

Cluster diagrammatic analysis of the RISM equation†

by DAVID CHANDLER‡

School of Chemical Sciences, University of Illinois,
Urbana, Illinois 61801

(Received 27 October 1975)

The interaction site cluster theory and the method of topological reduction are applied to determine the infinite class of cluster diagrams summed by the reference interaction site model (RISM) integral equation. It is shown that, along with summing a subset of allowed cluster graphs for the site-site correlation functions of molecular fluids, the equation also sums classes of graphs which are unallowed in a rigorous theory. The relationship between the RISM equation for molecular fluids and the Percus-Yevick equation for simple atomic fluids is analysed diagrammatically.

1. INTRODUCTION

During the past few years we have developed [1-3] and applied [4-6] a qualitatively successful theory for the equilibrium intermolecular structure of polyatomic fluids. The foundation for the theory is the reference interaction site model (RISM) integral equation. In this article we present a cluster diagrammatic formulation of the RISM equation. In particular, the infinite class of interaction site cluster diagrams [1] summed by the equation is derived.

The development begins in § 2 where the interaction site cluster series [1] for the equilibrium pair correlation functions of molecular fluids is reviewed. In § 3 the topologies of graphs involved in the RISM equation are determined. From this analysis, it is shown in § 4 that the RISM equation sums classes of diagrams that are not allowed in a rigorous theory. In § 5 the analogy between the Percus-Yevick equation for simple fluids and the RISM equation for molecular fluids is discussed.

This article was written assuming the reader is familiar with concepts of topological reduction and the material in reference [1]. Stell [7] and Morita and Hiroike [8] provide excellent texts on topological reduction.

2. EXACT INTERACTION SITE CLUSTER SERIES

The interaction site cluster expansion [1] provides a convenient language with which one may formulate equilibrium theories for molecular liquids. In this section we review the features of the interaction site cluster theory which are relevant to the analysis of the RISM equation.

† This research was supported by the National Science Foundation, the Alfred P. Sloan Foundation, and the Petroleum Research Fund as administered by the American Chemical Society.

‡ Alfred P. Sloan Foundation Fellow.

2.1. Statistical mechanical functions

The pair correlation functions described by the interaction site cluster series are the set of site-site functions

$$h_{\alpha\gamma}(\mathbf{r}) = g_{\alpha\gamma}(\mathbf{r}) - 1, \quad (2.1)$$

where

$$g_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) = \rho^{-2} \langle N(N-1) \delta(\mathbf{r}_1^{(\alpha)} - \mathbf{r}) \delta(\mathbf{r}_2^{(\gamma)} - \mathbf{r}') \rangle. \quad (2.2)$$

Here, ρ is the molecular density, the pointed brackets denote the equilibrium ensemble average, and $\mathbf{r}_i^{(\alpha)}$ denotes the position of the α th interaction site in molecule i . There are N molecules in the system (which, for notational simplicity, we take to be a one-component system), and each molecule has m interaction sites.

The interaction site cluster series expresses $h_{\alpha\gamma}(\mathbf{r})$ as a functional of the site-site cluster functions, $f_{\alpha\gamma}(\mathbf{r})$, and intramolecular distribution functions, $s_{\alpha\gamma\dots\eta}^{(n/m)}(\mathbf{r}, \mathbf{r}', \dots, \mathbf{r}'')$. These quantities are defined as follows:

$$f_{\alpha\gamma}(\mathbf{r}) = -1 + \exp[-\beta w_{\alpha\gamma}(\mathbf{r})], \quad (2.3)$$

where $w_{\alpha\gamma}(\mathbf{r})$ is the site-site potential, and β^{-1} is Boltzmann's constant times the temperature,

$$\begin{aligned} s_{\alpha\gamma}^{(2/m)}(\mathbf{r}, \mathbf{r}') &= (1 - \delta_{\alpha\gamma}) \rho^{-1} \langle N \delta(\mathbf{r}_1^{(\alpha)} - \mathbf{r}) \delta(\mathbf{r}_1^{(\gamma)} - \mathbf{r}') \rangle \\ &= (1 - \delta_{\alpha\gamma}) (4\pi L_{\alpha\gamma}^2)^{-1} \delta(|\mathbf{r} - \mathbf{r}'| - L_{\alpha\gamma}), \end{aligned} \quad (2.4)$$

and most generally,

$$\begin{aligned} s_{\alpha_1\alpha_2\dots\alpha_n}^{(n/m)}(\mathbf{r}, \mathbf{r}', \dots, \mathbf{r}'') &= \left[\prod_{i>j=1}^n (1 - \delta_{\alpha_i\alpha_j}) \right] \rho^{-1} \\ &\times \langle N \delta(\mathbf{r}_1^{(\alpha_1)} - \mathbf{r}) \delta(\mathbf{r}_1^{(\alpha_2)} - \mathbf{r}') \dots \delta(\mathbf{r}_1^{(\alpha_n)} - \mathbf{r}'') \rangle. \end{aligned} \quad (2.5)$$

The second equality in equation (2.4) holds for rigid molecules only; i.e., the distance between sites α and γ within the same molecule is a constant $L_{\alpha\gamma}$. For rigid molecules, equation (2.5) is equivalent to equation (4.1) of reference [1].

2.2. Diagrammatic notation

There are two types of bonds used in the interaction site cluster series—intermolecular interaction bonds which stand for the $f_{\alpha\gamma}(\mathbf{r})$ functions, and intramolecular distribution bonds. The following graphical symbols are used for these functions:

$$f_{\alpha\gamma}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_2^{(\gamma)}) = \overset{\circ}{1^{(\alpha)}} \text{---} \overset{\circ}{2^{(\gamma)}}, \quad (2.6)$$

$$s_{\alpha\gamma}^{(2/m)}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_1^{(\gamma)}) = \overset{\circ}{1^{(\alpha)}} \text{---} \overset{\circ}{1^{(\gamma)}}, \quad (2.7)$$

$$s_{\alpha\gamma\eta}^{(3/m)}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_1^{(\gamma)}, \mathbf{r}_1^{(\eta)}) = \begin{array}{c} \overset{\circ}{1^{(\eta)}} \\ \diagup \quad \diagdown \\ \overset{\circ}{1^{(\alpha)}} \quad \overset{\circ}{1^{(\gamma)}} \end{array}, \quad (2.8)$$

etc. The white circles are labelled since they represent particular interaction sites at specific locations.

An interaction site cluster diagram is a collection of white and black circles connected by **f** and **s** bonds. The black circles are white circles which have been integrated over space and summed over interaction sites ; i.e.,

$$\bullet = \sum_{\alpha=1}^m \int d\mathbf{r}_i^{(\alpha)} [\bigcirc_i^{(\alpha)}]. \quad (2.9)$$

The value of a diagram is determined by performing the sums and integrations implied by the black circles and then multiplying by $\nu^{-1}\rho^n$. Here, ν is the symmetry number of the diagram, and $n + 2$ is the number of different molecules (not sites) involved in the diagram. For example,

$$\begin{array}{c} \text{---} \\ \diagup \quad \diagdown \\ \text{---} \end{array} \begin{array}{c} \text{---} \\ \diagdown \quad \diagup \\ \text{---} \end{array} = (\rho/2) \sum_{\eta, \lambda, \nu=1}^m \int d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' s_{\alpha\eta\lambda}^{(3/m)}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}, \mathbf{r}') \\ \times f_{\eta\nu}(|\mathbf{r} - \mathbf{r}''|) f_{\lambda\nu}(|\mathbf{r}' - \mathbf{r}''|) f_{\nu\gamma}(|\mathbf{r}'' - \mathbf{r}_2^{(\gamma)}|). \quad (2.10)$$

An *allowed* diagram is a graph which does not violate any of the following restrictions :

- (a) The graph must be connected.
- (b) Any two circles may be connected directly to one another by at most one bond (i.e. the graph is 'simple').
- (c) All black circles must be intersected by at least one **f**-bond.
- (d) No circle is intersected by two or more different **s**-bonds.
- (e) There are no articulation circles and no articulation **s**-bonds.

The terminology used here is described in reference [1]. For example, an articulation circle is a circle whose removal leaves a disconnected graph with one or more of the disconnected portions containing no white circle. An articulation **s**-bond does the same thing as an articulation circle except one now considers what happens if an entire **s**-bond and the circles attached to it are removed.

For examples of allowed and unallowed interaction site diagrams, see figures 9 and 10 of reference [1].

2.3. Exact cluster series

Let $y_{\alpha\gamma}(\mathbf{r})$, the indirect correlation function, be defined as

$$y_{\alpha\gamma}(\mathbf{r}) = \exp [+ \beta w_{\alpha\gamma}(\mathbf{r})] g_{\alpha\gamma}(\mathbf{r}). \quad (2.11)$$

Clearly,

$$h_{\alpha\gamma}(\mathbf{r}) = f_{\alpha\gamma}(\mathbf{r}) + [1 + f_{\alpha\gamma}(\mathbf{r})][y_{\alpha\gamma}(\mathbf{r}) - 1]. \quad (2.12)$$

From reference [1], one knows that

$$y_{\alpha\gamma}(\mathbf{r}_1^{(\gamma)}, \mathbf{r}_2^{(\gamma)}) - 1 = \text{the sum of all allowed interaction site cluster diagrams with } \mathbf{f}\text{-bonds and } \mathbf{s}\text{-bonds, two white circles (labelled } 1^{(\alpha)} \text{ and } 2^{(\gamma)}), \text{ one or more black circles, and no bond connecting the white circles directly to each other,} \quad (2.13)$$

Alternatively,

$$y_{\alpha\gamma}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_2^{(\gamma)}) = 1 + \text{the sum of all indirect diagrams in } h_{\alpha\gamma}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_2^{(\gamma)}). \quad (2.14)$$

An 'indirect' diagram is one in which the white circles are not connected directly to one another by a bond. With these results, an analysis of the RISM integral equation can now be carried out.

3. THE RISM INTEGRAL EQUATION

3.1. Percus–Yevick like topology

The topology of the interaction site cluster diagrams which can be summed to give the RISM equation is similar to the topology of the graphs in the Percus–Yevick integral equation. See Stell's work [9] for the cluster diagrammatic analysis of the Percus–Yevick equation.

Let $\{D_{\alpha\gamma}\}$ denote the infinite set of interaction site cluster diagrams formed in the following way :

1. Place $n(\geq 3)$ circles around in a ring.
2. Colour two adjacent circles white, and all the rest black. Label the white circles $1^{(\alpha)}$ and $2^{(\gamma)}$.
3. Connect all adjacent circles, except the white pair, with either $\mathbf{s}^{(2)}$ -bonds or \mathbf{f} -bonds.

[Thus, one has formed a polygon with one edge missing ; the sides of the polygon are \mathbf{f} -bonds or $\mathbf{s}^{(2)}$ -bonds.]

4. Connect non-adjacent circles with zero or more \mathbf{f} -bonds.

Next, supplement this construction by requiring all the diagrams in $\{D_{\alpha\gamma}\}$ to obey the following restrictions :

5. The graph is a simple cluster diagram.
6. No pair of \mathbf{f} -bonds cross over one another (though they can intersect at the circles).
7. There are no black circles which are intersected by only $\mathbf{s}^{(2)}$ -bonds. As a result, all black circles must be intersected by at least one \mathbf{f} -bond.

Examples of diagrams that are in $\{D_{\alpha\gamma}\}$ are shown in figure 1. Examples of diagrams that are not members of this set are shown in figure 2.

Notice that not all graphs contained in $\{D_{\alpha\gamma}\}$ are allowed graphs as defined in § 2. For example, the diagram labelled (*d*) in figure 1 is not allowed in the rigorous cluster series for $h_{\alpha\gamma}(r)$ or $y_{\alpha\gamma}(r)$ since it contains a circle which is intersected by two different \mathbf{s} -bonds. Nevertheless, the graph is a member of $\{D_{\alpha\gamma}\}$, and it will be shown that it is a diagram that is summed in the RISM equation.

3.2. Summation of cluster graphs in $\{D_{\alpha\gamma}\}$

Let $[y_{\alpha\gamma}(r)]_{\text{RISM}}$ be defined as

$$[y_{\alpha\gamma}(r)]_{\text{RISM}} = 1 + \text{the sum of all the diagrams in } \{D_{\alpha\gamma}\}, \quad (3.1)$$

where $r = |\mathbf{r}_1^{(\alpha)} - \mathbf{r}_2^{(\gamma)}|$. Equation (3.1) provides a theory for the indirect correlation function. It will be shown that for hard-core interaction site model molecules (i.e., RISM molecules) this theory is equivalent to the RISM integral equation discussed in references [1–5].

To carry out the demonstration, note that according to equations (3.1) and (2.12)

$$[h_{\alpha\gamma}(r)]_{\text{RISM}} = f_{\alpha\gamma}(r) + [1 + f_{\alpha\gamma}(r)][\text{the sum of all the diagrams in } \{D_{\alpha\gamma}\}], \quad (3.2)$$

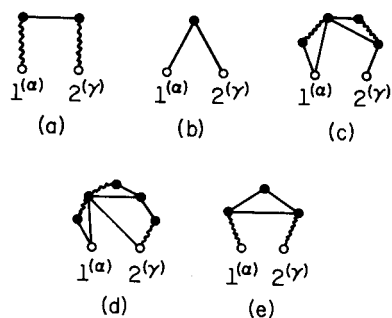


Figure 1. Examples of interaction site cluster diagrams in $\{D_{\alpha\gamma}\}$.

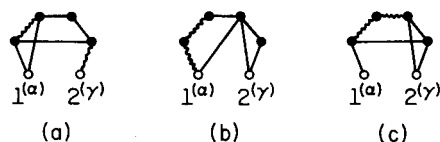


Figure 2. Examples of interaction site diagrams not contained in $\{D_{\alpha\gamma}\}$. In graph (a), two **f** bonds cross. In graph (b), a black circle is intersected by only two **s**⁽²⁾ bonds. In graph (c), a black circle is not intersected by an **f** bond, and two **f** bonds cross.

$$\begin{aligned}
 [h_{\alpha\gamma}(1^{(\alpha)}, 2^{(\gamma)})]_{\text{RISM}} &= \text{diagram 1} + \text{diagram 2} + \text{diagram 3} \\
 &+ \text{diagram 4} + \text{diagram 5} + \text{diagram 6} \\
 &+ \text{diagram 7} + \text{diagram 8} + \text{diagram 9} \\
 &+ \text{etc.} \\
 &= \text{diagram 1} + (1 + \text{diagram 1}) \left(\text{diagram 2} \right. \\
 &+ \text{diagram 4} + \text{diagram 6} + \text{diagram 8} \\
 &+ \text{diagram 7} + \text{diagram 9} + \text{diagram 10} \\
 &+ \text{etc.} \left. \right)
 \end{aligned}$$

Figure 3. Interaction site cluster graphs in $[h_{\alpha\gamma}(r)]_{\text{RISM}}$ with $r = |\mathbf{r}_1^{(\alpha)} - \mathbf{r}_2^{(\gamma)}|$. The second equality shows the factorization of $h_{\alpha\gamma}(r)$ into $f_{\alpha\gamma}(r) + [1 + f_{\alpha\gamma}(r)][y_{\alpha\gamma}(r) - 1]$.

or

$$[h_{\alpha\gamma}(r)]_{\text{RISM}} = \text{the graph with one } \mathbf{f}\text{-bond connecting two white circles plus the sum of all the graphs in } \{D_{\alpha\gamma}\} \text{ plus the sum of all the direct graphs formed by connecting with an } \mathbf{f}\text{-bond the white circles of the graphs in } \{D_{\alpha\gamma}\}. \quad (3.3)$$

The cluster diagrams summed in equation (3.3) are shown in figure 3.

3.3. The RISM direct correlation function, $[c_{\alpha\gamma}(r)]_{\text{RISM}}$

Notice that the indirect diagrams in equation (3.3) (i.e., the diagrams in $\{D_{\alpha\gamma}\}$) all contain nodes—black circles which are cutting points. The nodeless diagrams in $[h_{\alpha\gamma}(r)]_{\text{RISM}}$ are only those diagrams which have $f_{\alpha\gamma}$ bonds connecting the white circles directly. Let

$$[c_{\alpha\gamma}(r)]_{\text{RISM}} = \text{the sum of all the nodeless diagrams in equation (3.3)}. \quad (3.4)$$

From the preceding remarks it is clear that

$$[c_{\alpha\gamma}(r)]_{\text{RISM}} = f_{\alpha\gamma}(r) + f_{\alpha\gamma}(r)[\text{the sum of all the diagrams in } \{D_{\alpha\gamma}\}]. \quad (3.5)$$

Thus, by combining equations (3.5) and (3.1),

$$[c_{\alpha\gamma}(r)]_{\text{RISM}} = f_{\alpha\gamma}(r)[y_{\alpha\gamma}(r)]_{\text{RISM}}. \quad (3.6)$$

The first, third, fifth and seventh diagrams pictured in figure 3 are diagrams that contribute to $[c_{\alpha\gamma}(r)]_{\text{RISM}}$ as well as contributing to $[h_{\alpha\gamma}(r)]_{\text{RISM}}$.

3.4. Topological reduction

The $[c_{\alpha\gamma}(r)]_{\text{RISM}}$ function has been introduced because $[h_{\alpha\gamma}(r)]_{\text{RISM}}$ can be expressed as a functional of $[c_{\alpha\gamma}(r)]_{\text{RISM}}$ rather than $f_{\alpha\gamma}(r)$. In particular, by applying the standard methods of topological reduction, one may combine equations (3.5) and (3.2) to find

$$[h_{\alpha\gamma}(r)]_{\text{RISM}} = \text{the sum of all simple chains with one or more } \mathbf{c}\text{-bonds and any number of } \mathbf{s}^{(2)}\text{-bonds, two white circles } 1^{(\alpha)} \text{ and } 2^{(\gamma)}, \text{ any number of black circles, and all the black circles are intersected by at least one } \mathbf{c}\text{-bond}. \quad (3.7)$$

A 'simple chain' is a connected diagram for which there is only one path between the white circles. The \mathbf{c} -bonds are cluster bonds formed from the $m \times m$ set of $[c_{\alpha\gamma}(r)]_{\text{RISM}}$ functions. Figure 4 shows the sum of graphs in equation (3.7). A dashed line is used to represent a \mathbf{c} -bond graphically; i.e.,

$$[c_{\alpha\gamma}(\mathbf{r}_1^{(\alpha)}, \mathbf{r}_2^{(\gamma)})]_{\text{RISM}} = \overset{\circ}{1^{(\alpha)}} \text{-----} \overset{\circ}{2^{(\gamma)}} \quad (3.8)$$

As a book-keeping device it is convenient to introduce the 'hypervertex' function $\omega_{\alpha\gamma}(r)$ defined as

$$\begin{aligned} \omega_{\alpha\gamma}(r) &= \delta_{\alpha\gamma} \delta(\mathbf{r}) + s_{\alpha\gamma}^{(2/m)}(r) \\ &= \overset{\circ}{1^{(\alpha)}} \text{---} \text{---} \text{---} \overset{\circ}{1^{(\gamma)}} \end{aligned} \quad (3.9)$$

non-linear integral equations formed by combining equation (3.13) with the closure relation (3.6). For the special case of hard-core (but definitely aspherical) interaction site model molecules, this integral equation is the RISM integral equation discussed in previous publications [1-5]. In particular, for hard cores,

$$\begin{aligned} f_{\alpha\gamma}(r) &= -1, & r < d_{\alpha\gamma} \\ &= 0, & r \geq d_{\alpha\gamma}, \end{aligned} \quad (3.14)$$

where $d_{\alpha\gamma}$ is the distance of closest approach between two sites α and γ in different molecules. Then, from equation (3.6) it follows that

$$[c_{\alpha\gamma}(r)]_{\text{RISM}} = 0, \quad r \geq d_{\alpha\gamma}. \quad (3.15)$$

Further, from equation (3.2) it follows that

$$[h_{\alpha\gamma}(r)]_{\text{RISM}} = -1, \quad r < d_{\alpha\gamma}. \quad (3.16)$$

Equation (3.13) combined with equations (3.15) and (3.16) is the familiar form of the RISM equation.

Thus, we have isolated the interaction site cluster diagrams that are summed by the solutions of the RISM integral equation.

4. ALLOWED AND UNALLOWED DIAGRAMS

As was briefly discussed in § 3.1, many of the diagrams which are members of $\{D_{\alpha\gamma}\}$ are not allowed diagrams. The RISM equation sums all the graphs in $\{D_{\alpha\gamma}\}$. Thus, the RISM equation contains unallowed diagrams. In other words, the equation sums classes of graphs that cannot be contained in a rigorous theory. This aspect of the RISM equation is now examined in more detail.

Consider the density expansion of the RISM indirect correlation function :

$$[y_{\alpha\gamma}(r)]_{\text{RISM}} = 1 + y_{\alpha\gamma}^{(0)}(r) + \rho y_{\alpha\gamma}^{(1)}(r) + \rho^2 y_{\alpha\gamma}^{(2)}(r) + \dots, \quad (4.1)$$

where $\rho^n y_{\alpha\gamma}^{(n)}(r)$ is the sum of all graphs in equation (3.1) which involve density to the n th power. That is, $\rho^n y_{\alpha\gamma}^{(n)}(r)$ sums all the diagrams in $\{D_{\alpha\gamma}\}$ for which

$$n = n_b - n_s, \quad (4.2)$$

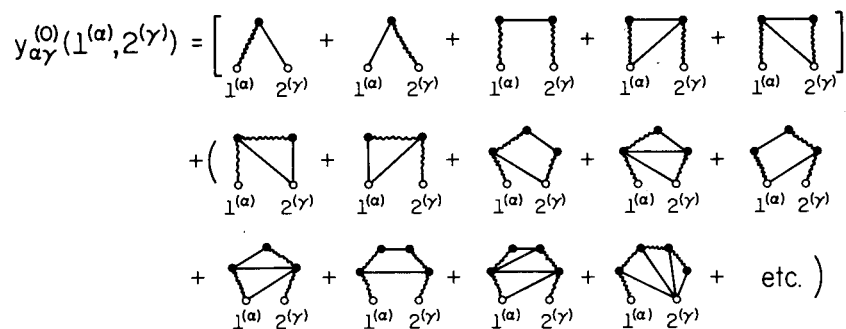


Figure 5. Interaction site cluster diagrams contributing to the low density limit of the RISM indirect correlation function.

where n_b is the number of black circles in the diagram and n_s is the number of $s^{(2)}$ -bonds. There are an infinite number of such diagrams!

The interaction site cluster graphs contributing to $y_{\alpha\gamma}^{(0)}(r)$ are shown in figure 5. These graphs are divided into two groups. The first, surrounded by square brackets, is the finite set of allowed graphs that do contribute to the low density limit of the exact $y_{\alpha\gamma}(r)$ function. Of course, these graphs in square brackets form only a subset of the entire *finite* set of allowed graphs in the low density limit for $y_{\alpha\gamma}(r)$. The second group of diagrams, surrounded by round brackets in figure 5, is an *infinite* set of unallowed interaction site cluster diagrams.

This behaviour is not confined to the low density limit. For the n th order term one has

$$\begin{aligned} \rho^n y_{\alpha\gamma}^{(n)}(r) = & [\text{the sum of the } \textit{finite} \text{ subset of allowed diagrams which} \\ & \text{are members of } \{D_{\alpha\gamma}\} \text{ and which are of the order of } \rho^n] \\ & + (\text{the sum of the } \textit{infinite} \text{ set of unallowed diagrams in} \\ & \{D_{\alpha\gamma}\} \text{ which are of the order of } \rho^n), \end{aligned} \quad (4.3)$$

while to that order in the density, the exact indirect correlation function is

$$\begin{aligned} & [\text{the sum of the } \textit{finite} \text{ set of allowed diagrams } \blacksquare \text{ in } \{D_{\alpha\gamma}\} \\ & \text{which are of the order of } \rho^n] \\ & + \{\text{the sum of the } \textit{finite} \text{ set of allowed diagrams not in } \{D_{\alpha\gamma}\} \\ & \text{which are of the order of } \rho^n\}. \end{aligned}$$

For the RISM equation to be useful, one hopes that

$$\begin{aligned} & (\text{the sum of the } \textit{infinite} \text{ set of unallowed diagrams in } \{D_{\alpha\gamma}\} \\ & \text{which are of the order of } \rho^n) \\ & \approx \{\text{the sum of the } \textit{finite} \text{ set of allowed diagrams not in } \{D_{\alpha\gamma}\} \\ & \text{which are of the order of } \rho^n\}. \end{aligned} \quad (4.4)$$

It is difficult to assess *a priori* the accuracy of this approximation. A great deal of empirical evidence exists which indicates that the RISM equation is fairly accurate, and thus equation (4.4) is probably qualitatively correct.

The explanations for why the RISM equation works fairly well are derived from physical arguments (like the ones used in the original developments of the equation [3]) or from mathematical arguments which view the equation more as an interpolation formula (as were presented in reference [1]). In the next section we attempt to bring these two types of arguments into one unified discussion by employing the results of § 3.

5. RELATIONSHIP WITH PERCUS-YEVICK THEORY

The Percus-Yevick (PY) integral equation is shown diagrammatically in figure 6. Also shown graphically in that figure is the RISM integral equation. This particular form of the RISM equation is obtained by direct topological reduction of equation (3.1), or equivalently, by combining equations (2.12), (3.6), and (3.13).

Empirically it is known that the PY equation is fairly accurate when the interactions between particles are harshly repulsive. Thus, the PY equation probably provides an accurate theory for the structural properties of a fluid composed of RISM molecules. However, the PY equation becomes so complicated when applied to such systems, it is impossible (with current generation

$$\begin{aligned}
 [y(1,2)-1]_{\text{PY}} &= \text{graph (a)} \\
 [y_{\alpha\gamma}(1^{(\alpha)},2^{(\gamma)})-1]_{\text{RISM}} &= \text{graph 1} + \text{graph 2} + \text{graph 3} \\
 &+ \text{graph 4} + \text{graph 5}
 \end{aligned}$$

(a)

(b)

Figure 6. The Percus–Yevick (PY) and RISM integral equations. In (a), which is the PY equation, the graph is a usual molecular cluster diagram with the black circle denoting a density field point, the solid line denoting a Mayer f -bond, and the bonds $-y-$ and $-h-$ represent the indirect correlation function, $y(1,2)$, and the pair correlation function, $h(1,2)$, respectively. In (b), the graphs are interaction site cluster diagrams with the bonds $-y-$ and $-h-$ denoting the RISM indirect and pair correlation functions, respectively.

computers) to obtain numerically liquid density solutions of the equation. It is for reasons like this one that the RISM equation (and more generally the interaction site cluster theory) was developed. In particular, one wants a computationally convenient theory. But in obtaining that theory, one does not want to sacrifice entirely what is known to be useful in the physics of simple fluids.

In view of figure 6 the RISM equation appears to be a straightforward generalization of the PY equation for atomic fluids. The topological structures of the two equations are nearly identical. The differences between them are due solely to the presence of the *intramolecular* pair bonds in the RISM equation and the necessary absence of these bonds in the PY equation.

The fourth RISM graph in figure 6 is the same as the PY graph. The first RISM graph is also identical to the PY graph except that the h -bond has been changed to an $s^{(2)}$ -bond. This alteration accounts for the fact that *intramolecular* correlations as well as intermolecular coupling provide a viable mechanism for atomic pair correlations in a molecular fluid. Once the first and fourth RISM graphs are used, the second, third, and fifth must also be included to ensure symmetry [i.e. $y_{\alpha\gamma}(r) = y_{\gamma\alpha}(r)$]. The resulting RISM equation is symmetric and it does not multiply-count distinct interaction site cluster graphs.

Not only does the RISM equation look like the PY equation, it reduces exactly to that equation in two limiting situations. In the first, imagine that the intramolecular lengths in a RISM molecule become very large compared to the range of the $f_{\alpha\gamma}(r)$ functions; i.e.

$$L_{\alpha\gamma} \rightarrow \infty, \quad 1 \leq \alpha < \gamma \leq m. \quad (5.1)$$

In this limit,

$$s_{\alpha\gamma}^{(2/m)}(r) \rightarrow 0, \quad (5.2)$$

and the RISM equation is identical to the PY equation for a mixture of spherical particles. (For an exact theory, this limit reduces the atomic pair correlations of a molecular liquid to the *exact* pair correlations for a mixture of spherical particles [1]).

In the other limit, imagine the situation in which the interaction spheres associated with the second through m th sites in each molecule are entirely enveloped by the interaction sphere of site 1. For this limit, it can be shown that the solutions of the RISM equation are

$$[h_{\alpha\gamma}(r)]_{\text{RISM}} = \omega_{\alpha 1} \star h^{(\text{PY})} \star \omega_{1\gamma}(r), \quad (5.3)$$

where $h^{(\text{PY})}(r)$ is the Percus–Yevick pair correlation function for the system with the pair potential $w_1(r)$. (In this limit, an exact theory for site–site pair correlations in molecular fluids reduces to equation (5.3) but with $h^{(\text{PY})}(r)$ replaced with the exact $h(r)$ [1]).

Along the interpolating to ‘correct’ end points (i.e., to the PY theory), the RISM equation also correctly predicts in the intermediate region the locations for nontrivial singularities in $y_{\alpha\gamma}(r)$. In particular, for RISM molecules the exact $y_{\alpha\gamma}(r)$ contains cusps (discontinuities in the first derivative) at specifiable positions [1]. These cusps arise from convolutions of intramolecular correlation bonds (which are delta functions) and intermolecular f -bonds (which are step functions for hard-core models). The RISM equation locates these cusps at the correct positions. In figure 6, the first and second RISM diagrams are the graphs which contribute cusps to $[y_{\alpha\gamma}(r)]_{\text{RISM}}$.

In summary, it appears that there is no rigorous foundation for the RISM equation. However, it is possible to understand why the RISM equation is qualitatively accurate. It is a generalization of the PY theory for simple fluids; and it is a generalization which incorporates the physically important coupling between intramolecular and intermolecular interactions. It may be possible to derive an alternative equation which sums only allowed diagrams and at the same time satisfies the features which seem to make the RISM equation accurate. If such an equation can be found it is likely that it will be more accurate and thus more useful than the RISM theory.

REFERENCES

- [1] LADANYI, B. M., and CHANDLER, D., 1974, *J. chem. Phys.*, **62**, 4308.
- [2] CHANDLER, D., 1973, *J. chem. Phys.*, **59**, 2749.
- [3] CHANDLER, D., and ANDERSEN, H. C., 1972, *J. chem. Phys.*, **57**, 1930.
- [4] LOWDEN, L. J., and CHANDLER, D., 1973, *J. chem. Phys.*, **59**, 6587; 1975, *Ibid.*, **62**, 4246.
- [5] LOWDEN, L. J., and CHANDLER, D., 1974, *J. chem. Phys.*, **61**, 5228.
- [6] LOWDEN, L. J., 1975, Ph.D. Thesis, University of Illinois (unpublished).
- [7] STELL, G., 1964, *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin).
- [8] MORITA, T., and HIROIKE, K., 1961, *Prog. theor. Phys.*, **25**, 537.
- [9] STELL, G., 1963, *Physica (Utr.)*, **29**, 517.