MOLECULAR PHYSICS, 1982, VOL. 46, NO. 6, 1335–1345

New and proper integral equations for site–site equilibrium correlations in molecular fluids†

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(*Received* 24 *December* 1981 ; *accepted* 12 *March* 1982)

We show that the often used site–site direct correlation function cannot be defined in terms of a sum over a subset of the diagrams in the interaction site cluster series for the equilibrium pair correlation functions of a molecular fluid. However, from an exact topological reduction, we arrive at a new class of site–site direct correct correlation functions that are properly defined in the diagrammatic sense. The class is composed of four topologically distinct functions which are related to each other and the pair correlation function through four coupled Ornstein–Zernike-like equations. These new integral equations are exact and provide a rigorous foundation for integral equation theories of molecular fluids. The formal solutions to the equations are constructed, and the utility of the formulation is illustrated by discussing one example of an approximate closure to the integral equations.

1. INTRODUCTION

The graphical cluster series for pair correlations between sites on different molecules in an equilibrium fluid have been analysed in a number of papers [1–3]. Outside of the low density regime, the series must be partially summed to infinite order to yield reasonably accurate descriptions of the fluid states. Such summations can be performed with integral equations. The purpose of this paper is to describe a rigorous framework for these equations.

When considering simple systems (or when all the coordinates in a molecule are accounted for explicitly), integral equation theories are often derived or motivated within the context of the Ornstein–Zernike (or Dyson) equation

$$h(1,2)=c(1,2)+\rho\int d3c(1,3)h(3,2) \tag{1.1}$$

which can be written in compact matrix form as

$$\begin{aligned}\mathbf{h}&=\mathbf{c}+\rho\mathbf{ch}\\&=(\mathbf{1}-\rho\mathbf{c})^{-1}\,\mathbf{c}.\end{aligned} \tag{1.1'}$$

† This research has been supported by grants from the National Science Foundation and from the Petroleum Research Fund as administered by the American Chemical Society.

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Here, $h(1, 2) = g(1, 2) - 1$ is the pair correlation function between particles 1 and 2, $c(1, 3)$ is the direct correlation function, and ρ is the particle density. [For notational simplicity, throughout this paper we consider uniform one component systems only. Generalizations to the non-uniform and multicomponent cases are straightforward.] Since the inverse of $\mathbf{1} + \rho\mathbf{h}$ exists for any stable system, (1.1) can be inverted to yield $\mathbf{c}$ in terms of $\mathbf{h}$. Hence, the equation serves as a definition of $c(1, 2)$.

A deeper and more meaningful definition of the direct correlation function arises from a topological reduction of the exact cluster series for $h(1, 2)$. See, for example, [4] and [5]. The Ornstein–Zernike equation expresses $h(1, 2)$ as the sum of all simple (singly connected) chains of c-bonds. It follows [4, 5], therefore, that $c(1, 2)$ is the sum of all nodeless (two particle irreducible) graphs which express $h(1, 2)$ in terms of the density and interparticle potentials. This graphical definition of $\mathbf{c}$ is an exact result (provided some arrangement of the cluster series has a finite radius of convergence). Integral equations which sum infinite sets of graphs contributing to $h(1, 2)$ can be deduced by expressing a subset of the nodeless graphs in terms of $\mathbf{h}$ and the interparticle potentials.

When considering pair correlations between sites in different molecules in a molecular fluid, a different class of integral equations has been devised [6] which is based upon the relationship

$$\begin{aligned} \mathbf{h} &= \boldsymbol{\omega}\mathbf{c}\boldsymbol{\omega} + \rho\boldsymbol{\omega}\mathbf{c}\mathbf{h} \\ &= (\mathbf{1} - \rho\boldsymbol{\omega}\mathbf{c})^{-1}\, \boldsymbol{\omega}\mathbf{c}\boldsymbol{\omega}. \end{aligned} \tag{1.2}$$

Here,

$$h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = g_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) - 1 \tag{1.3}$$

is the equilibrium correlation function between site α at $\mathbf{r}$ and site γ in another molecule at $\mathbf{r}'$;

$$\omega_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = \delta_{\alpha\gamma}\delta(\mathbf{r} - \mathbf{r}') + s_{\alpha\gamma}{}^{(2)}(|\mathbf{r} - \mathbf{r}'|), \tag{1.4}$$

where $s_{\alpha\gamma}{}^{(2)}(r)$ is the intramolecular pair distribution function between two different sites α and γ within the same molecule; $c_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = c_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|)$ is the site–site direct correlation function; and we employ the matrix multiplication rule

$$(\mathbf{AB})_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = \sum_{\eta} \int d\mathbf{r}'\, A_{\alpha\eta}(\mathbf{r}, \mathbf{r}'')B_{\eta\gamma}(\mathbf{r}'', \mathbf{r}'). \tag{1.5}$$

We will use this notation throughout this paper. Further explanation of notation is found in [1–3].

According to (1.2), $h_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|)$ is the sum of all simple chains connecting the roots $(\alpha, \mathbf{r})$ and $(\gamma, \mathbf{r}')$ with one or more $\mathbf{c}$ bonds and any number of $\mathbf{s}^{(2)}$ bonds subject to the restriction that no circle is intersected by more than one $\mathbf{s}^{(2)}$ bond. This series, depicted graphically in figure 1, provides a physical picture in which pair correlations are 'propagated' in a molecular fluid via sequences of intramolecular and intermolecular interactions. The latter are represented by the site–site direct correlation bonds. This physical interpretation has led to closure relations such as the RISM equation [7], and more recently Rossky's extended RISM equation [8], in which $c_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}')$ is expressed as a short ranged functional of site–site pair potentials (or renormalized potentials) and the pair correlation functions, $\mathbf{h}$. The resulting integral equations have been shown to be fairly accurate for a variety of molecular liquids [6].

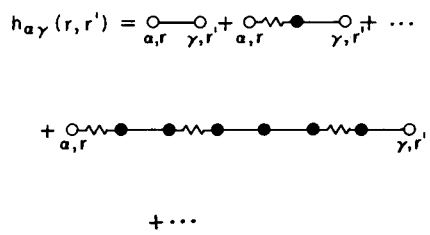


Figure 1. Simple chains summed by (1.2). The straight bonds represent the $c_{\alpha\gamma}(r)$ functions, and the wavy bonds depict $s_{\alpha\gamma}{}^{(2)}(r)$. The black circles are field points which indicate a summation over common site label and integration over common coordinate. The power of density associated with each graph is the number of intermediate molecules associated with the graph (i.e. number of black circles minus the number of $\mathbf{s}^{(2)}$ bonds). Thus, for example, the value of the second diagram is $\sum_{\eta} \int d\mathbf{r}''\, s_{\alpha\eta}{}^{(2)}(|\mathbf{r}-\mathbf{r}''|)c_{\eta\gamma}(|\mathbf{r}''-\mathbf{r}'|)$.

Yet, quantitative deficiencies exist, and some of them hint at fundamental problems with (1.2). For example, the RISM integral equation equates certain long wavelength pair correlation factors to the corresponding ideal uncorrelated values [9]; this error is related to difficulties encountered when applying theories like the RISM equation to calculate the dielectric constant [9, 10].

We believe the source of these difficulties is most easily identified by considering the origin of (1.2). The relationship seems plausible on physical grounds, and it can be viewed as simply the definition of the site–site direct correlation function. Indeed, Stell and coworkers have argued [11] that (1.2) is nothing more nor less than the standard Ornstein–Zernike equation since one can define $\mathbf{c}_{\text{in}}$ by $(\mathbf{1}-\rho\mathbf{c}_{\text{in}})^{-1}=\boldsymbol{\omega}$ from which one may then write $[\mathbf{1}-\rho(\mathbf{c}_{\text{in}}+\mathbf{c})]^{-1}=\boldsymbol{\omega}+\rho\mathbf{h}$. In this view, (1.2) arises simply from a division of the direct correlation function into two parts: an intramolecular piece and an intermolecular piece. If we were to adopt this attitude, we might seek improvements of the RISM or extended RISM theories by retaining (1.2) and improving the RISM closure relations. For example, one might imagine building in the exact long wavelength behaviour by adding a long ranged tail to $c_{\alpha\gamma}(r)$ in much the same spirit as Waisman generalized the mean spherical approximation for simple fluids [12]. Cummings and Stell [13] have recently proposed just this type of scheme in an effort to improve the RISM theory for dielectrics.

Unfortunately, serious problems are ignored with this approach. For one thing, the inverse of $\boldsymbol{\omega}$ is not necessarily well defined. In fact, due to stoichiometric constraints (i.e. normalization) which make all the elements of $\boldsymbol{\omega}$ equal to unity in the long wavelength limit, $\boldsymbol{\omega}$ is non-invertible in this limit. In addition even when $\boldsymbol{\omega}$ is invertible, $\mathbf{c}_{\text{in}}$ would appear ill-defined as $\rho\to 0$. Most serious, however, though perhaps related to the above, is the limitation of (1.2) already apparent in several publications, most notably [7] and [14]. The problem has to do with whether one can arrive at (1.2) from a topological reduction of the exact cluster series for $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$. If not, then $c_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ cannot be defined as a sum over a subset of graphs in $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$, and therefore integral equations based upon (1.2) will almost certainly contain contributions from

'unallowed graphs'—topologies which are not permitted in an exact theory for $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$.

In § 2, we show that, indeed, no topological reduction can be performed to define the site–site direct correlation function of (1.2) in terms of a subset of the diagrams contributing to $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$. In this sense, (1.2) is not a diagrammatically proper integral equation. While this fact has been well known [1], no explicit proof has been published before.

To improve upon the RISM and related theories, we believe it is important to consider generalizations of (1.2) which do have a proper foundation in graph theory. Such a generalization is deduced in § 3. We show that it is possible to define a set of four topologically distinct site–site direct correlation functions which are related to one another and the pair correlation functions by a set of four coupled Ornstein–Zernike-like equations. These new equations are exact and follow from a topological reduction. In § 4, we show that the equations can provide useful improvements upon the existing RISM theories.

2. Nonexistence of a topological reduction

Consider the cluster series for $\mathbf{h} = \mathbf{h}[\mathbf{f}, \rho\mathbf{s}]$, where $1 + f_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ is the Boltzmann factor for the intermolecular site–site potentials, and $\mathbf{s}$ refers to the set of all the intramolecular distribution functions: $s_\alpha^{(1)}(\mathbf{r}) = 1$ (for a uniform system), $s_{\alpha\gamma}^{(2)}(\mathbf{r}, \mathbf{r}')$, etc. Representative terms in this cluster series are shown in figure 2.

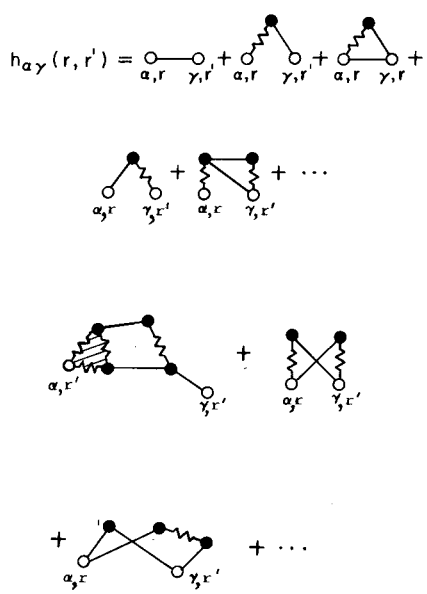
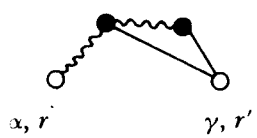


Figure 2. Cluster series for $\mathbf{h}$ as a functional of the site–site cluster function, $f_{\alpha\gamma}(|\mathbf{r}-\mathbf{r}'|)$ and the intramolecular distribution functions, $s_{\alpha\gamma}^{(2)}(|\mathbf{r}-\mathbf{r}'|)$, $s_{\alpha\gamma\eta}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$, etc. These functions are represented by the straight lines, wavy lines, and wavy filled triangles, respectively. See [1–3] for derivations and further discussion of this series and notational conventions.

Let us suppose a topological reduction of this series can be performed to yield (1.2). As seen from figure 1, (1.2) implies

$$h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') = c_{\alpha\gamma}(\mathbf{r}, \mathbf{r}') + [\text{sum of graphs with one or more nodal circles}], \quad (2.1)$$

where a node or nodal circle is a black circle whose removal from a connected graph produces a graph in which the two white root circles are now disconnected. Therefore, if (1.2) is to represent a partitioning of the graphical series for $\mathbf{h}[\mathbf{f}, \rho\mathbf{s}]$, then $c_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ must sum all the graphs in that series that contain no nodal circles. The first, third, seventh, and eighth graphs are examples of such diagrams. If we insert the first and last of these into (1.2), we get an infinity of graphs, each one of which is an allowed diagram. But the third, fifth and sixth diagrams pictured in figure 2 present problems since their use in (1.2) will yield unallowed graphs like



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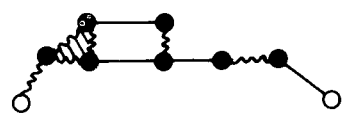
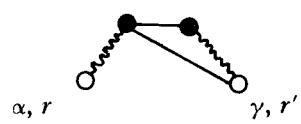


in addition to allowed contributions like



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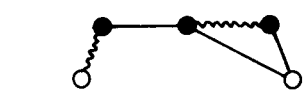
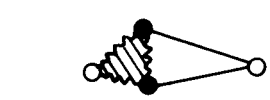


[The first two are described as 'unallowed' since they contain **s** circles intersected by more than one **s** vertex bond. For obvious reasons, such graphs are not found in the exact cluster series. For example, the first unallowed graph pictured above only approximately describes integrals which are properly described with



further, the first unallowed graph contains one integral in which a field point refers to the same site as the root point. That is to say, due to the summation over sites implied by the black circles, the field point not directly connected

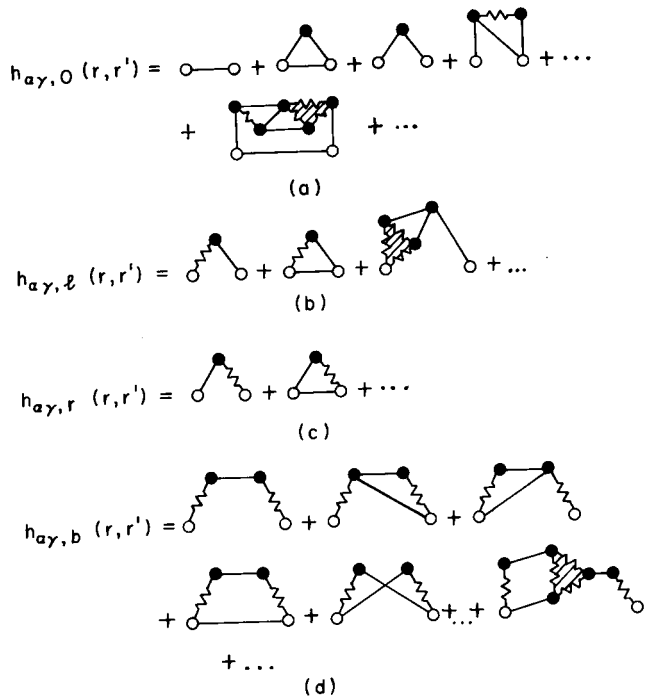


Figure 3. Cluster series for topologically distinct contributions to **h** as a function of **f** and the intramolecular distributions, ρ**s**. See caption to figure 2 for conventions. (*a*) Series for $\mathbf{h}_0$; (*b*) series for $\mathbf{h}_l$; (*c*) series for $\mathbf{h}_r$; (*d*) series for $\mathbf{h}_b$. In each diagram, the root circle on the left refers to site α at **r**, and the root circle on the right refers to site γ at **r**′.

to the root α will, for one term in the sum, be α. See [1] for thorough discussion of the distinctions between allowed and unallowed graphs.]

Since (1.2) forces us to add contributions that are not contained in the original series for $\mathbf{h}[\mathbf{f}, \rho\mathbf{s}]$, it follows that no topological reduction of the exact series can yield (1.2). Therefore, it is not possible to define $c_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ in terms of a subset of the topologies of diagrams contributing to $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$.

3. Topological reduction and a new integral equation

We now derive a generalization of (1.2) which does follow from a topological reduction Our analysis begins by separating the contributions to $\mathbf{h}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ into four classes of graphs:

$$\mathbf{h} = \mathbf{h}_0 + \mathbf{h}_l + \mathbf{h}_r + \mathbf{h}_b. \tag{3.1}$$

Here, **h** is the matrix with elements $h_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$; $\mathbf{h}_0$ is the sum of all graphs in **h** for which neither root is an **s** circle; $\mathbf{h}_l$ is the sum of all graphs for which the left root is an **s** circle [i.e. site α at position **r** in all the graphs contributing to $h_{\alpha\gamma,l}(\mathbf{r}, \mathbf{r}')$ is a white circle intersected by an s vertex bond]; $\mathbf{h}_r = \mathbf{h}_l^{\dagger}$ is the sum of all graphs for which the right root is an **s** circle; and $\mathbf{h}_b$ is the sum of all the graphs contributing to **h** for which both roots are **s** circles. The four diagrammatic series are illustrated in figure 3.

In each of these series, there are both nodeless diagrams and diagrams with one or more nodal circles. We shall define the set of auxiliary functions $\mathbf{c}_0$, $\mathbf{c}_l$, $\mathbf{c}_r$ and $\mathbf{c}_b$ as the sum of nodeless graphs contributing to $\mathbf{h}_0$, $\mathbf{h}_l$, $\mathbf{h}_r$ and $\mathbf{h}_b$, respectively. For example, the first, second and fourth diagrams in figure 3 (*a*) contribute to $\mathbf{c}_0$; the second in figure 3 (*b*) contributes to $\mathbf{c}_l$; the fourth and fifth diagrams in figure 3 (*d*) contribute to $\mathbf{c}_b$. Due to the topological characterization of these auxiliary functions, which we shall call direct correlation functions, it is straightforward to show that

$$\begin{aligned}\mathbf{h} &= (\mathbf{c}_0+\mathbf{c}_l+\mathbf{c}_r+\mathbf{c}_b)+(\text{sum of graphs with one or more nodes})\\ &= \text{sum of all allowed simple chains with two white circles, any number}\\ &\qquad\qquad \text{of black circles, } \mathbf{c}_0,\ \mathbf{c}_l,\ \mathbf{c}_r,\ \mathbf{c}_b \text{ and } \mathbf{s}^{(2)} \text{ bonds.}\end{aligned} \tag{3.2}$$

This sum is illustrated in figure 4. An 'allowed simple chain' is a singly connected chain between the two white root circles, and no circle can be intersected by more than one *s* vertex bond. This means that with the diagrammatic notation adopted in figure 4, we do not allow black circles of the following form:

The chain diagrams can be grouped and summed as shown in figure 5. In matrix notation, these equations are

$$\mathbf{h}_0 = \mathbf{c}_0 + \rho\mathbf{c}_0\mathbf{h}_0 + \rho\mathbf{c}_0\mathbf{h}_l + \rho\mathbf{c}_r\mathbf{h}_0, \tag{3.3 a}$$

$$\mathbf{h}_l = \mathbf{c}_l + \mathbf{s}^{(2)}\mathbf{h}_0 + \rho\mathbf{c}_b\mathbf{h}_0 + \rho\mathbf{c}_l\mathbf{h}_0 + \rho\mathbf{c}_l\mathbf{h}_l, \tag{3.3 b}$$

and

$$\mathbf{h}_b = \mathbf{c}_b + \mathbf{c}_l\mathbf{s}^{(2)} + \mathbf{s}^{(2)}\mathbf{h}_r + \rho\mathbf{c}_l\mathbf{h}_r + \rho\mathbf{c}_b\mathbf{h}_r + \rho\mathbf{c}_l\mathbf{h}_b. \tag{3.3 c}$$

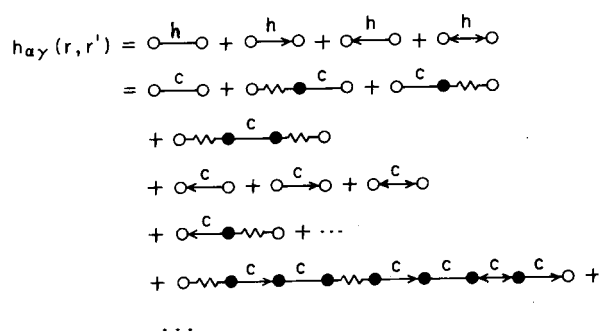


Figure 4. Cluster series for $\mathbf{h}$ as a functional of the four direct correlation functions, $\mathbf{c}_0$, $\mathbf{c}_l$, $\mathbf{c}_r$, $\mathbf{c}_b$, and of the intramolecular pair distribution functions, $\mathbf{s}^{(2)}$. The bonds labelled $\bigcirc\overset{c}{—}\bigcirc$, $\bigcirc\overset{c}{\rightarrow}\bigcirc$, $\bigcirc\overset{c}{\leftarrow}\bigcirc$ and $\bigcirc\overset{c}{\leftrightarrow}\bigcirc$ refer to $\mathbf{c}_0$, $\mathbf{c}_r$, $\mathbf{c}_l$, and $\mathbf{c}_b$, respectively. Similar conventions are used for the four components to $\mathbf{h}$, namely $\mathbf{h}_0$, $\mathbf{h}_l$, $\mathbf{h}_r$, and $\mathbf{h}_b$. In each diagram, the root circle on the left is for site α, $\mathbf{r}$, and the root on the right is for γ, $\mathbf{r}'$.

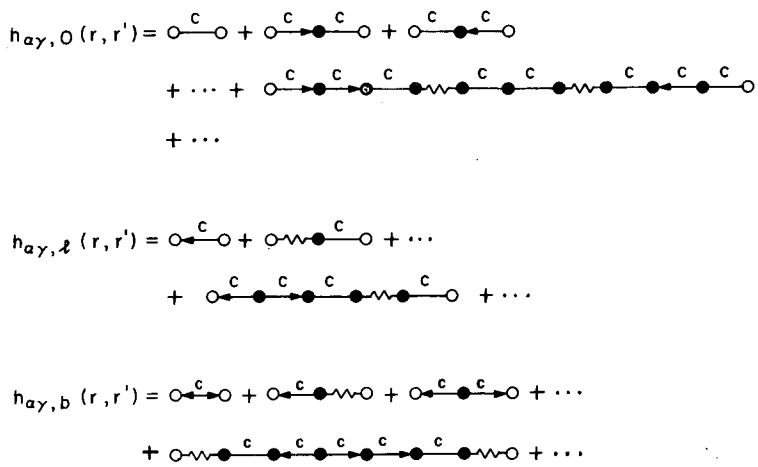


Figure 5. Cluster series for the topologically distinct components to h as functionals of $\mathbf{c}_0$, $\mathbf{c}_l$, $\mathbf{c}_r$, $\mathbf{c}_b$ and $\mathbf{s}^{(2)}$. See caption to figure 4 for notational conventions.

The solution of these equations is straightforward though tedious. The result is most easily stated by introducing the quantities

$$\begin{aligned}\mathbf{\Omega} &= (\mathbf{1}-\rho\mathbf{c}_l)^{-1}(\mathbf{1}+\mathbf{s}^{(2)}+\rho\mathbf{c}_b)(\mathbf{1}-\rho\mathbf{c}_r)^{-1}\\ &\equiv \mathbf{1}+\mathbf{s}^{(2)}+\Delta\mathbf{\Omega}.\end{aligned} \tag{3.4}$$

One finds

$$\boldsymbol{\omega}+\rho\mathbf{h} = (\mathbf{1}-\rho\mathbf{\Omega}\mathbf{c}_0)^{-1}\,\mathbf{\Omega} \tag{3.5}$$

or

$$\mathbf{h} = (\Delta\mathbf{\Omega}/\rho)+(\mathbf{1}-\rho\mathbf{\Omega}\mathbf{c}_0)^{-1}\,\mathbf{\Omega}\mathbf{c}_0\mathbf{\Omega} \tag{3.5$'$}$$

which is remarkable in its striking resemblance to (1.2). However, unlike (1.2), (3.5) follows from an exact topological reduction. When cast in the form of an integral equation, it takes the form

$$\mathbf{h} = \Delta\mathbf{\Omega}/\rho+\Omega\mathbf{c}_0(\boldsymbol{\omega}+\rho\mathbf{h}). \tag{3.5$''$}$$

Another way of deriving (3.5) begins by defining $\mathbf{\Omega}$ as

$\mathbf{\Omega} = \boldsymbol{\omega}+$(the sum of all allowed simple chains with one or more $\mathbf{c}_l$, $\mathbf{c}_r$, or $\mathbf{c}_b$ bonds, any number of $\mathbf{s}^{(2)}$ bonds and no $\mathbf{c}_0$ bonds). (3.6)

Equation (3.4) follows from this definition. Further, $\mathbf{\Omega}$ can be decomposed into a portion in which only the left root is an $\mathbf{s}$ circle,

$$\mathbf{\Omega}_l = \rho(\mathbf{1}-\rho\mathbf{c}_l)^{-1}\,\mathbf{c}_l, \tag{3.7 a}$$

a part in which only the right root is an $\mathbf{s}$ circle,

$$\mathbf{\Omega}_r = \rho(\mathbf{1}-\rho\mathbf{c}_r)^{-1}\,\mathbf{c}_r \tag{3.7 b}$$

and the remainder in which both roots are $\mathbf{s}$ circles,

$$\mathbf{\Omega}_b = \mathbf{s}^{(2)}+\rho\mathbf{c}_b+\mathbf{\Omega}_l\mathbf{\Omega}_r+\mathbf{\Omega}_l(\mathbf{s}^{(2)}+\rho\mathbf{c}_b)\mathbf{\Omega}_r+\mathbf{\Omega}_l(\mathbf{s}^{(2)}+\rho\mathbf{c}_b)+(\mathbf{s}^{(2)}+\rho\mathbf{c}_b)\mathbf{\Omega}_r. \tag{3.7 c}$$

Clearly,

$$\mathbf{\Omega} = \mathbf{1} + \mathbf{\Omega}_r + \mathbf{\Omega}_l + \mathbf{\Omega}_b. \tag{3.7 d}$$

Next, we introduce

$$\mathbf{H}_0 = (\mathbf{1} - \rho \mathbf{c}_0 \mathbf{\Omega})^{-1}\, \mathbf{c}_0, \tag{3.8}$$

which is the sum of all simple chains which begin and end with $\mathbf{c}_0$ bonds. With these definitions we have

$$\mathbf{h}_0 = (\mathbf{1} + \mathbf{\Omega}_r)\, \mathbf{H}_0 (\mathbf{1} + \mathbf{\Omega}_l), \tag{3.9 a}$$

$$\mathbf{h}_l = \rho^{-1}\, \mathbf{\Omega}_l + (\mathbf{\Omega}_l + \mathbf{\Omega}_b)\, \mathbf{H}_0 (\mathbf{1} + \mathbf{\Omega}_l), \tag{3.9 b}$$

$$\mathbf{h}_r = \rho^{-1}\, \mathbf{\Omega}_r + (\mathbf{1} + \mathbf{\Omega}_r)\, \mathbf{H}_0 (\mathbf{\Omega}_r + \mathbf{\Omega}_b), \tag{3.9 c}$$

and

$$\mathbf{h}_b = \rho^{-1}(\mathbf{\Omega}_b - \mathbf{s}^{(2)}) + (\mathbf{\Omega}_l + \mathbf{\Omega}_b)\, \mathbf{H}_0 (\mathbf{\Omega}_b + \mathbf{\Omega}_r). \tag{3.9 d}$$

By combining (3.8) and (3.9), we arrive again at (3.5), the principal result of this paper.

4. Approximate theories

Equations (3.5) and the definitions of the auxiliary functions provide an exact foundation for developing and improving upon approximate integral equations for the site–site correlation functions of a molecular fluid. As an example, we will construct here possible analogues of the Percus–Yevick theory [15].

Let the function $t_{\alpha\gamma}(r)$ be defined by the relation

$$h_{\alpha\gamma,0}(r) = [1 + f_{\alpha\gamma}(r)][1 + t_{\alpha\gamma}(r)] - 1. \tag{4.1}$$

Diagrammatically, $\mathbf{t}$ is the sum of all the indirect graphs contributing to $\mathbf{h}_0$ in the series with $\mathbf{f}$ bonds and $\mathbf{s}$ vertex bonds. Many of these graphs contain nodal circles, but if we multiply $t_{\alpha\gamma}(r)$ by $f_{\alpha\gamma}(r)$, all the graphs are direct and nodeless. Thus, a reasonable choice for $\mathbf{c}_0$ is

$$c_{\alpha\gamma,0}(r) \approx f_{\alpha\gamma}(r) + f_{\alpha\gamma}(r) t_{\alpha\gamma}(r), \tag{4.2 a}$$

which is equivalent to the approximation $\mathbf{h}_0 - \mathbf{c}_0 \approx \mathbf{t}$. In the same spirit, we can take

$$c_{\alpha\gamma,l}(r) \approx f_{\alpha\gamma}(r)(\mathbf{h}_l - \mathbf{c}_l)_{\alpha\gamma}(r), \tag{4.2 b}$$

and

$$c_{\alpha\gamma,b}(r) \approx f_{\alpha\gamma}(r)(\mathbf{h}_b - \mathbf{c}_b)_{\alpha\gamma}(r), \tag{4.2 c}$$

which can be combined with (3.5), (3.9) and $\mathbf{c}_l = \mathbf{c}_r^{\dagger}$ to yield a closed set of integral equations for the intermolecular correlation functions.

Figure 6 depicts these relations in diagrammatic form. In the low density limit, the integral equation theory formed with the closure relations (4.2) reduces to an approximation analysed in [1] where it is shown that this approximation is very accurate for hard core models of diatomic molecules. Outside of the low density limit, the integral equation theory sums all the allowed classes of graphs included in the RISM equation [7] and does not sum any unallowed graphs.

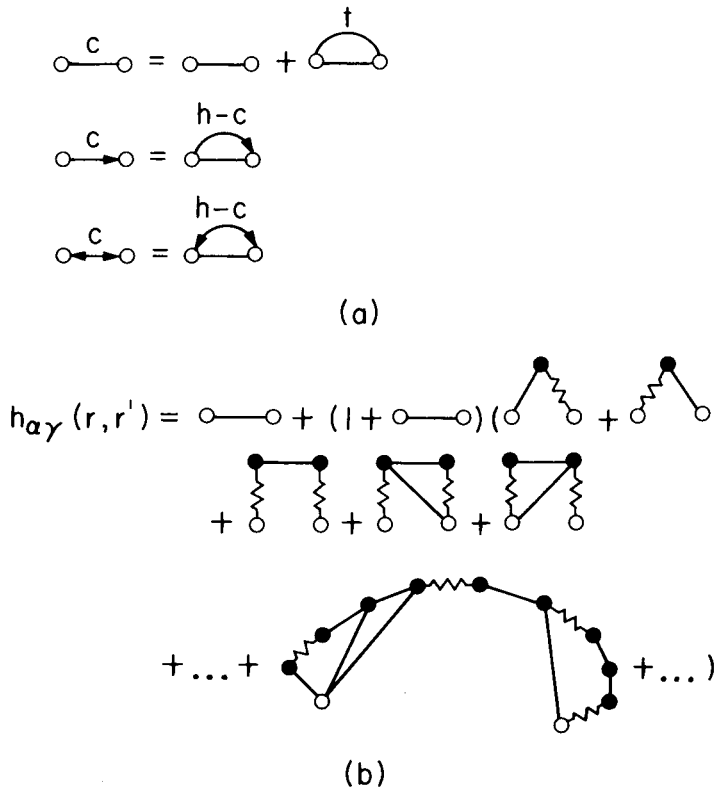


Figure 6. Approximate integral equation theory. (*a*) The closure relations, (*b*) resulting series with $\mathbf{s}^{(2)}$ bonds and $\mathbf{f}$ bonds. The unlabelled straight bonds refer to $\mathbf{f}$ bonds, while the functions $\mathbf{c}_0$, $\mathbf{c}_r$, $\mathbf{c}_b$, $\mathbf{h}_0$, $\mathbf{h}_l$, $\mathbf{h}_r$ and $\mathbf{t}$ are depicted with labelled bonds. All but the last diagram in (*b*) comprise the low density limit in this theory. The last pictured graph is sixth order in the density. For each diagram, the root circle on the left refers to site α, $\mathbf{r}$ and the root circle on the right refers to site γ, $\mathbf{r}'$.

Many other integral equation theories can be constructed in this way. For each case, a proper theory must distinguish the four topologically distinct direct correlation function matrices $\mathbf{c}_0$, $\mathbf{c}_l$, $\mathbf{c}_r$ and $\mathbf{c}_b$. The RISM theory based upon (1.2) does not make this distinction. For this reason, the RISM theory is somewhat simpler numerically though probably less accurate than many theories which employ (3.5).

Of course, one may always *define* a $\mathbf{c}$ such that the exact $\mathbf{h}$ is given by (1.2); this is merely a tautology unless another independent equation for $\mathbf{c}$ is given. Even when such an equation is given, the important question is whether $\mathbf{c}$ as defined in this way is a sum over a subset of graphs in $\mathbf{h}$, and is thus the result of a topological reduction. We can relate the RISM $\mathbf{c}$ of (1.2) to the four different direct correlation functions by comparing (1.2) and (3.5) and forcing the two to coincide. The comparison yields

$$\begin{aligned}\mathbf{c} &= \mathbf{c}_0 - \rho^{-1}(\mathbf{\Omega}^{-1} - \boldsymbol{\omega}^{-1}) \\ &= \mathbf{c}_0 + \mathbf{c}_r\boldsymbol{\omega}^{-1} + \boldsymbol{\omega}^{-1}\,\mathbf{c}_l \\ &\qquad + (\mathbf{1} - \rho\mathbf{c}_r)\boldsymbol{\omega}^{-1}\,\mathbf{c}_b(\mathbf{1} + \rho\boldsymbol{\omega}^{-1}\,\mathbf{c}_b)^{-1}\,\boldsymbol{\omega}^{-1}(\mathbf{1} - \rho\mathbf{c}_l) - \rho\mathbf{c}_r\boldsymbol{\omega}^{-1}\,\mathbf{c}_l. \qquad (4.3)\end{aligned}$$

Notice how the right-hand side of (4.3) both adds and subtracts diagrams. Presumably, the subtraction would account for the cancellation of unallowed diagrams that must occur in a proper theory [14]. By ignoring the topological distinctions between different contributions to **h** or **c**, one may arrive at theories like the RISM equation which can be considered as useful numerical compromises. But such theories will undoubtedly contain topologies of graphs which will not be found in an exact theory. We believe that for some applications the added numerical complexity of the new class of theories described herein may favour the use of the RISM equation. However in many circumstances, the additional complexity will not be significant enough to favour the compromise, and for these cases the new theories should provide an important advance in accuracy.

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