening it, labelling it 1 and labelling the remaining circles in any way. Consider a particular labelled graph occurring in (5.2). If the whitened circle of this graph lies in orbit i of Γ, we know from (2.3) and (3.3) that the value of the graph is

$$|\Gamma^{(i)}|\Gamma^{(i)} = |\Gamma|\Gamma^{(i)}/n_i \tag{5.3}$$

where $\Gamma^{(i)}$ has the same meaning as in Section 3 and n_i is the length of the orbit. Orbit i contributes n_i terms to the sum in brackets on the right-hand side of (5.2), each term having the same value. Thus, multiplying (5.3) by n_i, summing over the t orbits of Γ and introducing the result into Eq. (5.2) we find that

$$\begin{aligned}\gamma(1)\frac{\delta\Gamma}{\delta\gamma(1)} &= \frac{1}{|\Gamma|}\sum_{i=1}^{t} n_i(|\Gamma|\Gamma^{(i)}/n_i) \\ &= \sum_{i=1}^{t}\Gamma^{(i)}\end{aligned} \tag{5.4}$$

The lemma is now proved by dividing through by $\gamma(1)$, which is equivalent to replacing the white γ-circle of each $\Gamma^{(i)}$ by a white 1-circle.

Corollary If Γ is a graph composed of m black γ-circles, bonds and faces then

$$\int d1\gamma(1)\frac{\delta\Gamma}{\delta\gamma(1)} = m\Gamma \tag{5.5}$$

Proof Equation (5.4) can be rewritten as

$$\gamma(1)\frac{\delta\Gamma}{\delta\gamma(1)} = \sum_{i=1}^{t}\frac{1}{|\Gamma^{(i)}|}\tilde{\Gamma}^{(i)} = \sum_{i=1}^{t}\frac{n_i}{|\Gamma|}\tilde{\Gamma}^{(i)} \tag{5.6}$$

where $\tilde{\Gamma}^{(i)}$ is a labelled version of $\Gamma^{(i)}$ and we have substituted for $|\Gamma^{(i)}|$ from (3.2). Integrating with respect to the coordinate 1 is equivalent to blackening the white circle labelled 1. But blackening the white circle of any $\Gamma^{(i)}$ yields a labelled version of Γ, $\tilde{\Gamma}$ say, the value of which is simply $|\Gamma|\Gamma$. Thus

$$\sum_{i=1}^{t}\int d1\,\frac{n_i}{|\Gamma|}\tilde{\Gamma}^{(i)} = \sum_{i=1}^{t} n_i\Gamma = m\Gamma \tag{5.7}$$

5.2 Differentiation with respect to a two-point function

Lemma IV Let Γ be a simple graph composed of black circles, p B-bonds and faces. Then

$$\frac{\delta\Gamma}{\partial B(1,2)} = \tfrac{1}{2}\{\text{the sum of all topologically distinct graphs obtained by removing a } B\text{-bond of } \Gamma\text{, whitening the black circles at each end and labelling the whitened circles 1 and 2}\} \tag{5.8}$$

Proof From (2.3) and (4.15) we see, after multiplication by $B(1,2)$, that

$$B(1,2)\frac{\delta\Gamma}{\delta B(1,2)} = \frac{1}{2|\Gamma|}(\tilde{\Gamma}_{B_1} + \cdots + \tilde{\Gamma}_{B_p}) \tag{5.9}$$

where the graphs $\tilde{\Gamma}_{B_1}, \ldots, \tilde{\Gamma}_{B_p}$ are obtained from Γ by choosing each bond in turn, whitening the black circles at each end, labelling the whitened circles 1 and 2 and labelling the remaining circles in any one way. Consider a particular graph occurring in (5.9). If the circle labelled 1 in this graph is in orbit i of Γ and if the circle labelled 2 is in orbit i' of $\Gamma^{(i)}$, then in the notation already used the value of this graph, from (2.3) and (3.3), is

$$|\Gamma^{(i,i')}|\Gamma^{(i,i')} = |\Gamma|\Gamma^{(i,i')}/n_i n_{i'} \tag{5.10}$$

where n_i and $n_{i'}$ are the lengths of the orbits in question. There are a total of $n_i n_{i'}$ such graphs in (5.9), so their total contribution is $|\Gamma|\Gamma^{(i,i')}$. Summing over orbits we find that

$$\begin{aligned} B(1,2)\frac{\delta\Gamma}{\delta B(1,2)} &= \frac{1}{2|\Gamma|}\sum_{i=1}^{t}\sum_{i'}{}' |\Gamma|\Gamma^{(i,i')} \\ &= \frac{1}{2}\sum_{i=1}^{t}\sum_{i'}{}' \Gamma^{(i,i')} \end{aligned} \tag{5.11}$$

where t is again the number of orbits in Γ and the sum on i' is restricted to orbits of $\Gamma^{(i)}$ in which the circles are connected to the white circle in orbit i by a B-bond. Division through by $B(1,2)$, which is equivalent to deleting the $B(1,2)$ bond in each $\Gamma^{(i,i')}$, leads immediately to the result (5.8).

Corollary If Γ is a simple graph composed of black circles, p B-bonds and faces then

$$\iint d1d2B(1,2)\frac{\delta\Gamma}{\delta B(1,2)} = p\Gamma \tag{5.12}$$

Proof This proceeds as in the corollary to Lemma III. By making use of (2.3) we see that eqn. (5.11) can be rewritten in the form

$$B(1,2)\frac{\delta\Gamma}{\delta B(1,2)} = \frac{1}{2}\sum_{i=1}^{t}\sum_{i'}{}' \frac{1}{|\Gamma^{(i,i')}|}\tilde{\Gamma}^{(i,i')} = \frac{1}{2}\sum_{i=1}^{t}\sum_{i'}{}' \frac{n_i n_{i'}}{|\Gamma|}\tilde{\Gamma}^{(i,i')} \quad (5.13)$$

where $\tilde{\Gamma}^{(i,i')}$ is a labelled version of $\Gamma^{(i,i')}$. Double integration of (5.13) with respect to 1 and 2 is equivalent to blackening the two white circles of $\tilde{\Gamma}^{(i,i')}$, giving rise to a graph of value $|\Gamma|\Gamma$. Integration therefore yields the result

$$\frac{1}{2}\sum_{i=1}^{t}\sum_{i'}{}' \iint d1d2\,\frac{n_i n_{i'}}{|\Gamma|}\tilde{\Gamma}^{(i,i')} = \frac{1}{2}\sum_{i=1}^{t}\sum_{i'}{}' n_i n_{i'}\Gamma \quad (5.14)$$

But $n_i n_{i'}$ is simply the number of bonds linking circles in orbit i of Γ to those in orbit i' of $\Gamma^{(i)}$ and in forming the double sum in (5.13) each bond is counted twice. Thus

$$\sum_{i=1}^{t}\sum_{i'}{}' n_i n_{i'} = 2p \quad (5.15)$$

and the proof is complete.

5.3 Differentiation with respect to an s-point function

Lemma V Let Γ be a simple graph composed of black circles, bonds and ξ_s-faces. Then for any given s

$$\frac{\delta\Gamma}{\delta\xi_s(1,\ldots,s)} = (1/s!)\{\text{the sum of all topologically distinct graphs obtained by removing an } \xi_s\text{-face of } \Gamma\text{, whitening the circles at the vertices of the face and labelling the whitened circles } 1,\ldots,s\} \quad (5.16)$$

As the proof proceeds on almost identical lines to that of Lemma IV, we shall omit the details; we also omit the statement of the corollary analogous to (5.5) and (5.12), since this has not yet found any practical application.

5.4 Some applications

There exist many important examples of functional derivatives, including in particular those which yield the probability distribution functions of the system. For example, the n-particle densities $\rho^{(n)}(1,\ldots,n)$ can be written as functional derivatives of the grand partition function in the form

$$\rho^{(n)}(1,\ldots,n) = \frac{1}{\Xi} z^*(1)\ldots z^*(n)\frac{\delta^n\Xi}{\delta z^*(1)\ldots\delta z^*(n)} \quad (5.17)$$

which for $n = 1$ simplifies to

$$\rho^{(1)}(1) = z^*(1)\frac{\delta \log \Xi}{\delta z^*(1)} \tag{5.18}$$

The relation (5.17) can be deduced directly from the basic definition of $\rho^{(n)}(1, \ldots, n)$ in the grand canonical ensemble.[27] The grand partition function is said to be a *generating functional* for the densities, by analogy with the generating functions of combinatorial analysis.[29] In almost the same fashion, $\log \Xi$ is the generating functional[5,16] for the Ursell cluster functions $U^{(n)}(1, \ldots, n)$:

$$U^{(n)}(1, \ldots, n) = z^*(1) \ldots z^*(n)\frac{\delta^n \log \Xi}{\delta z^*(1) \ldots \delta z^*(n)} \tag{5.19}$$

The Ursell functions are related to the densities by the expression

$$\rho^{(n)}(1, \ldots, n) = \Sigma[\Pi U^{(s)}(1, \ldots, s)] \tag{5.20}$$

where the sum is taken over all products of the $U^{(s)}$ corresponding to distinct partitions of the set $\{1, \ldots, n\}$, and to the n-particle correlation functions $h^{(n)}(1, \ldots, n)$ by

$$U^{(n)}(1, \ldots, n) = h^{(n)}(1, \ldots, n)\rho^{(1)}(1) \ldots \rho^{(1)}(n), \quad n \geq 2 \tag{5.21}$$

Thus

$$U^{(1)}(1) = \rho^{(1)}(1) \tag{5.22}$$

$$U^{(2)}(1, 2) = \rho^{(2)}(1, 2) - \rho^{(1)}(1)\rho^{(1)}(2) \tag{5.23}$$

$$\begin{aligned} h^{(2)}(1, 2) &= \rho^{(2)}(1, 2)/\rho^{(1)}(1)\rho^{(1)}(2) - 1 \\ &= g^{(2)}(1, 2) - 1 \end{aligned} \tag{5.24}$$

where $g^{(2)}(1, 2)$ is the pair distribution function.

Applying Lemma III to the expansion (2.7) we find from Eq. (5.18) that

$$\begin{aligned} \rho^{(1)}(1) = \{&\text{the sum of all topologically distinct, simple,} \\ &\text{connected graphs consisting of one white} \\ &z^*\text{-circle labelled 1, black } z^*\text{-circles and} \\ &f\text{-bonds}\} \end{aligned} \tag{5.25}$$

an expansion which begins as shown in Figure 9(a), and from (5.19) that

$$\begin{aligned} U^{(2)}(1, 2) = \{&\text{the sum of all topologically distinct, simple,} \\ &\text{connected graphs consisting of two white} \\ &z^*\text{-circles labelled 1 and 2, black } z^*\text{-circles} \\ &\text{and } f\text{-bonds}\} \end{aligned} \tag{5.26}$$

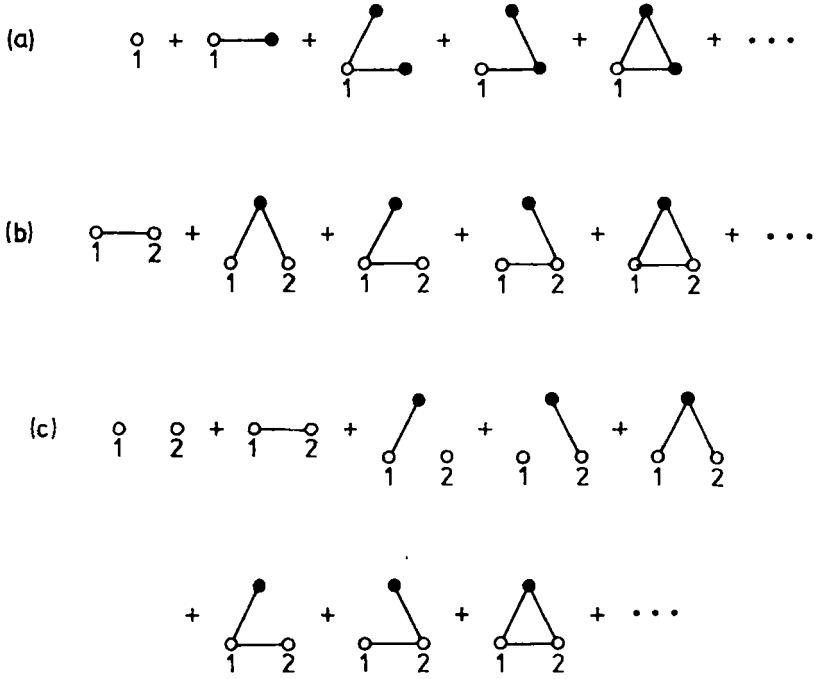

FIGURE 9 The first few graphs in the z^*-circle, f-bond expansion of (a) $\rho^{(1)}(1)$, (b) $U^{(2)}(1, 2)$ and (c) $\rho^{(2)}(1, 2)$.

which begins as shown in Figure 9(b). We can now derive the z^*-circle, f-bond expansion of $\rho^{(2)}(1, 2)$ by substituting the expansions (5.25) and (5.26) into Eq. (5.23). As an intermediate step we obtain the expansion of $\rho^{(1)}(1)\rho^{(1)}(2)$ as the sum of star products of graphs contributing separately to $\rho^{(1)}(1)$ and $\rho^{(1)}(2)$. This is a legitimate operation, since two such graphs have no factor in common. The final result can be expressed in the form

$$\rho^{(2)}(1, 2) = \{\text{the sum of all topologically distinct, simple graphs consisting of two white } z^*\text{-circles labelled 1 and 2, black } z^*\text{-circles and } f\text{-bonds, such that there is a path from each black circle to a white circle}\} \tag{5.27}$$

The graphs in (5.27) (the first few are shown in Figure 9(c)) occur in pairs, differing only in the presence or absence of an f-bond between the white circles. Two such graphs can be combined to form a single graph in which two white circles are linked by an e-bond, where $e(1, 2) = 1 + f(1, 2)$.

Now consider the effect of taking the functional derivative of $\log \Xi$ with respect to $f(1, 2)$. Applying Lemma IV to the expansion (2.7) we find that

$$2\frac{\delta \log \Xi}{\delta f(1,2)} = \{\text{the sum of all topologically distinct, simple graphs consisting of two white } z^*\text{-circles labelled 1 and 2, black } z^*\text{-circles and } f\text{-bonds, such that there is a path from each black circle to a white circle but the white circles are not adjacent}\} \tag{5.28}$$

But the graphs appearing in (5.28) are just the subset of graphs in (5.27) for which there is no f-bond between the white circles. Thus by multiplying through Eq. (5.28) by $e(1, 2)$ we generate all the graphs appearing in (5.27), showing that

$$\begin{aligned}\rho^{(2)}(1,2) &= 2[1 + f(1,2)]\frac{\delta \log \Xi}{\delta f(1,2)} \\ &= 2\frac{\delta \log \Xi}{\delta \log[1 + f(1,2)]} \\ &= -2k_B T\frac{\delta \log \Xi}{\delta v(1,2)}\end{aligned} \tag{5.29}$$

We have therefore succeeded in expressing the pair density as a functional derivative of $\log \Xi$ with respect to the pair potential.

The graphs in the expansion (5.25) are of two types: those which are star irreducible and those in which the white circle is an articulation circle. The latter can all be written as star products of star irreducible graphs which appear at a lower order in the expansion and can therefore be eliminated by use of the exponentiation theorem. The expansion of the function $h^{(1)}(1)$ defined by

$$h^{(1)}(1) = \log \rho^{(1)}(1) - \log z^*(1) \tag{5.30}$$

is therefore obtained by discarding the reducible graphs in (5.25) and replacing the white z^*-circle by a white 1-circle. Use of the symbol $h^{(1)}(1)$ for the function defined in Eq. (5.30) is justified by the fact that for *any* n we find that

$$h^{(n)}(1, \ldots, n) = \{\text{the sum of all topologically distinct, simple graphs consisting of } n \text{ white 1-circles labelled } 1, \ldots, n, \text{ black } z^*\text{-circles and } f\text{-bonds, such that there are no white articulation circles}\} \tag{5.31}$$

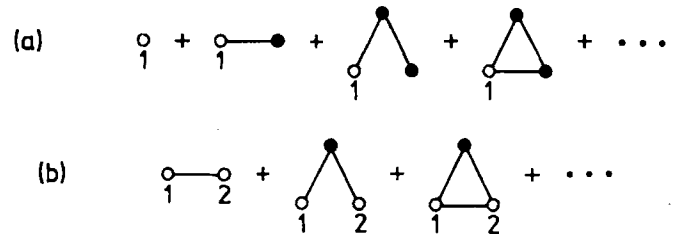

FIGURE 10 The first few graphs in the z^*-circle, f-bond expansion of (a) $h^{(1)}(1)$ and (b) $h^{(2)}(1, 2)$. The white circles are all 1-circles.

For $n = 1$ the absence of white articulation circles is equivalent to the statement, already proved, that the graphs are star irreducible. For $n \geq 2$ the result is proved by substituting the expansions (5.25) and (5.31) into the right-hand side of Eq. (5.21); this yields the generalization of (5.26) to all n. The first few graphs in (5.31) for $n = 1$ and $n = 2$ are shown in Figure 10. Note in particular the simplicity of the expansion of $h^{(2)}(1, 2)$ relative to that of $\rho^{(2)}(1, 2)$, Figure 9(c); it is for this reason that the theory is developed in terms of correlation functions rather than densities.

The significance of the corollaries to Lemmas III and IV is that they allow the functional to be expressed as a linear combination of the graphs used to characterize another. For example, taking account of Eq. (2.7), the corollary to Lemma III applied to (5.18) shows that

$$\int \rho^{(1)}(1)d1 = \{\text{the sum of all topologically distinct, simple, connected graphs consisting of black } z^*\text{-circles and } f\text{-bonds, each weighted by the number of circles it contains}\} \tag{5.32}$$

The corollary to Lemma IV can be exploited in a similar fashion.

6 TOPOLOGICAL REDUCTION

We turn now to a different type of graph theoretic operation, that of topological reduction.[5] To gain some understanding of what is involved, consider the following problem. Suppose that $\mathscr{F}$ is a known functional of $\gamma(\mathbf{r})$ and $B(\mathbf{r}, \mathbf{r}')$, so that it can be written as a (possibly infinite) sum of graphs with γ-circles and B-bonds. If $\gamma'(\mathbf{r})$ is a second known functional of $\gamma(\mathbf{r})$ and $B(\mathbf{r}, \mathbf{r}')$, it is possible, at least in principle, to transform the graphical prescription for $\mathscr{F}$ in terms of γ-circles to a different expression in terms of γ'-circles by eliminating $\gamma(\mathbf{r})$ between the two functional relations. There

are two obvious reasons why such a transformation could be useful. First, the function $\gamma'(\mathbf{r})$ may be physically more meaningful or mathematically simpler to handle than $\gamma(\mathbf{r})$. Second, the transformation may lead to a reduction (hence the name) in either the total number of graphs which must be considered, or the number of graphs which appear at a given order in, say, an expansion parameter. In the same way one might wish to convert from a relation in terms of $B(\mathbf{r}, \mathbf{r}')$ to a new expression involving a different two-point function. The process of topological reduction is in this case sometimes referred to as *bond renormalization*. The origin of the term is not difficult to find. The two-point functions in question invariably represent, in some sense, interactions between particles, so that bond renormalization can be regarded as a procedure for rewriting the quantities of interest in terms of a new, "renormalized" interaction. Bond renormalization plays a particularly important part in the graph theoretic formulation of many perturbation theories of fluids. We shall give examples of the use of topological reduction in Section 6.4, but we must first derive the basic lemmas[3] which are needed in solving the formal elimination problem.

6.1 Coloured and decorated graphs

Let Γ be a simple connected graph consisting of n white γ-circles, m black 1-circles and p B-bonds, and let $g \equiv \{g_i(\mathbf{r})\}$ be a (possibly infinite) set of distinct functions of one variable. Consider the colouring of Γ which results from associating a function drawn from g with each black circle of Γ; the functions chosen need not all be different. If the black circles are labelled $1, \ldots, m$ in some arbitrary way, the colouring of Γ is fully characterized by its connections and the ordered set $\sigma \equiv \{i_1, \ldots, i_m\}$, where g_{i_k} is the function associated with the circle labelled k; we shall call this set the *colouring set*. Thus the coloured free graph may conveniently be denoted by the symbol $\Gamma(g; \sigma)$ and a labelled version by $\tilde{\Gamma}(g; \sigma)$.

Any permutation of the labels $1, \ldots, m$ of $\tilde{\Gamma}(g; \sigma)$ will induce a permutation on the ordered set σ. If this permutation is made on circles of the same colour, i.e. on circles associated with the same function, the resulting graph is characterized by the same colouring set and to that extent the permutation is a trivial one. However, the same permutation does not necessarily leave the connections of the graph unaltered. The graph group of a coloured graph is defined as the group of permutations which not only leave the connections unaltered but also induce only trivial permutations on the colouring set. With this modified definition of what constitutes the graph group, the previous definitions of topological equivalence, symmetry number and the value of a free graph can be taken over unaltered to the case of coloured graphs.

It is easy to see that the graph group of $\Gamma(g;\sigma)$ is always a subgroup of the graph group of Γ, and that the two groups will be the same only when the colouring set is such that each circle in any orbit of Γ is given the same colour. Lagrange's theorem tells us now (cf. Eq. (2.2)) that

$$\begin{aligned}|\Gamma| &= |\Gamma(g;\sigma)| \times \{\text{the number of elements in the graph group of } \Gamma \text{ which when applied to } \Gamma(g;\sigma) \text{ yield topologically inequivalent graphs}\} \\ &= |\Gamma(g;\sigma)| \times \{\text{the number of distinct, non-trivial permutations induced on } \sigma \text{ by elements of the graph group of } \Gamma\} \\ &= |\Gamma(g;\sigma)| n(\sigma), \text{ say} \qquad (6.1)\end{aligned}$$

Thus the effect of colouring Γ is to reduce its symmetry number by a factor $n(\sigma)$.

Let g' be the set of all possible labelled colourings of Γ which are obtained by associating distinct ordered subsets of m functions drawn from g with the black circles of a particular labelled version of Γ. No two graphs in g' are topologically equivalent, since the colouring sets are distinct. Furthermore, given a graph characterized by the particular colouring set σ, the $n(\sigma) - 1$ topologically (but not completely) inequivalent graphs which are also topologically (but not completely) inequivalent to the given one appear in g' exactly once. All other graphs in g' are completely inequivalent to the given one. Thus g' can be partitioned into subsets containing $n(\sigma)$ topologically inequivalent graphs, graphs in different subsets being completely inequivalent. By choosing one element from each subset of g' and removing the labels from the black circles we obtain a further set, G say, made up of topologically distinct graphs.

Now consider the set $h \equiv \{h_i\}$ composed of topologically distinct, simple, connected graphs with one white γ-circle labelled $\mathbf{r}$, black γ-circles and B-bonds, the integral associated with h_i being the function $g_i(\mathbf{r})$ in g, i.e. $h_i = g_i(\mathbf{r})/|h_i|$. Let each black circle of Γ have one of the elements in h attached to it in such a way that the white circle of the graph in h is superimposed on the black circle of Γ and then blackened. We speak of the graphs in h being *hung on* at the black circles of Γ, or that Γ is *decorated* with graphs drawn from h. It is also possible to visualize a reverse process whereby *articulation pieces* are detached from a graph containing one or more white circles, an articulation piece being a subset of the black circles and bonds which connects with the remainder of the graph at an articulation circle. The effect of detaching all articulation pieces is to reduce the graph to a 1-irreducible subgraph which contains all the white circles.

The graph obtained by decorating Γ can be characterized in the same manner as a colouring of Γ, that is to say by the distinct ordered set $\sigma \equiv \{i_1, \ldots, i_m\}$, where h_{i_k} is the graph hung on at the circle labelled k in Γ. We shall denote this graph by the symbol $\Gamma(h; \sigma)$ and the set of all such graphs which are topologically distinct by H. Since the elements of h are in one-to-one correspondence with the elements of g, there is also a one-to-one correspondence between the decorated graphs in H and the coloured graphs in G, but the symmetry number of a graph $\Gamma(h; \sigma)$ will always be greater than or equal to that of the corresponding graph $\Gamma(g; \sigma)$.

These ideas can be more readily grasped by looking at a simple example. Let Γ be the graph (having a symmetry number of two) shown in Figure 11(a), and let the set h be composed of the three graphs pictured in Figure 11(b). Then the set g consists of three functions and the set g' contains nine elements, since there are nine distinct choices of the colouring set. There are three cases for which $n(\sigma) = 1$ (when both circles in are coloured in the same way) and six for which $n(\sigma) = 2$. Thus the set G contains only six graphs, three with a symmetry number of two and three with a symmetry number of one; the corresponding graphs in H, shown in Figure 11(c), have much higher symmetry numbers: 2, 2, 8, 2, 4 and 8. All graphs in H have two black articulation circles and by detaching the articulation pieces connected to these circles we recover, in every case, the graph Γ.

Graphs can also be hung on at bonds. Let $t \equiv \{t_i\}$ be a set of topologically distinct, simple, connected graphs with two white γ-circles labelled $\mathbf{r}$ and $\mathbf{r}'$, black γ-circles and B-bonds. A decorated graph can now be built up from Γ by hanging on a graph drawn from t at each bond of Γ, that is to say by superimposing the two white circles of the graph in t on the circles with which the bond is incident, blackening any circle which is black in Γ and erasing the bond. The procedure we describe is sometimes referred to as the *replacement* of bonds in Γ by graphs in t. Once again we can visualize the reverse process of detaching articulation pieces from rooted graphs if we broaden the concept of an articulation piece to include any subset of the black circles and bonds which connects with the rest of the graph at any set of circles forming an articulation subset in the complete graph. When the articulation pieces are detached from all articulation pairs, the subgraph which remains contains all the white circles but is not necessarily connected.

Let T be the set of all topologically distinct graphs which can be obtained by replacing bonds in Γ by graphs in t. If $s \equiv \{s_i(\mathbf{r}, \mathbf{r}')\}$ is a set of distinct functions of two variables such that $s_i(\mathbf{r}, \mathbf{r}')$ is the integral associated with the ith element in t, i.e. $t_i = s_i(\mathbf{r}, \mathbf{r}')/|t_i|$, and if s' is the set of all topologically inequivalent labelled graphs which can be built up by associating a function $s_i(\mathbf{r}, \mathbf{r}')$ with each bond of a labelled version of Γ, it is clear that the graphs in s' can be partitioned into subsets in the same manner as those in g'. Then,

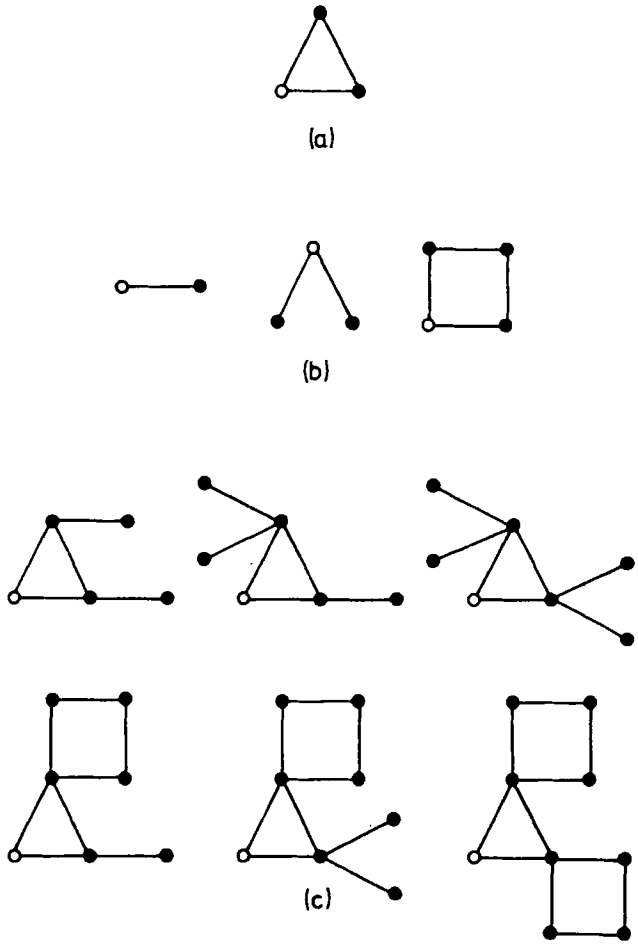

FIGURE 11 Decorating the black circles of the graphs shown in (a) with graphs in the set (b) yields the set (c).

by choosing one representative from each subset and removing the labels from the black circles, we obtain a set S of topologically distinct graphs which are in one-to-one correspondence with those in T. It should be easy for the reader to construct an example similar to that used to illustrate the process of decorating the black circles of a given graph. Note, however, that in general the graph Γ cannot be recovered simply by detaching articulation pieces at the articulation pairs of graphs in S, since this necessarily causes the disappearance of any bond linking the two circles.

The further generalization to the case of faces is straightforward.

6.2 Hanging on of graphs at circles

Lemma VI Let Γ be the graph and let g, h and H be the sets introduced in Section 6.1. Then if $\mathscr{H}(\mathbf{r})$ is the sum of all graphs in h and if each graph in H is uniquely decomposable into its constituent parts, then

$$\{\text{the sum of all graphs in } H\} = \{\text{the graph obtained by associating the function } \mathscr{H}(\mathbf{r}) \text{ with each black circle of } \Gamma\} \tag{6.2}$$

Proof The function $\mathscr{H}(\mathbf{r})$ is given by

$$\mathscr{H}(\mathbf{r}) = \sum_i h_i = \sum_i g_i(\mathbf{r})/|h_i| \tag{6.3}$$

and the value of the graph Γ is

$$\Gamma = \frac{\gamma(1)\dots\gamma(n)}{|\Gamma|}\int\cdots\int d(n+1)\dots d(n+m)\prod_{(k,l)}{}' B(k,l) \tag{6.4}$$

where m is the number of black circles in Γ and $\prod'$ ranges over all pairs (k, l) which are linked by a bond. Then we can rewrite the right-hand side of (6.2) either in the form

$$\begin{aligned}
&\frac{\gamma(1)\dots\gamma(n)}{|\Gamma|}\int\cdots\int d(n+1)\dots d(n+m)\prod_{(k,l)}{}' B(k,l)\prod_{j=1}^{m}\sum_{g} g_i(j)/|h_i| \\
&\quad = \gamma(1)\dots\gamma(n)\int\cdots\int d(n+1)\dots d(n+m)\sum_{\sigma}{}'\prod_{(k,l)}{}' B(k,l) \\
&\qquad \times g_{i_1}(1)\dots g_{i_m}(m)/|\Gamma||h_{i_1}|\cdots|h_{i_m}| \\
&\quad = \sum_{\sigma}{}'\frac{1}{|\Gamma||h_{i_1}|\cdots|h_{i_m}|}\tilde{\Gamma}(g;\sigma)
\end{aligned} \tag{6.5}$$

where $\sum'$ ranges over all distinct choices of the colouring set σ, or as

$$\sum_{\sigma}{}''\frac{n(\sigma)}{|\Gamma||h_{i_1}|\cdots|h_{i_m}|}\tilde{\Gamma}(g;\sigma) \tag{6.6}$$

where $\sum''$ is restricted to the sets σ which generate completely inequivalent graphs.

Since the graphs in H (the left-hand side of (6.2)) are all distinct and those in (6.6) are all completely inequivalent, they must be in one-to-one correspondence. As the integrals associated with corresponding graphs are clearly the same, it remains only to show that the corresponding coefficients are equal. This is a straightforward task. By construction, the graphs in H are

uniquely decomposable. Thus the graph group of a graph $\Gamma(h;\sigma)$ in H is the direct product of the graph group of the corresponding coloured graph $\Gamma(g;\sigma)$ in G with the graph groups of $h_{i_1},\ldots,h_{i_m}$. The symmetry number of $\Gamma(h;\sigma)$ is therefore given by

$$\begin{aligned}|\Gamma(h;\sigma)| &= |\Gamma(g;\sigma)||h_{i_1}|\cdots|h_{i_m}| \\ &= |\Gamma||h_{i_1}|\cdots|h_{i_m}|/n(\sigma)\end{aligned} \tag{6.7}$$

Thus the factor multiplying the associated integral on the left-hand side of (6.2) is $n(\sigma)||\Gamma||h_{i_1}|\cdots|h_{i_m}|$, which is the same as that appearing in the corresponding term in (6.6). The lemma is therefore proved.

The limitation that the graphs in H must be uniquely decomposable is an important one, since the product property of the graph groups is essential to the proof of the lemma. In simpler language the restriction means that knowing the structure of Γ and of the graphs in h it must be possible by inspection of any graph in H to recognize which graph in h has been hung on at each black circle of Γ. For the lemma to be applicable this clearly restricts the class of graphs which can be used to decorate a particular graph Γ, but there is never any difficulty when Γ is free of black articulation circles. The lemma can be cast in more general form, for example by including the case when Γ itself is a coloured graph, but the simpler version given here is sufficient for most purposes.

6.3 Replacement of bonds by graphs

Lemma VII Let Γ be the graph and let s, t and T be the sets introduced in Section 6.1. Then if $\mathscr{T}(\mathbf{r},\mathbf{r}')$ is the sum of all graphs in t, with $\mathscr{T}(\mathbf{r},\mathbf{r}')=\mathscr{T}\mathbf{r}(\mathbf{r}',\mathbf{r})$, and if each graph in T is uniquely decomposable into its constituent parts, then

$$\begin{aligned}\{\text{the sum of all graphs in } T\} = \{&\text{the graph obtained by} \\ &\text{associating the function} \\ &\mathscr{T}(\mathbf{r},\mathbf{r}') \text{ with each bond of } \Gamma\}\end{aligned} \tag{6.8}$$

Proof This is almost identical to the proof of Lemma VI. Given any labelled version of Γ, the bonds can be labelled in some way (it does not matter how) and also given a particular direction (again it does not matter how). Since there are p bonds, the result of this ordering is a list $\vec{b}_1,\ldots,\vec{b}_p$. A graph built up by replacing each bond of Γ by a graph drawn from t can now be completely characterized by the ordered set $\sigma\equiv\{i_1,\ldots,i_p\}$, where the i_jth element in t is hung on at the jth bond in Γ, the circle labelled $\mathbf{r}$ being superimposed at the beginning of the bond and the circle labelled $\mathbf{r}'$ superimposed at the end. We now proceed as in Lemma VI, the analogue of the

quantity $n(\sigma)$ being the factor by which the symmetry number of Γ is reduced when the B-bonds are replaced by two-point functions drawn from the set s.

Note that a given graph has two forms, depending on the order in which the labels are attached to the white circles. If the value of the graph changes when the labels $\mathbf{r}$ and $\mathbf{r}'$ are interchanged, both graphs must appear in the set T. This ensures the symmetry of the function $\mathscr{T}(\mathbf{r}, \mathbf{r}')$ with respect to interchange of the variables.

6.4 Some applications

Lemmas VI and VII provide the tools we need in solving problems of the type discussed in the introduction to this section. For example, by Lemma VI, the sum of all graphs in Figure 11(c) can be represented by the single graph Γ of 11(a) with its black γ-circles replaced by black $\mathscr{H}(\mathbf{r})$-circles. Thus the transformation of variables ($\gamma(\mathbf{r}) \to \mathscr{H}(\mathbf{r})$) is accompanied by a reduction in the total number of graphs.

We must look now at some examples of more practical importance. Consider first the z^*-circle, f-bond expansion of $h^{(1)}(1)$ given by Eq. (5.31), taken for $n = 1$. Each graph contains a 1-irreducible rooted subgraph, obtained by locating each black articulation circle and detaching the corresponding articulation pieces. From Lemmas II.1 and II.2 it follows that each graph has a unique maximal such subgraph, Γ_m say, consisting wholly or in part of the one white circle, the black circles adjacent to it, and the bonds linking these circles. It is then easy to see that the effect of decorating Γ_m with graphs drawn from the expansion (5.25) of $\rho^{(1)}(1)$ in terms of z^*-circles is to build up graphs in the expansion of $h^{(1)}(1)$. For example, in Figure 12, we show (a) a particular choice of Γ_m and (b) the way this can be decorated with graphs drawn from (5.25) to yield, in (c), a subset of the graphs in (5.31). Since the graphs in $h^{(1)}(1)$ can be uniquely decomposed to leave a maximal 1-irreducible subgraph, it follows from Lemma VI that for any particular choice of Γ_m

$$\{\text{the sum of all graphs in } h^{(1)}(1) \text{ with the same } \Gamma_m\} = \{\Gamma_m \text{ with its black } z^*\text{-circles replaced by black } \rho^{(1)}\text{-circles}\} \quad (6.9)$$

But the fact that the maximal subgraphs are unique also means that every graph in $h^{(1)}(1)$ can be built up only from a specific Γ_m. Thus by summing the left-hand side of (6.9) over all topologically distinct Γ_m we generate each graph in $h^{(1)}(1)$ exactly once. It follows that the expansion of $h^{(1)}(1)$ in terms of $\rho^{(1)}$-circles is given solely by graphs which are free of black articulation circles. Essentially the same argument can be pursued for arbitrary n, the relevant maximal subgraphs being those which contain all the white circles but no black articulation circles; these are unique by virtue of Lemma II.1.

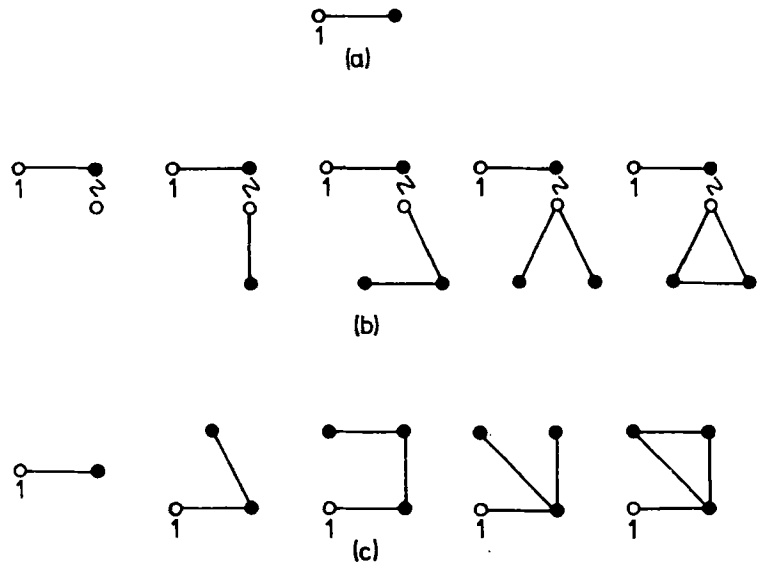

FIGURE 12 Decorating the black circles of the graph Γ_m shown in (a) with graphs (b) in the z^*-circle, f-bond expansion of $\rho^{(1)}(1)$ yields in (c) a subset of graphs in the $\rho^{(1)}$-circle, f-bond expansion of $h^{(1)}(1)$.

The expansion (5.31) can therefore be recast in the form

$$h^{(n)}(1,\ldots,n) = \{\text{the sum of all topologically distinct, simple, 1-irreducible graphs consisting of } n \text{ white 1-circles labelled } 1,\ldots,n, \text{ black } \rho^{(1)}\text{-circles and at least one } f\text{-bond}\} \tag{6.10}$$

We have therefore passed from an expansion in terms of z^*-circles to another in terms of $\rho^{(1)}$-circles, discarding in the process all graphs with black articulation circles. The uniqueness of the maximal subgraph is clearly crucial to the argument, underlining the importance of results such as those contained in Lemma II.

The corresponding reduction of the z^*-circle expansion of $\log \Xi$ given by Eq. (2.7) is a little more complicated. We shall follow the method of de Dominicis,[4] since this provides further examples of the application of the lemmas both of this section and of Section 5.

We first define a functional of $\rho^{(1)}$ and f by the expression

$$\mathscr{E} = \{\text{the sum of all topologically distinct, simple, 1-irreducible graphs consisting of black } \rho^{(1)}\text{-circles and } f\text{-bonds}\} \tag{6.11}$$

Let Γ be a graph appearing in (6.11). Now consider the effect of decorating Γ in all possible ways with graphs drawn from the expansion of $\rho^{(1)}(1)$ in terms of z^*-circles. From Lemma VI, applied in reverse, it follows that

$$\Gamma = \{\text{the sum of all topologically distinct, simple, connected graphs consisting of black } z^*\text{-circles and } f\text{-bonds, and which contain a maximal 1-irreducible subgraph identical to } \Gamma \text{ except that the } \rho^{(1)}\text{-circles are replaced by } z^*\text{-circles}\} \tag{6.12}$$

Each graph appearing in (6.12) is a graph in the expansion (2.7). Furthermore, by summing (6.12) over all possible choices of Γ, thereby obtaining the functional $\mathscr{E}$, we generate every graph appearing in (2.7), but each such graph may appear more than once. In fact

$$\mathscr{E} = \{\text{the sum of all graphs in (2.7), each weighted by the number of 1-irreducible subgraphs it contains}\} \tag{6.13}$$

We now take the functional derivative of (6.11) with respect to $\rho^{(1)}(1)$. From Lemma III it follows that the result is a sum of graphs with one white circle labelled 1, which by comparison with Eq. (6.10) is found to be identical to the $\rho^{(1)}$-circle, f-bond expansion of $h^{(1)}(1)$. Thus

$$h^{(1)}(1) = \frac{\delta \mathscr{E}}{\delta \rho^{(1)}(1)} \tag{6.14}$$

and, consequently, from the corollary to Lemma III

$$\int h^{(1)}(1)\rho^{(1)}(1)d1 = \{\text{the sum of all graphs in (6.11), each weighted by the number of circles it contains}\} \tag{6.15}$$

But we already know that each graph in (6.11) is itself a sum of graphs in the expansion of $\log \Xi$. Thus the functional defined by (6.15) can be written as a linear combination of the graphs in (2.7), each graph being weighted by a coefficient obtained by summing over all maximal 1-irreducible subgraphs in the graph, the contribution from each subgraph being the number of circles which it contains. This is equivalent to summing over all circles in the graph, counting one for each maximal 1-irreducible subgraph in which it appears. In other words

$$\int h^{(1)}(1)\rho^{(1)}(1)d1 = \{\text{the sum of all graphs in (2.7), each weighted by its total multiplicity}\} \tag{6.16}$$

the "total multiplicity" being the quantity μ appearing in Eq. (2.8). From Eqs. (5.32), (6.13) and (6.16) we see finally that $\log \Xi$ is given as a functional of $\rho^{(1)}$ and f by the expression

$$\log \Xi = \int \rho^{(1)}(1)d1 - \int h^{(1)}(1)\rho^{(1)}(1)d1 + \mathscr{E} \tag{6.17}$$

since by the rule (2.8) each graph in the expansion (2.7) appears exactly once in the combination on the right-hand side of (6.17) when the three quantities appearing there are treated as functionals of z^* and f. In the homogeneous case Eq. (6.17) becomes the usual virial expansion of the equation of state in powers of the density.

We want finally to show how Lemma VII can be used in the process of bond renormalization. Consider the class of graphs defined by the prescription

$$\begin{aligned} x_n(1, \ldots, n) = \{&\text{the sum of all topologically distinct,} \\ &\text{1-irreducible, simple graphs consisting of} \\ &n \text{ white 1-circles labelled } 1, \ldots, n, \text{ black} \\ &\rho^{(1)}\text{-circles and } f\text{-bonds, such that there} \\ &\text{are no white articulation pairs and no two} \\ &\text{white circles are adjacent}\} \end{aligned} \tag{6.18}$$

The case $n = 2$ is particularly important, since it yields[5,27] the graphical expansion of the function $\log y(1, 2)$, where

$$y(1, 2) = g^{(2)}(1, 2)/e(1, 2) \tag{6.19}$$

and the case $n = 3$ becomes of interest when, for example, we seek a graphical interpretation of the Kirkwood superposition approximation for the three-body distribution function.[16] The expansions for $n = 2$ and $n = 3$ begin as shown in Figure 13.

Consider first the case when $n \geq 3$. The graphs contributing to $x_n(1, \ldots, n)$ are free of white articulation pairs, but may contain articulation pairs made up of one white and one black circle or of two black circles. However, for any graph Γ in (6.18) (for $n \geq 3$), a 2-irreducible graph can be constructed by proceeding as follows. First locate an articulation pair and detach the articulation piece connecting with the rest of the graph at these two circles; next insert a bond between the two circles in question, irrespective of whether such a bond is present in Γ itself; then repeat the operation until no articulation pairs remain. The result is a graph, Γ'_m say, which is 2-irreducible and contains all the white circles. The fact that the construction of Γ'_m may involve the creation of bonds not present in Γ means that Γ'_m is not, in general, a subgraph of Γ. On the other hand, it is clear that Γ'_m is a maximal 2-irreducible subgraph of a graph Γ' which differs from Γ only by the insertion of a bond between

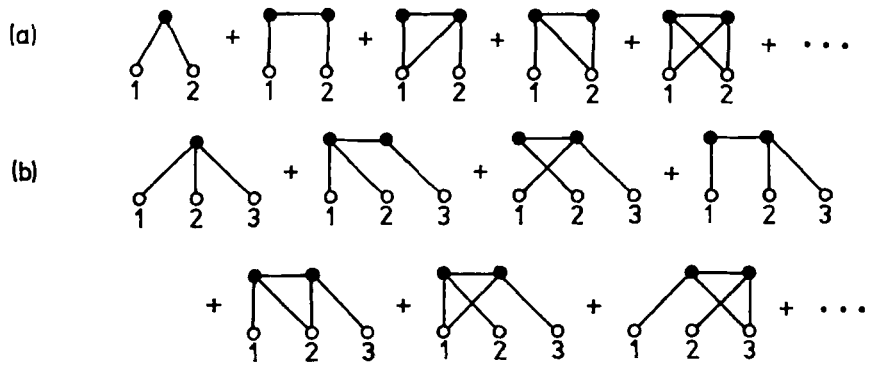

FIGURE 13 The first few graphs in the $\rho^{(1)}$-circle, f-bond expansion of (a) $x_2(1, 2)$ and (b) $x_3(1, 2, 3)$. The white circles are all 1-circles.

pairs of nonadjacent circles which form an articulation pair in Γ. (This means that the white circles remain non-adjacent.) Since Γ'_m contains at least three circles, it follows from Lemma II.3 that it is a unique maximal such subgraph. In other words, the order in which articulation pieces are detached in constructing Γ'_m is irrelevant. Any graph in (6.18) for $n \geq 3$ can now be built up from a specific Γ'_m by the process of replacing its f-bonds by graphs drawn from the $\rho^{(1)}$-circle, f-bond expansion of $h^{(2)}(1, 2)$ (Eq. (6.10), taken for $n = 2$); remember that such graphs are free of articulation circles. The way in which this can be done in a simple case is illustrated in Figure 14. Lemma VII can be applied to each Γ'_m, and summing over all topologically distinct choices of Γ'_m gives the $\rho^{(1)}$-circle, $h^{(2)}$-bond expansion of $x_n(1, \ldots, n)$ for $n \geq 3$ in the form

$$x_n(1, \ldots, n) = \{\text{the sum of all topologically distinct, 2-irreducible, simple graphs consisting of } n \text{ white circles labelled } 1, \ldots, n, \text{ black } \rho^{(1)}\text{-circles and } h^{(2)}\text{-bonds, such that no two white circles are adjacent}\} \tag{6.20}$$

We see that the elimination of f-bonds in favour of $h^{(2)}$-bonds leads to the disappearance of articulation pairs of any colour.

For $n = 2$ the situation is more complicated because in that case the procedure we have described for constructing Γ'_m does not yield a unique result for graphs containing nodal circles. One solution is to write $x_2(1, 2)$ as the sum

$$x_2(1, 2) = b(1, 2) + d(1, 2) \tag{6.21}$$

where $d(1, 2)$ (the "bridge" graphs) is the subset consisting of graphs which are free of nodal circles. Lemma II.4 is now applicable and Lemma VII

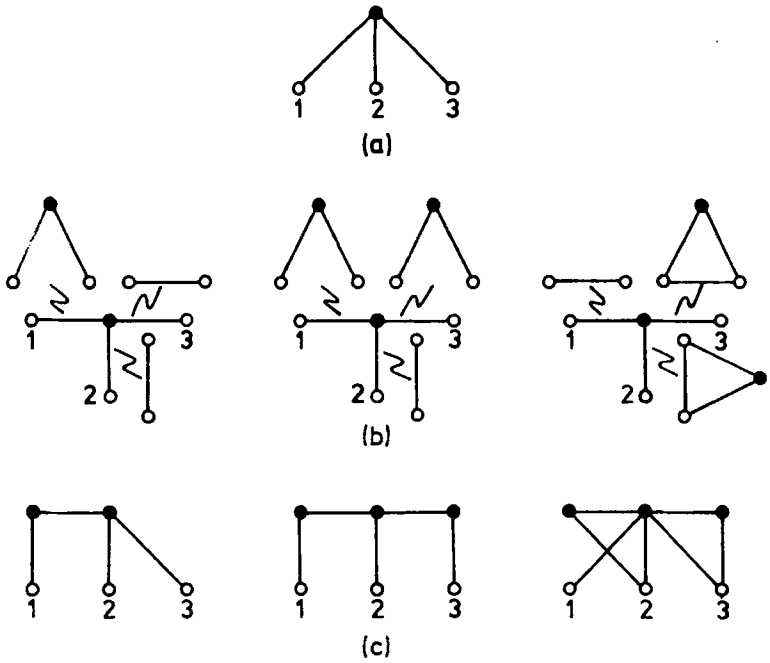

FIGURE 14 Replacing the bonds of the graph Γ'_m shown in (a) with graphs (b) in the $\rho^{(1)}$-circle, f-bond expansion of $h^{(2)}(1, 2)$ yields in (c) a subset of graphs in the $\rho^{(1)}$-circle, $h^{(2)}$-bond expansion of $x_3(1, 2, 3)$.

can therefore be used in the topological reduction of all graphs in $d(1, 2)$, but different methods[5,27] must be used for $b(1, 2)$ (the "series" graphs).

More detailed discussion of the topological reduction of the f-bond expansion of $x_2(1, 2)$ would lead us too far afield, and in any event the subject is treated thoroughly elsewhere. We therefore take our last examples of bond renormalization from the more recently developed field of perturbation theory. Let us suppose that the pair potential can be separated into two parts in the form

$$v(1, 2) = v_0(1, 2) + v_1(1, 2) \tag{6.22}$$

where v_0 defines a reference system and v_1 represents a perturbation which may, in some sense, be regarded as "weak." Then the Mayer f-function can be written as

$$f(1, 2) = f_0(1, 2) + [1 + f_0(1, 2)] \sum_{n=1}^{\infty} [\Phi(1, 2)]^n/n! \tag{6.23}$$

where $\Phi(1, 2) = -\beta v_1(1, 2)$ and

$$f_0(1, 2) = \exp[-\beta v_0(1, 2)] - 1 \tag{6.24}$$

is the f-function for the reference system. Then the pair correlation function of the reference system, $h_0^{(2)}(1, 2)$ say, is given as a functional of $\rho^{(1)}$ and f_0 by Eq. (6.10) (taken for $n = 2$), with f-bonds replaced by f_0-bonds.

We now substitute the expansion (6.23) into Eq. (6.10) (again taken for $n = 2$) and obtain, for each graph in (6.10), an infinite set of graphs consisting of black $\rho^{(1)}$-circles, f_0-bonds and Φ-bonds. (This amounts to applying Lemma VII in reverse.) The subset of graphs which contain only f_0-bonds is equal to $h_2^{(0)}(1, 2)$, so the pair correlation of the full system can be written as

$$h^{(2)}(1, 2) = h_0^{(2)}(1, 2) + h_1^{(2)}(1, 2) \tag{6.25}$$

with

$$h_1^{(2)}(1, 2) = \{\text{the sum of all topologically distinct, 1-irreducible, } \Phi\text{-bond composite graphs consisting of two white 1-circles labelled 1 and 2, black } \rho^{(1)}\text{-circles, } f_0\text{-bonds and at least one } \Phi\text{-bond}\} \tag{6.26}$$

where a Φ-bond composite graph is one in which each pair of circles is linked by an arbitrary number of Φ-bonds but at most one f_0-bond. From the rule given in Section 2.3 we know that the symmetry number of the graphs in (6.26) must be increased by a factor $n!$ for each pair of circles joined by n Φ-bonds; this takes account of the factors $1/n!$ appearing in (6.23).

An articulation pair in a graph containing reference system bonds is said to form a *reference articulation pair* if there is an articulation piece connected to the pair which consists solely of black circles and reference bonds. The graphs in (6.26) can be partitioned into subsets, each consisting of a) a graph Γ in which the white circles are not a reference articulation pair and b) all possible star products of Γ with one of the graphs in the expansion of $h_0^{(2)}(1, 2)$. The sum of all graphs in a given subset can therefore be represented by Γ with a $[1 + h_0^{(2)}(1, 2)]$-bond between its white circles. Thus we can eliminate graphs in (6.26) which contain white articulation pairs by writing

$$h_1^{(2)}(1, 2) = [1 + h_0^{(2)}(1, 2)]\ \{\text{the sum of all topologically distinct, 1-irreducible, } \Phi\text{-bond composite graphs consisting of two white 1-circles labelled 1 and 2, } f_0\text{-bonds and at least one } \Phi\text{-bond, such that the white circles are not linked by an } f_0\text{-bond and do not form an articulation pair, and graphs containing one or more black circles have at least one } \Phi\text{-bond incident with a black circle}\} \tag{6.27}$$

Graphs defined by the expression in curly brackets in Eq. (6.27) are of two types: those consisting solely of two white circles linked by Φ-bonds, and those containing at least three circles. In every case, therefore, it is possible to construct a graph which is free of all reference articulation pairs but contains both white circles by proceeding in a manner analogous to the construction of Γ'_m in the topological reduction of graphs contributing to $x_n(1, \ldots, n)$, that is to say by locating in turn all reference articulation pairs, detaching the appropriate articulation piece and inserting a reference bond between the two circles. Uniqueness of the resulting graph is guaranteed by a trivial generalization of Lemma II.3, graphs with nodal circles posing no special problem. Lemma VII can therefore be applied in much the same way as before, with the result that the expression for the pair distribution function of the system of interest can be written in the form

$$g^{(2)}(1, 2) = 1 + h^{(2)}(1, 2)$$
$$= g_0^{(2)}(1, 2)\,\{1 + \text{the sum of all topologically distinct, 1-irreducible, Φ-bond composite graphs consisting of two white 1-circles labelled 1 and 2, } h_0\text{-bonds and at least one Φ-bond, such that the white circles are not linked by an } h_0\text{-bond, there are no reference articulation pairs, and graphs consisting of three or more circles have at least one Φ-bond incident with a black circle}\} \tag{6.28}$$

where we have exploited the relation between $g^{(2)}$ and $h^{(2)}$ given by Eq. (5.24).

Equation (6.28) is exact and forms the basis of a variety of approximation schemes. To zeroth order in Φ we find that $g^{(2)}(1, 2) = g_0^{(2)}(1, 2)$, as is to be expected, and corrections to this result could be obtained by summing graphs containing increasingly large numbers of Φ-bonds. In practice, however, this is rarely the best way to proceed, and the graphs in (6.28) are generally ordered (and summed) according to schemes based on more detailed consideration of their topological structure. A particularly important role is played by the so-called chain graphs, i.e. the graphs in (6.28) which consist of two white circles linked by a single path of black circles, Φ-bonds and h_0-bonds. In a homogeneous system, provided the perturbation is sufficiently weak, the sum of all such graphs, $\mathscr{C}(\mathbf{r})$ say, can be evaluated by Fourier transform techniques. The function $-k_B T\mathscr{C}(\mathbf{r})$ can be regarded as a renormalized potential in the sense already discussed; in the limit $h_0(\mathbf{r}) \to 0$ it reduces to the bare potential $v_1(\mathbf{r})$. By a further topological reduction the Φ-bonds in the graphs in (6.28) can be replaced by $\mathscr{C}$-bonds, with the disappearance of all graphs containing articulation pairs which have articula-

tion pieces consisting of a chain of bonds and black circles. Once again the result is exact and can be used as a basis for approximations. It should now be clear that any bond renormalization is invariably accompanied by the disappearance of a certain class of articulation pairs, the classification being made on the basis of the topological character of the associated articulation pieces.

As an alternative to the Φ-bond expansion, the graphs in $h^{(2)}(1, 2)$ can be expressed in terms of f-bonds and δf-bonds, where $\delta f(1, 2) = f(1, 2) - f_0(1, 2)$. Elimination (by topological reduction) of δf-bonds in favour of $y_0 \delta f$-bonds then yields a result from which the "blip-function" theory of Andersen *et al.*[30] is easily derived. This is the standard method of treating the perturbation involved in "softening" a hard-core potential.

CONCLUDING REMARKS

For the reasons indicated in the introduction, our discussion of applications has been kept deliberately brief. Thus we have said nothing at all about the very successful "optimized cluster theory" of Andersen and Chandler,[9] we have made only brief reference to the blip-function theory, and we have mentioned only in passing a topic of considerable practical importance, namely the way[16,17] in which graphs can be ordered (and hence, with luck, summed) according to different topological criteria. Nor have we said anything on the subject of many-body forces, but the manner in which these can be incorporated should be fairly clear, requiring for the most part a straightforward generalization of earlier arguments to the case of non-linear graphs; functional derivatives, for example, can be handled with the help of results such as that of Lemma V. All these questions are very well treated in one or other of the review articles already cited.

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