

Transformation and Topological Reduction of Cluster Expansions Using m -Bonds

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We introduce the notion of an " m -bond" and show how it may be used to manipulate the cluster expansions that describe the equilibrium properties of classical fluids. An m -bond has a constant value of -1 , and its presence affects the sign and symmetry number of a graph. We further define an " m -product," which is formed by summing all graphs obtained by adding m -bonds to join field points in the (usual) product graph. It is shown that the logarithm of a sum of graphs can be written in terms of their m -products. The formalism is used to demonstrate a few well-known results concerning cluster expansions. Also, a generalization of the m -product is introduced, and with it a theorem is presented that relates graphs composed of f -bonds to those that contain both f - and $(f + 1)$ -bonds. Such "frustrated" graphs are useful in understanding approximations such as the Percus-Yevick formula, and also in performing numerical calculations.

KEY WORDS: Cluster series; diagrammatic methods; topological reduction; graph theory.

1. INTRODUCTION

The statistical treatment of fluids has advanced greatly over recent decades, and much of this progress has been facilitated by the development of diagrammatic methods.⁽¹⁻⁴⁾ These methods provide an intuitive, visual means to categorize and manipulate the many (in fact, infinite) integrals that arise when equilibrium thermodynamic and structural properties are expressed in terms of the intermolecular potential. Present applications have come a long way from the early successful treatments of hard spheres and models for argon. Molecular fluids, polymers, inhomogeneous fluids, electrolytes, gels, and random media are but some examples of the systems we have come to understand better by applying diagrammatic techniques.

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Equilibrium properties are given in terms of the intermolecular potential by multibody integrals, termed cluster integrals. A cluster integral may be represented diagrammatically by a graph, which is a collection of points connected by bonds. The relation between the cluster integral and its graph is straightforward, but it is not briefly stated. Moreover, there exists a wide array of techniques for categorizing graphs by their topology, and for reducing their sums to a simpler form. We refer the reader to standard references⁽²⁻⁴⁾ for this background information, which is essential to understanding what follows.

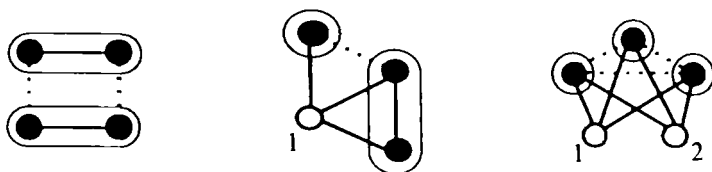
This report presents a new tool for transforming and reducing cluster sums or series. A key element of the treatment is the "*m*-bond," and with it a new multiplication operator, the "*m*-product." These devices permit us to derive a new topological reduction that expresses the sum of many graphs in terms of the logarithm of the sum of fewer graphs. This development is presented in the following section, while in Sections 3 and 4 we provide a few simple applications.

2. FORMALISM

2.1. Definitions

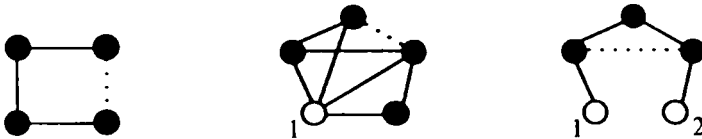
The following definitions apply to connected, simple graphs composed of black γ_k -points, some or no labeled white root points, and *B*-bonds and *m*-bonds.

An *m*-bond connecting two points has a constant value of -1 , regardless of the value of the coordinates represented by the points. The effect of an *m*-bond on the value of a graph is twofold: it affects the sign of the graph (i.e., whether it has a positive or negative value), and it affects the symmetry number of the graph. Two field points are *m*-adjacent if they are joined directly by an *m*-bond. An *m*-bond is not usually joined to a root point. Two field points are said to be in the same *region* if they can be joined by a path that does not pass through any white points or traverse any *m*-bonds; i.e., points in the same region remain connected upon removal of all white points and *m*-bonds. The following graphs give examples of regions, each of which is enclosed in a curve (throughout this paper we designate an *m*-bond by a dotted line):



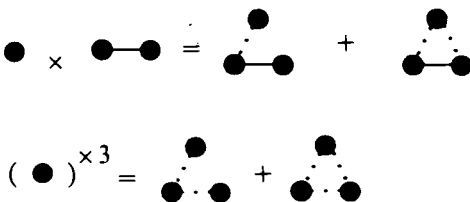
Two distinct regions of a graph are *m-connected* if there is a path connecting them (i.e., connecting any point in one to any point in the other) that does not go through any white points. A graph in which all regions are *m-connected* remains a connected graph upon removal of all white points. Two regions are *m-adjacent* if any two points from each region are *m-adjacent*. Regions that are *m-connected* need not be *m-adjacent*.

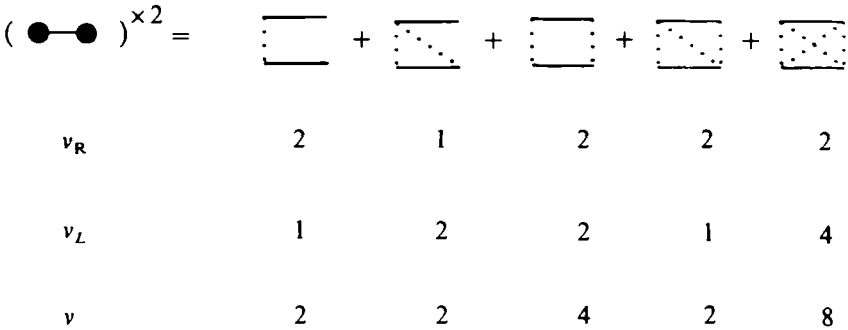
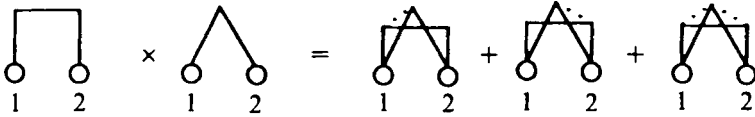
A graph is *properly m-connected* if no two field points in the same region can be connected by a path that traverses an *m-bond*, without going through another region of the graph. Furthermore, all pairs of regions of a properly *m-connected* graph are *m-connected*. The graphs in the examples above are properly *m-connected*; the following graphs are not:



The *product* of two graphs Γ_1 and Γ_2 (denoted $\Gamma_1 * \Gamma_2$) is formed by overlaying any common white circles. If the two graphs have no common white circles (or have no white circles at all), the product is a disconnected graph (this is the standard definition of the product).

The *m-product* of two graphs Γ_1 and Γ_2 (denoted $\Gamma_1 \times \Gamma_2$) is the sum of all topologically distinct, properly *m-connected* graphs that can be formed by adding one or more *m-bonds* to the product $\Gamma_1 * \Gamma_2$ (“adding” an *m-bond* means to join any pair of field points by an *m-bond*). Note that if Γ_1 and Γ_2 are star-irreducible, each such graph will have exactly two regions—composed of the fields points from Γ_1 and Γ_2 respectively—and that *m-bonds* will be added connecting field points from (what was) Γ_1 to field points from Γ_2 . The *m-product* of several graphs is defined similarly: the sum of all properly *m-connected* graphs formed by adding one or more *m-bonds* to the product graph. We write $\Gamma^{\times p}$ to represent the *p-fold m-product* $\Gamma \times \Gamma \times \dots \times \Gamma$ (*p* terms). Further, we write $\prod_{i=1}^p \Gamma_i$ to represent the *m-product* $\Gamma_1 \times \Gamma_2 \times \dots \times \Gamma_p$. Examples follow:





The numbers following the last example will be explained shortly.

2.2. Labeled and Unlabeled Regions and Field Points

The value of a graph Γ equals the integral it represents (I) divided by its symmetry number (v): $\Gamma = I/v$. If the graph is said to have labeled field points, then its field points are distinguishable (but still integrated upon); the symmetry number of a graph with labeled field points is unity, and its value is just I .

The only effect of labeling the field points is to eliminate the symmetry number, and to render distinct what would otherwise be topologically equivalent graphs. In particular, the product of graphs with labeled field points is formed in the usual manner, by overlapping only the labeled white points. Any conflict in the labeling is resolved by relabeling the field points of the product graph. The m -product of graphs with labeled field points will in general include more terms in the sum used to form the m -product. It should be clear that in taking the product of graphs that each consist of a single field point,

$$\begin{aligned}
 & (m\text{-product with unlabeled field points}) \\
 &= \frac{1}{p} (m\text{-product with labeled field points})
 \end{aligned}$$

where p is the number of field points in the product graphs. The reasoning is as follows: Each graph Γ of the sum has the value I/ν , and upon labeling its points it may potentially give rise to $p!$ distinct graphs, each of value I . However, ν of these labeled graphs will not be distinct, so instead of giving rise to $p!$ graphs, it will give rise to only $p!/\nu$. The sum of these graphs will then be $p! I/\nu$, which is of course $p!$ times the original graph.

We will sometimes find it convenient to consider graphs with labeled regions, but with field points that are not necessarily labeled. Labeling the regions has an effect similar to that of labeling the field points: graphs that were previously equivalent become distinct. We define for an unlabeled graph a *region-symmetry number* ν_R as the number of ways that the region labels may be permuted while leaving the graph topologically unchanged. Moreover, we define the symmetry number ν_L of a region-labeled graph as the number of ways that the field points may be labeled and permuted while remaining in their respective regions, and while leaving the graph topologically unchanged. For a properly m -connected graph, $\nu = \nu_R \nu_L$. The various symmetry numbers are demonstrated in the last example above.

2.3. Lemmas

We derive three lemmas that will assist in the proof of the logarithmic reduction to be presented shortly.

Lemma A. Let Γ be the graph comprising a single unlabeled field point. Then the multiple m -product $\Gamma^{\times p}$ has the value

$$\Gamma_{\text{unlabeled}}^{\times p} = \frac{(-)^{p-1}}{p} I^p$$

Equivalently, if Γ comprises a single *labeled* field point, then

$$\Gamma_{\text{labeled}}^{\times p} = (-)^{p-1} (p-1)! I^p$$

Before proving the lemma, we will demonstrate with very simple examples. All bonds in the graphs below are m -bonds; the number above each graph represents its contribution to the m -product (upon division by I^p):

$$\begin{array}{ll}
 p=2 & \text{unlabeled:} \\
 & \begin{array}{c} -1/2 \\ \bullet \cdots \bullet \end{array} = -\frac{1}{2} I^2 \\
 \\
 & \text{labeled:} \\
 & \begin{array}{c} -1 \\ \bullet \cdots \bullet \\ 1 \quad 2 \end{array} = -I^2
 \end{array}$$

$$p=3 \quad \text{unlabeled:} \quad \begin{array}{c} +1/2 \\ \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \end{array} + \begin{array}{c} -1/6 \\ \bullet \quad \bullet \\ \diagup \quad \diagdown \\ \bullet \end{array} = +\frac{1}{3} I^3$$

$$\text{labeled:} \quad \begin{array}{c} +1 \\ \bullet \quad 3 \\ \diagup \quad \diagdown \\ \bullet \end{array} + \begin{array}{c} +1 \\ \bullet \quad 2 \\ \diagup \quad \diagdown \\ \bullet \end{array} + \begin{array}{c} +1 \\ \bullet \quad 1 \\ \diagup \quad \diagdown \\ \bullet \end{array} + \begin{array}{c} -1 \\ \bullet \quad 1 \\ \diagup \quad \diagdown \\ \bullet \end{array} = +2I^3$$

Proof. The proof is most easily performed for the lemma stated in terms of labeled graphs. In this case, all graphs formed in the m -product have the same absolute value, namely I^p . What remains is to determine the number of connected graphs with a given number of bonds, and to sum these with their appropriate signs. Letting $C_{p,b}$ represent the number of connected diagrams having p points and b bonds, we introduce the generating function $C_p(y)$

$$C_p(y) = \sum_b C_{p,b} y^b$$

Gilbert⁽⁵⁾ has presented a general solution for $C_p(y)$, but we need only $C_p(-1)$, which gives us precisely the sum we seek. According to his solution, $C_p(-1) = (-)^{p-1} (p-1)!$, and the proof follows directly.

Lemma A can be stated more generally.

Lemma A (General form). Let $\Gamma_1, \Gamma_2, \dots, \Gamma_i, \dots$ each be a graph that comprises a single unlabeled black γ_i -point. Then the multiple m -product $\mathbf{M}_{i=1}^p \Gamma_i$ has the value

$$\mathbf{M}_{i=1}^p \Gamma_i = \frac{(-)^{p-1}}{p} \prod_{i=1}^p I_i$$

The proof proceeds as before, with trivial modification.

Lemma B. Let R_1 and R_2 be two regions of a graph Γ that has labeled regions, unlabeled field points, some or no labeled white points, B -bonds, and some or no m -bonds; R_1 and R_2 should not be m -adjacent, although Γ may have m -bonds connecting regions elsewhere, or connecting R_1 and/or R_2 to other regions. Let r_1 and r_2 be subsets (possibly the entire

set) of the field points in R_1 and R_2 , respectively. Let G be the sum of all distinct simple graphs obtained from Γ by joining field points in r_1 to field points in r_2 using one or more m -bonds. Then

$$G = -\Gamma$$

Proof. Label all of the n_1, n_2 resp. field points of r_1, r_2 and consider the sum over all distinct graphs obtained from this labeled graph by permuting the new labels within each region and/or adding *some or no* m -bonds joining points in r_1 to those in r_2 . This sum is equal to $n_1! n_2!$ times the same sum of (point-)unlabeled graphs (using reasoning similar to that presented above). This sum is also equal to zero (reasoning: single out any pair of points, one each from r_1 and r_2 ; for every graph in the sum that has an m -bond joining these two points, there will be an otherwise identical graph that does not, and which exactly cancels the former's contribution to the sum). Consequently, the sum of all unlabeled graphs obtained by adding some or no m -bonds joining r_1 and r_2 is zero, and thus G —the same sum but without the graph that has *no* added m -bonds (i.e., Γ itself)—equals $-\Gamma$.

Loosely speaking, we may replace the sum of all diagrams having m -bonds joining field points in r_1 and r_2 by a single diagram having one m -bond “joining” the (sub)regions r_1 and r_2 .

Lemma C. Let G be a set of distinct, star-irreducible graphs, $\Gamma_1, \Gamma_2, \dots, \Gamma_n$, each consisting of one or more (unlabeled) field circles, some or no white 1-circles, and some or no B -bonds. The multiple m -product

$$\phi = \Gamma_1^{\times p_1} \times \Gamma_2^{\times p_2} \times \dots \times \Gamma_n^{\times p_n}$$

has the value

$$(-)^{p-1} (p-1)! \prod_{i=1}^n \frac{I_i^{p_i}}{v_i^{p_i} p_i!}$$

where $p = \sum p_i$, and all other symbols are defined as above.

Proof. We begin by labeling the *regions* of the product diagram

$$\phi = \Gamma_1^{*p_1} * \Gamma_2^{*p_2} * \dots * \Gamma_n^{*p_n}$$

and summing all distinct, properly m -connected diagrams that can be obtained from it by adding one or more m -bonds. It should be clear that this sum equals ϕ times $\prod_{i=1}^n p_i!$. We now group all terms in the sum according to their m -adjacency, i.e., if two regions are m -adjacent in one diagram of the group, they are m -adjacent in every diagram of the group.

Lemma B then implies that the sum of all diagrams in a group may be replaced a single diagram: each region R_i from the sum becomes a labeled, black γ_i -point, where $\gamma_i = I_i/\nu_i$, and with an m -bond joining points that represent m -adjacent regions (the value of γ_i may depend on the coordinates of any root points in ϕ , but this does not invalidate the proof). Thus the sum of all diagrams in the m -product maps exactly onto the sum obtained in taking the m -product of labeled field points. Lemma A then shows that this sum gives rise to a factor of $(-)^{p-1} (p-1)!$, and subsequent division by $\prod_{i=1}^n p_i!$ to recover ϕ yields the stated result.

2.4. The Logarithm Theorem

Let G be a set of distinct, star-irreducible, connected graphs $\Gamma_1, \Gamma_2, \dots, \Gamma_n$ each consisting of black circles, some or no white 1-circles, and some or no B -bonds. Then

$$\ln[1 + (\text{sum of all graphs in } G)] = (\text{sum of all } m\text{-products of graphs in } G)$$

Proof. A typical term in the expansion of the logarithm is

$$\frac{(-)^{p-1}}{p} \left[\sum_{i=1}^n \frac{I_i}{\nu_i} \right]^p$$

where I_i is the value of the integral represented by Γ_i and ν_i is its symmetry number. Upon expansion of the p products, terms arise of the form

$$(-)^{p-1} (p-1)! \prod_{i=1}^n \frac{I_i^{p_i}}{\nu_i^{p_i} p_i!}$$

where $\sum p_i = p$. Lemma C has demonstrated that this is precisely the m -product of the corresponding graphs; thus the sum of all such m -products is equivalent to the expansion of the logarithm, and the theorem is proved.

3. INVERSION OF THE URSELL FUNCTIONS

The Ursell functions are a sequence of symmetric functions $U_1(1), U_2(1, 2), \dots$ that can be defined implicitly in terms of another of functions $W_1(1), W_2(1, 2), \dots$ through the relation⁽⁶⁾

$$W_s(1, 2, \dots, s) = \sum \prod U_a(i_1, \dots, i_{n_a})$$

where the sum over products is carried out over all partitions of the set $\{1, \dots, s\}$. Uhlenbeck and Ford⁽⁷⁾ note that this relation may be inverted to

give the U_s explicitly in terms of the W_α ; the result has exactly the same form as the original equation, except that a coefficient $(-)^{p-1} (p-1)!$ is associated with each term of the sum, where p is the number of terms of the corresponding product. This result with Lemma C allows us to write immediately

$$U_s(1, 2, \dots, s) = \sum \mathbf{M} W_\alpha(i_1, \dots, i_{m\alpha})$$

where \mathbf{M} represents an m -product, and the sum is taken over all partitions as in the original formula. The m -product here is taken as if the points of the graphs represented by the W_α functions were labeled field points, i.e., although the graph representing W_α has a *white* points which should not be joined to anything new upon taking the m -product, they are regardless joined to the white points of other W -graphs as if they were all labeled field points (in fact, the graph representing W_α is just a W_α -face joining α root points, and it has no field points at all).

The grand canonical partition can be expressed in terms of the graphs for W ,⁽⁶⁾

$$\mathcal{E} = 1 + \text{sum of all diagrams containing } n \geq 1 \text{ black } z\text{-points} \\ \text{joined by a } W_n\text{-face}$$

where z is the activity. Thus, according to the logarithm theorem presented above, $\ln \mathcal{E}$ is the sum of all m -products of the W -diagrams in \mathcal{E} . Application of the inversion formula for the Ursell functions then leads to the well-known result⁽⁶⁾

$$\ln \mathcal{E} = \text{sum of all diagrams containing } n \geq 1 \text{ black } z\text{-points} \\ \text{joined by a } U_n\text{-face}$$

4. FRUSTRATED GRAPHS

Perhaps the most fruitful application of the m -bond formalism will be to aid the reintroduction of e -bonds into cluster expansions that are written in terms of f -bonds, where $f = e - 1$ is the Mayer function, and $e = \exp(-u/kT)$ with u the pair potential, k Boltzmann's constant, and T the temperature. Of course, f -bonds normally are preferred because they have a finite range, so integrals given in terms of them are also finite. Thus the key to this manipulation is the selective replacement of f -bonds. An example of the type of diagram we seek to generate is



where a solid line represents an f -bond and the dashed line is an e -bond. The e -bond requires that the field points not overlap (considering, for example, the hard-sphere potential), while the f -bonds require that each field point overlap both of the rooted points. Compared to diagrams that contain f -bonds exclusively, relatively few configurations of the field points therefore contribute to the integral that the graph represents. We shall use the designation "frustrated graphs" to describe such graphs which contain "conflicting" f - and e -bonds; diagrams comprising h - and g -bonds will be considered similarly (where h is the pair correlation function and $g = h + 1$ is the radial distribution function); in many cases we will use capitals to denote generic bonds F and $E = F + 1$.

The notion of diagrams composed of both F - and E -bonds was present in the early development of cluster-diagram methods,⁽⁸⁻¹⁰⁾ most notably in the work of Ree and Hoover,⁽¹¹⁾ who evaluated virial coefficients of hard spheres and hard disks by summing these frustrated graphs or, in their nomenclature, modified stars. Attard and Patey⁽¹²⁾ recently revived the idea to help in the computation of some sums of graphs, but otherwise the approach has received little attention. In this section we describe how some of the results presented above can help in the generation and manipulation of frustrated graphs. Our goal is more to motivate those results rather than to present a treatment for frustrated graphs, so this development will be incomplete. Despite the great similarity of our development to the work of Ree and Hoover,⁽¹¹⁾ we have not found a direct connection between the two (i.e., we have not been able to rederive their results using the formalism we present here).

We will find it useful to generalize the notion of an m -product and define a similar operation in terms of bonds other than m -bonds. Thus, for example, we will speak of the F -product of two graphs Γ_1 and Γ_2 , which we define as the sum of all topologically distinct, "properly F -connected" graphs that can be formed from the product $\Gamma_1 * \Gamma_2$ by adding one or more F -bonds (distinguishing these F -bonds from any that already might be present in Γ_1 or Γ_2). The E -product, etc., follow similarly. Clearly, the diagrams created in taking these products will not sum to a simple result as the m -product does. Additionally, we introduce the *tight m -product* (tight F -product, etc.) of Γ_1 and Γ_2 as the single graph obtained from $\Gamma_1 * \Gamma_2$ when all field points in one region (i.e., those from Γ_1) are joined by m -bonds to all field points in the other region (comprising the field points from Γ_2). Multiple products follow in an obvious fashion.

Let us now consider the following theorem:

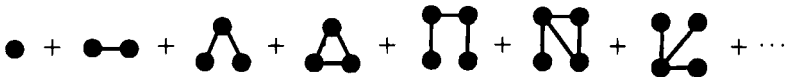
F2E Theorem. Let G be a set of distinct, star-irreducible, connected graphs $\Gamma_1, \Gamma_2, \dots, \Gamma_n$ each consisting of black circles, some or no labeled white 1-circles, and some or no B -bonds. Then

$$\begin{aligned} & \text{the sum of all graphs in } G \text{ and all } F\text{-products of graphs in } G \\ &= \ln[1 + \text{sum of all graphs in } G \text{ and all} \\ & \quad \text{tight } E\text{-products of graphs in } G] \end{aligned}$$

where $F = E - 1$ and B is neither F nor E .

Proof. We take all the graphs described in the sum on the left-hand side of the equality, and we replace the F -bonds that were introduced to form the F -product by an E -bond plus an m -bond. The resulting sum is now over all distinct, properly (E, m) -connected graphs obtained by taking products of the graphs in G and joining the field points from the component graphs by an m -bond or an E -bond. These diagrams will not necessarily be properly m -connected or properly E -connected. However, some can be viewed as properly m -connected “islands” of properly E -connected regions; all graphs in the sum can be obtained from these graphs by joining the regions within each island by some or no m -bonds. If we focus now on one of these islands of E -connected regions, we consider the sum of all graphs obtained by joining field points from different regions of the island by some or no m -bonds. Unless the island is a tight E -product (and thus no m -bond can be added within it), this sum is zero (more precisely, the sum will be zero once we do this for all islands). The only graphs that remain to sum are G , tight E -products of G , and m -products of tight E -products of G . Application of the logarithm theorem yields the stated result.

As a simple demonstration, let $G = \{\cdot\}$, the diagram composed of a single black z -point. The sum of G with all its f -products is



and it is well known that this is the activity expansion for the $\ln \Xi$, where Ξ is the grand-canonical partition function.⁽³⁾ The sum of G with its tight e -products is



which is also well known to be Ξ itself (minus unity), consistent with the F2E theorem.

These manipulations take on more interest when applied to graphs that contain root points. In particular, the graphs that contain two root points describe the pair structure, and have been the subject of intense

study. Important classes of diagrams include “*h*-allowable diagrams”—all distinct connected simple graphs consisting of two white 1-circles, labeled 1 and 2, respectively, some or no ρ -circles, and at least one *f*-bond, such that the graphs are free of articulation circles—which sum to give *h*(*r*). The *h*-allowable diagrams are classified further according to whether they contribute to various pair functions: nodal diagrams, which sum to the series function *b*(*r*); nonnodal diagrams, which sum to the direct correlation function *c*(*r*); bridge or elementary diagrams, which sum to the bridge function *d*(*r*). The elementary diagrams are very difficult to evaluate, and their treatment (or lack thereof) is the sole source of approximation in most integral equation theories for classical, pairwise-additive model systems.

Turning to the present context, we wish to point out that all of the elementary graphs can be written as an *f*-product of nodal graphs and, conversely, every graph generated in taking the *f*-product of a set of nodal graphs is an elementary graph. It is tempting therefore to state

$$d(r) \text{ equals the sum of all } f\text{-products of diagrams in } b(r)$$

which with the F2E theorem results in

$$b(r) + d(r) = \ln[1 + b(r) + \text{the tight } e\text{-product of diagrams in } b(r)]$$

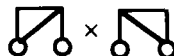
or

$$b(r) + d(r) = \ln \left[1 + b(r) + \begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagdown \quad \diagup \\ \circ \quad \circ \end{array} + \begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ \diagdown \quad \diagup \\ \diagdown \quad \diagup \\ \circ \quad \circ \end{array} + \dots \right]$$

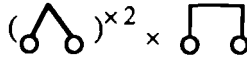
The Percus–Yevick approximation would then result by setting the *e*-products to zero. Unfortunately this statement is incorrect, for two reasons. First, the decomposition of a graph in *d*(*r*) is not necessarily unique. For example, the diagram



is generated from the *f*-product of



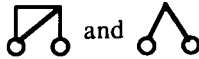
and also from the f -product of



Thus the f -product of graphs in $b(r)$ contains duplicates of graphs in $d(r)$. Second, the F2E theorem applies only if the f -bonds introduced by taking the f -product are distinguished—for the purpose of defining the symmetry number—from any f -bonds already present in the original graphs. Thus for example, the diagram

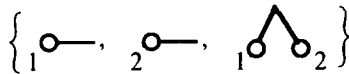


which arises in taking the f -product of



has a symmetry number of 2 when considered as one of the diagrams in d , but is given a symmetry number of only 1 when the new f -bond is distinguished from those in the original diagrams (as required by the theorem). We can see no simple and elegant way to bypass these problems.



Alternative decompositions of the graphs in $d(r)$ are possible. A variable approach involves the h -bond expansion of $d(r)$: all diagrams with two root points, one or more black p -points, and h -bonds, with no nodal points and no articulation pairs. Many of the graphs in this formulation of $d(r)$ are generated by taking all possible h -products of the three graphs




(here and in all of what follows we will use a solid line to represent an h -bond, and a dashed line to represent a g -bond). There remain however, several complications. First, not all graphs in $d(r)$ can be generated this way. These we will simply ignore, as an approximation; since the first such diagram, e.g.,




has four field points, their neglect affects the sixth and higher virial coefficients.




Second, the h -product generates unconnected graphs when only  or only  are in the product graph. These may be subtracted out easily.

Third, the h -product generates graphs having articulation pairs, and thus which are not in $d(r)$. The problem arises when  multiplies itself or




without an added h -bond joining the field point from  to another region



or a  region. The problem is compounded in diagrams with many such  bonds, and of course by the fact that the same occurs with the  graphs. We can define a new function $j(r)$ to eliminate this difficulty; it is defined implicitly:

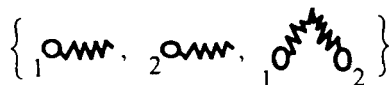
$j(r) = h(r)$ minus { the sum of all graphs containing two white 1-circles labeled 1 and 2, respectively, and some or no black ρ -circles, such that there is a j -bond joining the white circles to each other, a j -bond from every black circle to the root point labeled 1, h -bonds joining any of the field points to each other, one or more h -bonds joining field points to the root point labeled 2, and no articulation circles }

The quantity in braces equals the sum of all diagrams obtained by taking the h -product of all products of  and coloring one of the black points white and labeling it "2." The first few graphs in the h -bond expansion of $j(r)$ are

$$\underbrace{\text{wavy line}}_j = \underbrace{\text{line}}_h - \left[\begin{array}{c} \text{h-bonds} \\ \text{triangle} \\ \text{square} \\ \dots \end{array} \right]$$

which displays the necessary symmetry of the root points. We have not investigated further the nature of this function.

Now, we let G be the set of diagrams



where the wavy bonds are j -bonds and, within the approximation discussed in the first point above, we have

$$b(r) + d(r) = \text{the sum of the diagrams in } G \text{ and all } h\text{-products of graphs in } G, \text{ minus all } h\text{-products of } \underset{1}{\text{O}} \text{---} \text{wavy}, \text{ minus all } h\text{-products of } \underset{2}{\text{O}} \text{---} \text{wavy}, \text{ minus the convolution } h*b$$

The last term is needed to account for the extra nodal graphs introduced with the convolution of h with itself. The h -products of $\underset{1}{\text{O}} \text{---} \text{wavy}$ and $\underset{2}{\text{O}} \text{---} \text{wavy}$, due to the definition of $j(r)$, are simply $\underset{1}{\text{O}} \text{---} \text{O}$ and $\underset{2}{\text{O}} \text{---} \text{O}$, respectively, and may be evaluated via the compressibility equation. Finally, application of the F2E theorem results in

$$b(r) + d(r) = \ln[1 + \text{the sum of the graphs in } G \text{ and all tight } g\text{-products of graphs in } G] - \underset{1}{\text{O}} \text{---} \text{O} - \underset{2}{\text{O}} \text{---} \text{O} - h*b$$

The utility of this formulation is questionable, as it depends greatly on the nature of $j(r)$: the feasibility of its evaluation, and the extent of its range (which impacts on the magnitude of the tight g -products of G). One should also not forget the graphs neglected early in the formulation. We present this development to spur further thought; no doubt other approaches to the transformation of the bridge diagrams can be developed.

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