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Auxiliary sites in the RISM approximation for molecular fluids

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Received 6 October 1980

Abstract. One of the interesting features of the RISM approximation for molecular fluids is that the results of the theory show dependence on the presence or absence of auxiliary (i.e. non-interacting) sites. In this paper, this dependence is examined both analytically and numerically. Using graph-theoretical methods, the diagrammatic expansions for the site-site correlation functions are examined in great detail in order to explain the way in which the dependence on auxiliary sites arises in the RISM approximation. This provides considerable insight into the nature of the RISM approximation itself.

1. Introduction

Two basic approaches are currently being pursued in the theory of the structure of molecular fluids (Egelstaff *et al* 1975, Gray and Gubbins 1980). The first approach is based on the *angular* pair correlation function $g(12) = g(r_{12}\omega_1\omega_2)$, where r_{12} is the vector connecting the molecular centres of molecules 1 and 2, and $\omega_i = \theta_i\phi_i\chi_i$ are the Euler angles specifying the orientation of molecule i with respect to some axes (space-fixed or intermolecular). Various perturbation and integral equation approximations for calculating $g(12)$ have been devised (see, for example, the literature cited by Gray (1978a)). This approach has various advantages and disadvantages (Gray 1978b) with respect to the one considered in this paper.

The second approach to the structure of molecular fluids is based on the *site-site* pair correlation functions $g_{\alpha\beta}(r_{\alpha\beta})$ between two sites in different molecules (Chandler and Andersen 1972, Gubbins *et al* 1973). For the case[‡] that the intermolecular pair potential $u(12) = u(r_{12}\omega_1\omega_2)$ can be represented as a sum of atom-atom or site-site terms $u_{\alpha\beta}(r_{\alpha\beta})$, Chandler and Andersen (1972) have developed an integral equation method (the reference interaction site model—RISM) for calculating $g_{\alpha\beta}(r)$ approximately. The RISM theory consists of an integral equation (see (5) below) between the $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ and corresponding site-site direct correlation functions $c_{\alpha\beta}(r)$, together with some approximate closure relation. As originally developed, and most often applied to date, one chooses $u_{\alpha\beta}$ to be a hard sphere potential, and takes a Percus-Yevick (PY)-type closure for the $c_{\alpha\beta}$ (see (8b) below and ensuing discussion).

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[‡] For a discussion of the various assets and liabilities of the site-site model potential, see e.g. Downs *et al* (1979). Note however that the discussion of the angular dependence of the site-site model for $N_2 - Ar$ is incorrect there. We thank F Mulder for discussions of this point.

Thus we have

$$u(12) = \sum_{\alpha\beta} u_{\alpha\beta}(r_{\alpha\beta}) \quad (1)$$

where

$$u_{\alpha\beta}(r) = \infty, \quad r < \sigma_{\alpha\beta}, \\ = 0, \quad r > \sigma_{\alpha\beta}, \quad (2)$$

where $r_{\alpha\beta} = |\mathbf{r}_1^{(\alpha)} - \mathbf{r}_2^{(\beta)}|$, with $\mathbf{r}_i^{(\alpha)}$ the position of site α in molecule i , and $\sigma_{\alpha\beta}$ is the hard sphere diameter for sites α and β . This situation is depicted pictorially in figure 1. A 'site' in a molecule of fused hard spheres is normally associated with the centre of one of the hard spheres, although this need not necessarily be so. In the RISM approximation the molecules are usually assumed to be rigid; hence the parameters $l_{\alpha\beta} = |\mathbf{l}_i^{(\alpha)} - \mathbf{l}_i^{(\beta)}|$ are constants, where $\mathbf{l}_i^{(\alpha)}$ is the vector joining the centre (\mathbf{R}_i) and the site α of molecule i (cf figure 1).

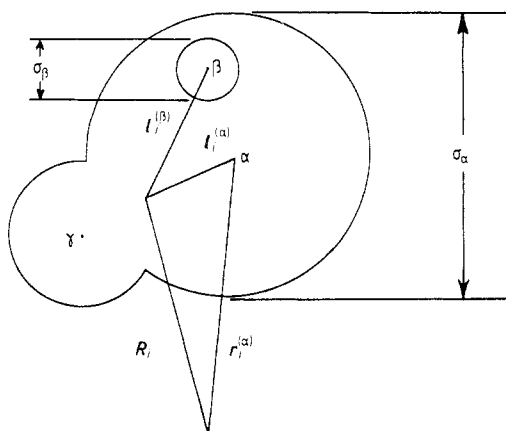


Figure 1. A typical RISM molecule—in this case a diatomic molecule with three sites. Site β is an auxiliary site.

The RISM approximation for molecular fluids enables the approximate evaluation of the site–site correlation functions $h_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = h_{\alpha\beta}(|\mathbf{r} - \mathbf{r}'|)$ defined in terms of $g(12)$ as (Ladanyi and Chandler 1975)

$$h_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \int d1 \int d2 h(12) \delta(\mathbf{r}_i^{(\alpha)} - \mathbf{r}) \delta(\mathbf{r}_i^{(\beta)} - \mathbf{r}') \quad (3)$$

where di is an abbreviation for $\Omega^{-1} \int d\mathbf{R}_i d\omega_i$, the integration over all positions and orientations of molecule i , Ω denotes the solid angle (i.e. $\Omega = 4\pi$ for linear molecules, $\Omega = 8\pi^2$ for nonlinear molecules) and $h(12)$, the molecular total correlation function, is given by

$$h(12) = g(12) - 1. \quad (4)$$

The RISM method for calculating the functions $h_{\alpha\beta}(r)$ consists of defining a site–site direct correlation function $c_{\alpha\beta}(r)$ via an extension to molecular fluids of the Ornstein–Zernike (OZ) equation for simple fluids (Ornstein and Zernike 1914). This matrix

equation, already shown (Stell *et al* 1980) to be simply the OZ equation transcribed into site-site language, has the following form in Fourier k -space:

$$\mathbf{h}(k) = \boldsymbol{\omega}(k)\mathbf{c}(k)\boldsymbol{\omega}(k) + \rho\boldsymbol{\omega}(k)\mathbf{c}(k)\mathbf{h}(k) \quad (5)$$

where $h_{\alpha\beta}(k) = [\mathbf{h}(k)]_{\alpha\beta}$ and $c_{\alpha\beta}(k) = [\mathbf{c}(k)]_{\alpha\beta}$ are the Fourier transforms of the functions $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$ respectively, ρ is the number density of molecules and

$$\begin{aligned} \omega_{\alpha\beta}(k) &= (\sin kl_{\alpha\beta})/kl_{\alpha\beta}, & \alpha \neq \beta, \\ &= 1, & \alpha = \beta. \end{aligned} \quad (6)$$

The function $\omega_{\alpha\beta}(k) = [\boldsymbol{\omega}(k)]_{\alpha\beta}$ is the Fourier transform of the intramolecular pair correlation function, $\omega_{\alpha\beta}(r)$, given by

$$\omega_{\alpha\beta}(r) = \delta_{\alpha\beta}\delta(r) + \frac{(1 - \delta_{\alpha\beta})}{4\pi l_{\alpha\beta}^2} \delta(r - l_{\alpha\beta}). \quad (7)$$

The RISM theory supplements the RISM OZ equation (5) with the closure relations

$$h_{\alpha\beta}(r) = -1, \quad r < \sigma_{\alpha\beta}, \quad (8a)$$

$$c_{\alpha\beta}(r) = 0, \quad r > \sigma_{\alpha\beta}, \quad (8b)$$

where the parameters $\sigma_{\alpha\beta}$ are defined in (2).

The RISM theory for molecular fluids is closely linked with the PY (Percus and Yevick 1958) approximation for hard spheres, where the atomic total and direct correlation functions ($h_{\text{HS}}(r)$ and $c_{\text{HS}}(r)$) satisfy the scalar OZ equation (Ornstein and Zernike 1914) in Fourier space,

$$h_{\text{HS}}(k) = c_{\text{HS}}(k) + \rho c_{\text{HS}}(k)h_{\text{HS}}(k), \quad (9)$$

and satisfy the closure relations

$$h_{\text{HS}}(r) = -1, \quad r < \sigma, \quad (10a)$$

$$c_{\text{HS}}(r) = 0, \quad r > \sigma, \quad (10b)$$

where ρ is the number density of atoms and σ is the hard sphere diameter. In certain limiting cases, the RISM approximation reduces to the PY approximation for hard spheres: clearly, one such case is that of a spherical molecule having one site only at its centre.

The RISM approximation enables the site-site correlation functions to be calculated in a computationally convenient fashion (Lowden and Chandler 1973), and has been applied to a large number of molecular fluids (e.g. Lowden and Chandler 1974), some of which can be regarded as models for quite complex molecules. In many of these applications, the RISM approximation has exhibited qualitative success in accounting for the *short-range* structural properties of the fluids studied; for exceptions see Streett and Tildesley (1978) and Murad *et al* (1979).

The RISM theory is an approximation to a formally exact treatment of molecular fluids where $u(12)$ satisfies (1) for general $u_{\alpha\beta}(r)$ (i.e. not restricted to hard sphere potentials); we shall refer to this formally exact treatment as the interaction site formalism (ISF). Ladanyi and Chandler (1975) have studied the ISF in great detail using diagrammatic expansions.

It is tempting to regard RISM as an approximation to the ISF for fused hard spheres in the same spirit that PY is an approximation to the formally exact Mayer cluster theory

(Hansen and MacDonald 1976) for the atomic fluid, an analogy reinforced by the similarity of the defining equations ((5), (8), (9) and (10)) for the two systems. To a certain extent, as shown in the Appendix, this is the case; however, the nature of molecular fluids is apparently such that the assumption of finite-ranged direct correlation functions (equation (8*b*)) is an approximation which leads to significantly larger errors in the case of fused hard spheres than it does for the atomic hard sphere fluid. This is evidenced by noting the following three facts.

(1) The agreement between the RISM results for the $h_{\alpha\beta}(r)$ and the results from machine simulation is considerably less satisfactory than that between the PY and simulation results for the atomic hard sphere fluid.

(2) As noted in the Appendix, the RISM approximation results not only in diagrams being dropped from $h_{\alpha\beta}(r)$, but also in the inclusion of an infinite class of diagrams at each order in density which are not allowed in the exact theory.

(3) Recently, it has been noted by Chandler (1978) (for G_2) and demonstrated by Sullivan and Gray (1981) that RISM gives incorrect results in evaluating the dielectric constant ϵ , and the angular correlation parameters G_l for linear molecules defined as

$$G_l = \rho \int P_l(\cos \gamma_{12}) h(r_{12}\omega_1\omega_2) \frac{d\omega_1}{4\pi} \frac{d\omega_2}{4\pi} dr_{12}, \quad (11)$$

where $P_l(x)$ is the Legendre polynomial of order l and γ_{12} is the angle between the symmetry axes of the two linear molecules. It has been shown (Sullivan and Gray 1981), by expressing G_l in terms of site-site correlation functions $h_{\alpha\beta}(r)$ and evaluating the latter in the RISM approximation, that G_1 is identically zero for any linear molecule, while G_2 is identically zero for any symmetric linear molecule. Neither of these results would be expected in a more exact treatment. The results of Sullivan and Gray (1981) are conditional only on the use of the RISM OZ equation and on the direct correlation functions decaying sufficiently fast to ensure that the Fourier transform of $c_{\alpha\beta}(r)$, $c_{\alpha\beta}(k)$, satisfies

$$c_{\alpha\beta}(k) = c_{\alpha\beta}^{(0)} + k^2 c_{\alpha\beta}^{(2)} + k^4 c_{\alpha\beta}^{(4)} + \dots \quad (12)$$

This will therefore, in particular, be the case for the RISM approximation for fused hard spheres, and will also be the case when various other closure approximations (Sullivan and Gray 1981, Cummings *et al* 1981) are employed, and in any extensions to soft-core potentials whenever the RISM OZ is used and (12) is satisfied.

In this paper we are interested in examining another anomaly of the RISM approximation which arises as a consequence of the errors introduced by the assumption (8*b*). This is the dependence on so-called 'auxiliary sites' i.e. an interaction site whose presence does not affect the total pair interaction $u(12)$ (Chandler 1973). In § 2, we examine the concept of an auxiliary site in detail and summarise the previously published results on the auxiliary site problem in both the ISF and RISM. Following this, in § 3, we examine, using the diagrammatic expansions given in the Appendix, the auxiliary site problem for the degenerate case of a single sphere with one auxiliary site; this problem makes possible a direct comparison between the ways in which RISM and ISF handle the auxiliary site problem. This analysis leads to conjectures regarding the sizes of auxiliary sites allowed in RISM which have the physical property of leaving results for correlations between real (non-auxiliary) sites unchanged; these conjectures are pursued in § 4 for a symmetric diatomic molecule.

Note that we expect that there will be dependence on auxiliary sites not only with the closure (8*b*), but also with any *approximate* closure to the RISM OZ equation; on the

other hand, the defects noted in (3) above can be remedied (in the sense that G_1, G_2 and ε are rendered non-trivial) by an improved (but nevertheless approximate) closure (see Sullivan and Gray 1981).

2. Auxiliary sites in RISM

An auxiliary site in the ISF is characterised by the following property of the intermolecular potential:

$$u(12)_{\text{with auxiliary site}} = u(12)_{\text{without auxiliary site}} \tag{13}$$

Consequently, in any rigorous theory, the inclusion of an auxiliary site can have no effect on the correlation functions of the fluid. That is, if α and β are real (non-auxiliary) sites we have

$$h_{\alpha\beta}(r)_{\text{with auxiliary sites}} = h_{\alpha\beta}(r)_{\text{without auxiliary sites}} \tag{14}$$

An example of an auxiliary site problem which received considerable attention in the work of Ladanyi and Chandler (1975) is that of a sphere (the centre of which is the only real site, site 1) with an arbitrary number of auxiliary sites (labelled 2, 3, . . . , m). The geometry of this problem is shown in figure 2.

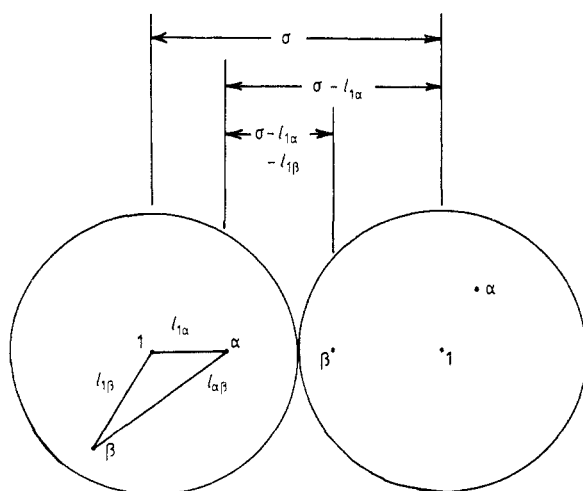


Figure 2. Two spheres with auxiliary sites shown with the real sites (sites 1 in each sphere) at their distance of closest approach.

It is clear that sites 2 to m remain auxiliary provided the site-site potentials satisfy

$$\begin{aligned} u_{\alpha\beta}(r) &= \infty, & r < \sigma_{\alpha\beta}, \\ &= 0, & r > \sigma_{\alpha\beta}, \end{aligned} \tag{15}$$

where

$$\sigma_{11} = \sigma, \quad \sigma_{1\alpha} = \sigma_{\alpha 1} \leq \sigma - l_{1\alpha}, \quad \sigma_{\alpha\beta} \leq \sigma - l_{1\alpha} - l_{1\beta}, \tag{16}$$

and σ is the diameter of the enveloping hard sphere.

In the ISF, it is clear that the result for $h_{\alpha\beta}(r)$ must be the same for all values of $\sigma_{\alpha 1}$ and $\sigma_{\alpha\beta}$ up to and including the limits in (16). Hence the results for $h_{\alpha\beta}(r)$ can be obtained by setting $\sigma_{1\alpha} = \sigma_{\alpha\beta} = 0$ for all $2 \leq \alpha, \beta \leq m$. Considering the expansion for $h_{\alpha\beta}(r)$ given in the Appendix (equation (A5)) it is straightforward to derive that (see Ladanyi and Chandler (1975, p 4317) for details)

$$h_{\alpha\beta}(k) = \omega_{1\alpha}(k)\omega_{1\beta}(k)h_{\text{HS}}(k) \quad (17)$$

where $h_{\text{HS}}(k)$ is the Fourier transform of the total correlation function for hard spheres of diameter σ and at density ρ , and $\omega_{\alpha\beta}(r)$ is defined in (7). Note that $\omega_{\alpha\beta}(r)$ is simply related to $s_{\alpha\beta}^{2/m}(r)$ defined in the Appendix (equation (A5)) by

$$\omega_{\alpha\beta}(r) = \delta_{\alpha\beta}\delta(r) + (1 - \delta_{\alpha\beta})s_{\alpha\beta}^{2/m}(r). \quad (18)$$

In particular, therefore, (17) implies (14) holds for $\alpha\beta = 11$.

It must be emphasised at this stage that (17) is derived by noting that in the formally exact ISF the auxiliary site results are independent of the diameters of the auxiliary sites provided that the inequalities (16) are satisfied, and hence can be derived for *all* cases by considering the *particular* set of $\sigma_{\alpha\beta}$ chosen ($\sigma_{1\alpha} = \sigma_{\alpha\beta} = 0$) to satisfy these inequalities.

In an approximate theory such as RISM we are no longer assured that, given (13), (14) follows. Hence for the particular case of the sphere with auxiliary sites it does not automatically follow that (17) holds (for some appropriate approximate $h_{\text{HS}}(k)$) given that the inequalities (16) hold. However, it has been pointed out by Ladanyi and Chandler (1975, p 4321) that the RISM approximation for a sphere with auxiliary sites yields

$$[h_{\alpha\beta}(k)]_{\text{RISM}} = \omega_{1\alpha}(k)\omega_{1\beta}(k)h^{\text{PY}}(k), \quad (19a)$$

$$[c_{\alpha\beta}(k)]_{\text{RISM}} = \delta_{1\alpha}\delta_{1\beta}c^{\text{PY}}(k), \quad (19b)$$

where $h^{\text{PY}}(k)$ and $c^{\text{PY}}(k)$ are the PY approximations for $h_{\text{HS}}(k)$ and $c_{\text{HS}}(k)$ respectively. This result cannot be derived directly in any obvious way; it must be accepted as being suggested by (17) or by the numerical solution using the Lowden programs (Lowden 1975). However, it can be verified analytically by noting that (19b) ensures that the closure (8b) is satisfied trivially, and inversion of (19a) to real space yields

$$h_{\alpha\beta}(r) = -1, \quad r < \sigma - l_{1\alpha} - l_{1\beta}, \quad (20a)$$

$$h_{1\alpha}(r) = -1, \quad r < \sigma - l_{1\alpha}. \quad (20b)$$

This ensures that the closure (8a) is satisfied. Since (19a) and (19b) also satisfy the RISM OZ equation, and we assume that the solution is unique, then (19) represents *the* solution of the RISM problem for the sphere with auxiliary sites.

The case of a sphere with auxiliary sites is unique in a number of ways: first, it represents the only auxiliary site problem in which the site-site correlation between real sites is unaffected by the presence of auxiliary sites in the RISM approximation; secondly, we see that, in the ISF, the solution to the RISM OZ equation for $c_{\alpha\beta}(r)$ in the present case is simply given by (19b), where $c^{\text{PY}}(k)$ is replaced by its exact hard sphere counterpart (this latter observation suggests that improvements to RISM can be made by more appropriate closures for $c_{\alpha\beta}(r)$); finally, it represents the only m -site RISM problem ($m > 1$) where an analytic solution has been found.

In the case of a symmetric diatomic molecule with an auxiliary site situated at the midpoint of the line joining the two real sites (sites 1 and 2) (the geometry of this

problem is shown in figure 3), the following observations were made by various authors (Hsu *et al* 1976, Hazoumé 1978, Chandler *et al* 1977).

(i) Whilst in the ISF there should be no dependence on the third auxiliary site provided

$$\sigma_{23} = \sigma_{13} \leq (\sigma_{11}^2 - l_{12}^2/4)^{1/2}, \quad \sigma_{33} \leq (\sigma_{11}^2 - l_{12}^2/2)^{1/2} \quad (21)$$

(the upper limits in (21) represent physically the distances of closest approach for interactions involving auxiliary sites), RISM does show dependence on the auxiliary sites for σ_{23} , σ_{33} in the ranges given in (21) (Hsu *et al* 1976).

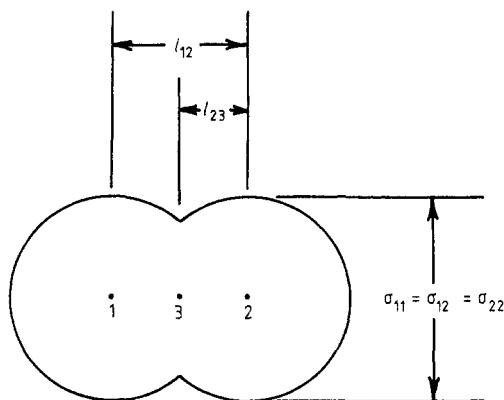


Figure 3. A symmetric diatomic molecule with two real sites (sites 1 and 2) and an auxiliary site (site 3) located at the centre of the molecule.

(ii) On the basis of comparison with simulation undertaken by Chandler *et al* (1977), Hazoumé (1978) concluded that the inclusion of an auxiliary site with interaction distances given by the upper limits in (21) leads to an improvement in the site-site correlation functions between real sites (i.e. $h_{11} = h_{12} = h_{21} = h_{22}$).

Although not discussed by these authors, there are a number of interesting questions regarding the auxiliary site problem for a diatomic molecule.

(1) Consider the particular case of the inequalities given in (21) when

$$\sigma_{13} = \sigma_{23} = \sigma_{33} = 0 \quad (22)$$

which in turn (via (8b)) yields

$$c_{13}(r) = c_{23}(r) = c_{33}(r) = 0 \quad \text{for all } r. \quad (23)$$

Substitution of this closure into the RISM OZ equation for a three-site problem yields

$$h_{11}(r) = h_{12}(r) = h_{21}(r) = h_{22}(r) = h_{ss}^{(d)}(r) \quad (24)$$

where $h_{ss}^{(d)}(r)$ is the site-site correlation function calculated via RISM for a symmetric diatomic molecule without an auxiliary site. Hence the RISM approximation satisfies (14) for at least one set of values of σ_{13} , σ_{23} , σ_{33} : an interesting question is: over what, if any, range of values for σ_{13} , σ_{23} , σ_{33} is (14) satisfied?

(2) What is the essential difference between the case of a sphere with auxiliary sites and a diatomic with an auxiliary site such that (14) is satisfied in RISM for the first case and not the second?

(3) Why should the site-site correlation functions calculated with interaction sites of physical diameter be superior to those calculated without auxiliary sites?

The answers to these questions are dealt with in the remainder of this paper. It turns out that by examining question (2) first, predictions can be made regarding the answer to question (1), and valuable insight is gained into the answer to question (3). Hence in § 3 we examine in detail the success of RISM in showing no dependence on auxiliary sites for the case of a sphere with auxiliary sites. In § 4, questions (1) and (3) are then dealt with in detail.

3. A sphere with an auxiliary site

In this section we consider the way in which the ISF and RISM deal with the case of a sphere with a single auxiliary site. The reason for considering this case is to simplify the graphical manipulation (although it is easily extended to cases where there is more than one auxiliary site), and to make the RISM/ISF comparison as straightforward as possible, since in higher-order problems it would be necessary to discuss $s_{\alpha\beta\dots\gamma}^{n/m}$ -bonds, $2 < n < m$ (refer to Appendix (A6)), which are not present in RISM.

It is our intention here to demonstrate that the RISM approximation shows no dependence on auxiliary sites for the problem under discussion, somewhat fortuitously: the most favourable result for RISM would be that it shows the correct behaviour because the class of diagrams it omits (APII, Appendix) and the class of diagrams it incorrectly includes (APIII, Appendix) are both trivially zero for the case of a sphere with an auxiliary site. If this were the case, then RISM's success for the present auxiliary site problem could be considered a strong point in favour of RISM, since it would mean that essentially RISM mimics the ISF in its treatment of this auxiliary site problem. Unfortunately we find that this is not the case.

The arguments leading to this conclusion unavoidably involve diagrammatic expansions in a detailed way. Our intention is to compare the ways in which the ISF and RISM expansions for $h_{11}(r)$ reduce to the expansion for $h_{HS}(r)$ and $h^{PY}(r)$ respectively. This comes about through widespread cancellation of graphs in each expansion.

To understand this cancellation, it is necessary to consider briefly the way in which the diagrams in the ISF expansion are obtained. We begin by noting that, in the case of any two-site problem, the molecular Mayer f -function can be written in terms of the site-site Mayer f -functions (see the Appendix, (A2)–(A4)) as

$$f(12) = f_{11} + e_{11}(f_{12} + f_{21} + f_{22} + f_{12}f_{22} + f_{21}f_{22} + f_{12}f_{21} + f_{12}f_{21}f_{22}) \quad (25)$$

where $f_{\alpha\beta}$ is shorthand for $f_{\alpha\beta}(r_{\alpha\beta})$ and $e_{11}(r)$ for the HS case is given by

$$\begin{aligned} e_{11}(r) = f_{11}(r) + 1 &= 0, & r < \sigma, \\ &= 1, & r > \sigma. \end{aligned} \quad (26)$$

Physically, it is straightforward now to see that $f(12)$ reduces to $f_{11}(r)$ only, since for $\alpha\beta \neq 11$ $f_{\alpha\beta}(r_{\alpha\beta})$ is non-zero only if $r_{\alpha\beta} < \sigma_{\alpha\beta} \leq -l_{1\alpha} - l_{1\beta}$ (note that for the present purposes it is convenient to consider that $l_{11} = 0$; cf (20)). From figure 2 it is clear that for any of the $f_{\alpha\beta}$ to be non-zero, $|\mathbf{r}_1^{(1)} - \mathbf{r}_2^{(1)}| < \sigma$. However, this is precisely the range over which $e_{11}(|\mathbf{r}_1^{(1)} - \mathbf{r}_2^{(1)}|)$ is zero; thus

$$f(12) \equiv f_{11}(|\mathbf{r}_1^{(1)} - \mathbf{r}_2^{(1)}|) = f_{11}(r). \quad (27)$$

Hence we expect that the ISF expansion for $h_{11}(r)$ should reduce to $h_{HS}(r)$ through the cancellation of all graphs generated in the site-site formalism except those required in the Mayer cluster expansion for $h_{HS}(r)$.

To follow the cancellation through to the level of the diagrammatic expansions, it is easiest to produce two expansions: one which arises from the use of both (25) and (26) in the definition for $h_{\alpha\beta}(r, r')$ (equation (3)), which leads to the expansion given in the Appendix (equation (A5)) in terms of $f_{\alpha\beta}$ -bonds alone; the second comes from using (25) only, which leads to an expansion in terms of $f_{\alpha\beta}$ -bonds and e_{11} -bonds. From the above discussion it is clear that all the diagrams containing e_{11} -bonds must have value zero; moreover it is clear from (25) that each diagram containing one e_{11} -bond may be obtained as the sum of two diagrams which differ only through the absence of an f_{11} -bond. This principle will be used to demonstrate the differences between the ISF and RISM treatments of the present auxiliary site problem.

Consider the ISF expansion for $h_{11}(r)$ at order ρ^0 : the diagrams contained in this expansion are shown in figure 4. It is straightforward at this level to see the cancellation mechanism: for example, diagrams 2 and 3 differ only by the absence and presence of an f_{11} -bond between the root (white) circles. Thus the sum of diagrams 2 and 3 is the diagram



where --- symbolises an e_{11} -bond, — an f -bond and $\text{---}\bigcirc\text{---}$ an $s^{2/2}$ -bond. That such a diagram is zero can be readily seen by noting that the black circle must be a 2-site (since sites at the ends of $s^{2/m}$ -bonds must be different). The integral corresponding to this diagram is thus

$$\int f_{12}(|\mathbf{x}|)s_{21}^{2/2}(|\mathbf{r}-\mathbf{x}|)e_{11}(|\mathbf{r}|) d\mathbf{x} \tag{29}$$

The s -bond function is given by (see the Appendix, equation (A6))

$$s_{21}^{2/2}(|\mathbf{r}-\mathbf{x}|) = \delta(|\mathbf{r}-\mathbf{x}|-l_{12})/4\pi l_{12}^2. \tag{30}$$

From (30), it can be seen that the effect of the $s_{21}^{2/2}$ -bond is to restrict the 2-site to lie on a sphere, radius l_{12} , centred at the root-point $2^{(1)}$. For our present purpose let us label the circles in the diagram (28) with letters as follows:



Hence the effect of the $s_{21}^{2/2}$ -bond in the integral (29) is to require that $BC = l_{12}$, where BC denotes the distance between the points B and C in the diagram (31). Similarly, from the discussion above concerning the non-zero range of $f_{\alpha\beta}$ it is clear that $AC < \sigma_{12} < \sigma - l_{12}$. Hence, from the triangle inequality

$$AB < AC + CB < \sigma - l_{12} + l_{12} = \sigma. \tag{32}$$

But for $AB < \sigma$, $e_{11}(|\mathbf{r}|)$ is zero (cf (26)); thus the integral (29) is zero. Consequently diagrams 2 and 3 in the ISF site-site cluster series for $h_{11}(r)$ cancel.

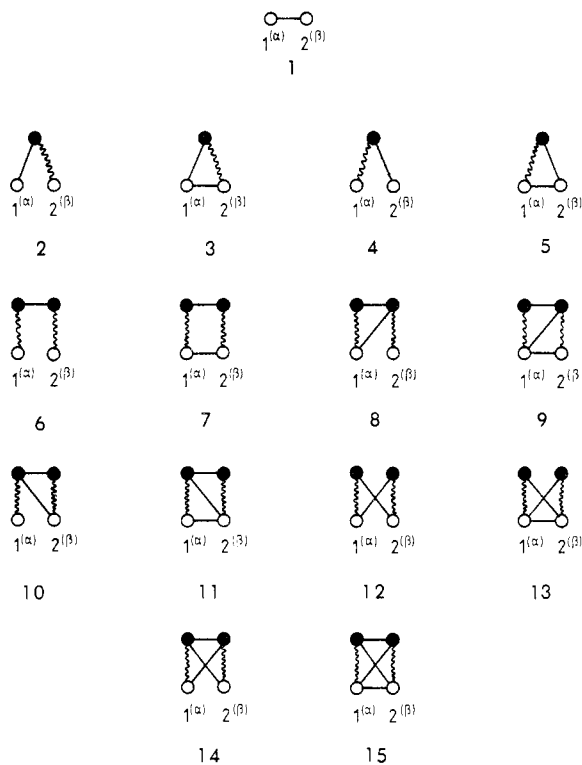


Figure 4. The diagrams generated in the ISF for a two-site problem by the molecular diagram $\bigcirc\text{---}\bigcirc$. Diagrams 12–15 inclusive are dropped in the RISM approximation.

Similar arguments to these may be provided for all the cancellations examined in this section; however, we will not go into any further details on the cancellations involved in this section, since they are easily derived by comparing the expansion for $h_{11}(r)$ in terms of f - and s -bonds only with that for $h_{11}(r)$ in terms of f -, s - and e_{11} -bonds. The argument we have given above is simply a reflection of that cancellation.

In table 1 we have given the complete cancellation table for the graphs in the ISF at order ρ^0 . As can be seen, the expected result is obtained—i.e. that the molecular diagram $1\text{---}2$ has precisely the value of the single diagram $1^{(1)}\text{---}2^{(1)}$, which is the first term in the Mayer cluster expansion for the $h_{HS}(r)$. Also it can be seen that the diagrams in figure 4 which are dropped in RISM (diagrams 12, 13, 14, 15) constitute a self-cancelling subset of the ISF. It is not difficult to see that the additional infinite set of diagrams summed in RISM (cf the Appendix) are self-cancelling as well, since they will

Table 1. Cancellation between pairs of site-site ISF diagrams given in figure 4.

| | | | |
|---|------------------|---|-----------------|
| $\left. \begin{array}{l} 2, 3 \\ 4, 5 \\ 6, 7 \\ 8, 9 \\ 10, 11 \end{array} \right\}$ | Retained in RISM | $\left. \begin{array}{l} 12, 13 \\ 14, 15 \end{array} \right\}$ | Dropped in RISM |
|---|------------------|---|-----------------|

occur in pairs of diagrams which are identical except for the presence or absence of an f_{11} -bond connecting the white circles.

Hence we have the following result:

$$\lim_{\rho \rightarrow 0} h_{11}(r) = \lim_{\rho \rightarrow 0} h_{HS}(r), \quad \lim_{\rho \rightarrow 0} [h_{11}(r)]_{RISM} = \lim_{\rho \rightarrow 0} h^{PY}(r). \quad (33)$$

At this point it is tempting to regard the process observed at order ρ^0 to be carried through at each order in density, hence yielding the known results discussed in § 2. If the process were to continue in this manner, RISM would have to be regarded in a very favourable light: the implication would be that in this auxiliary site problem RISM yields the physically correct result—i.e. (14)—because the contributions dropped in RISM (APII, Appendix) are trivially zero for the auxiliary site problem and the infinite class of disallowed diagrams additionally summed in RISM (APIII, Appendix) is also trivially zero.

That this is not the case is illustrated by considering the molecular diagram



which is $O(\rho^1)$. In the ISF for a two-site problem, this diagram generates 117 topologically distinct diagrams shown in figures 5 and 6. Since the black circles represent sums over possible sites, each diagram (except for those marked with an asterisk) corresponds to the sum of two diagrams with the black sites labelled. Some examples of this labelling are shown in figure 7.

Using the same principles as those used above at $O(\rho^0)$, a cancellation table can be drawn up and is shown in table 2. For the ISF the expected result is obtained—i.e. that all the diagrams generated by the molecular diagram (34) cancel, leaving the single diagram 1(f), which is precisely the diagram in the cluster expansion for $h_{HS}(r)$ to which diagram (34) corresponds. (The cancellation pairs given in table 2 can be checked by using the graphical results given in equations (40) below.)

The significant feature of table 2 which is different from table 1 is that *the diagrams dropped in RISM no longer form a self-cancelling subset of the ISF diagrams*. Hence, in order for the RISM approximation to show no dependence on the auxiliary site in this case, the diagrams in RISM, which in the ISF cancel with non-RISM graphs, must now cancel with a subset of the infinite set of disallowed diagrams (APIII, Appendix) which are additionally summed in RISM. (Note that there are a small number of additional cancellations possible among the allowed RISM graphs—e.g. 5(b), 20(f); 25(f), 26(f); 42(f), 44(f); 41(f), 45(f). Such cancellations are not expected, however, to reflect the true cancellation in RISM, since some hinge crucially on the restriction to a two-site problem and hence do not explain the cancellation in RISM in the problem of a sphere with more than one auxiliary site.) Plausible cancellations between these allowed RISM graphs and the disallowed infinite set are easily imagined. For example, consider 25(f): a plausible cancellation can be found by pairing this diagram with the diagram



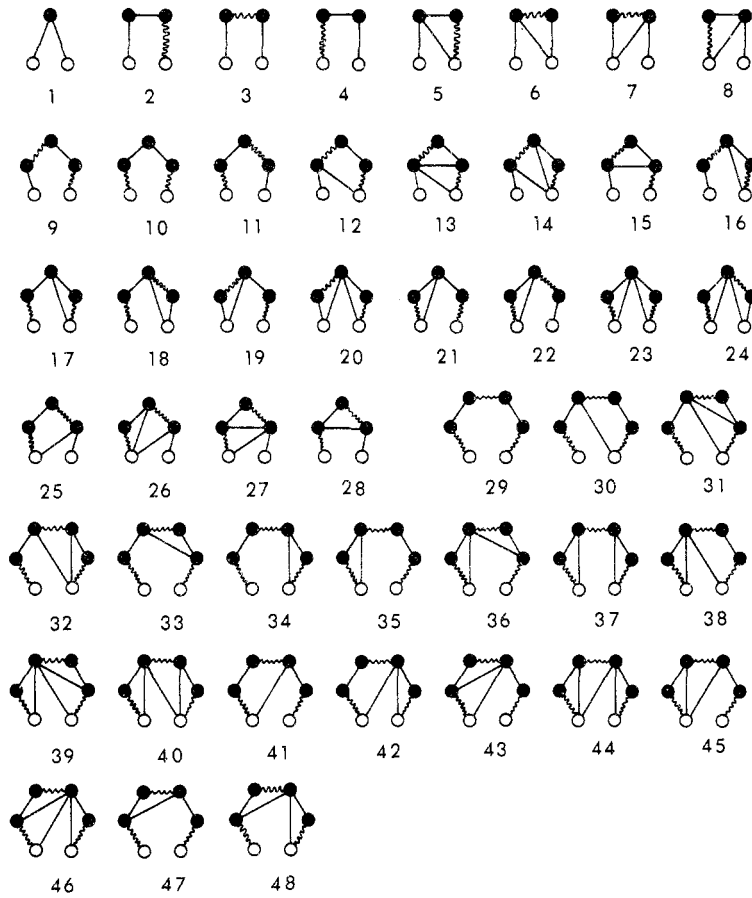



Figure 5. The diagrams generated by the molecular diagram  in the ISF for a two-site problem that are retained in the RISM approximation.

To verify this, consider any function $p(r)$ with the property

$$p(r) = 0, \quad r > R, \quad R < \sigma - l_{1\alpha}, \tag{36}$$

and consider also the function

$$P(r) = p(r) \int f_{11}(x) s_{1\alpha}^{2/2}(|\mathbf{x} - \mathbf{r}|) dx \tag{37}$$

where $r = |\mathbf{r}|$. Then from Ladanyi and Chandler (1975, equation (3.7)) we have

$$P(r) = p(r) \frac{1}{2rl_{1\alpha}} \int_{|r-l_{1\alpha}|}^{r+l_{1\alpha}} dx x f_{11}(x). \tag{38}$$

For $r < R < \sigma - l_{1\alpha}$, $r + l_{1\alpha} < \sigma$ and $f_{11}(x)$ takes the value -1 . Hence the integral in (37) may be performed, yielding

$$P(r) = -p(r), \quad r < R. \tag{39}$$

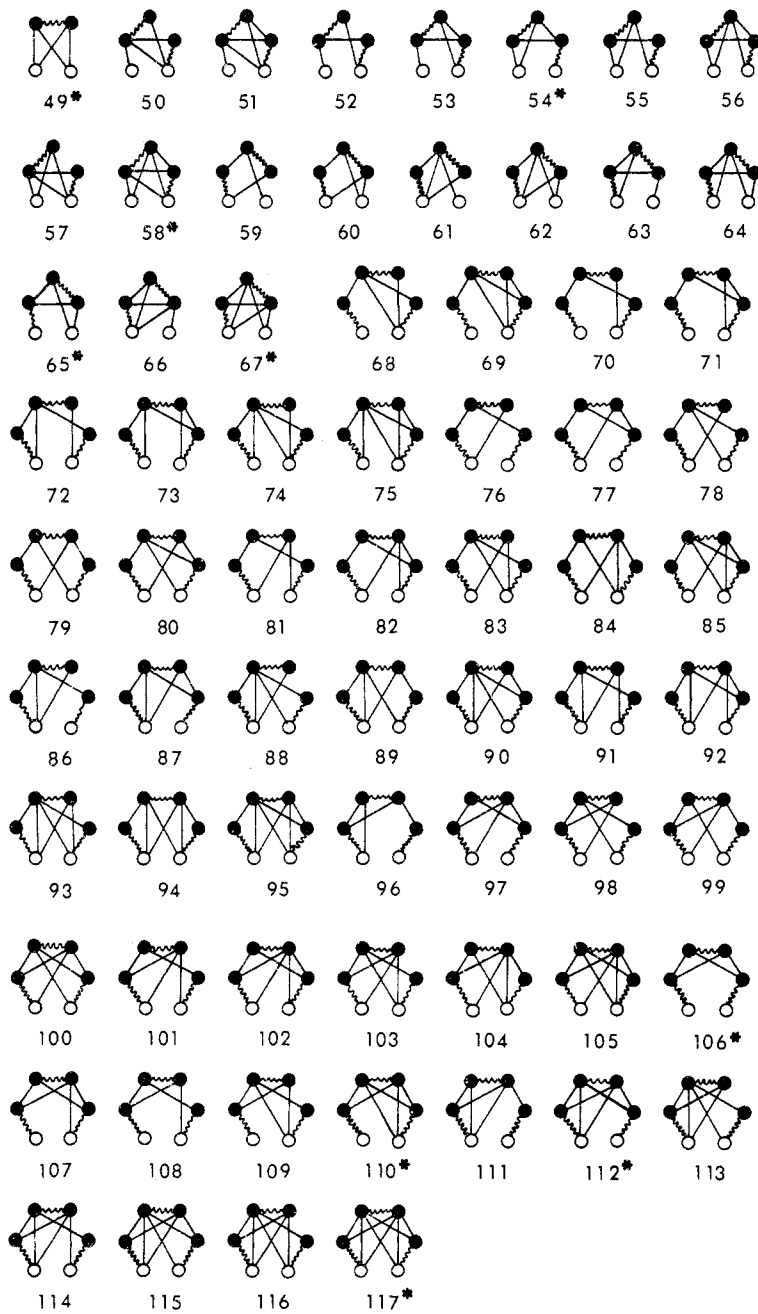



Figure 6. Diagrams generated by the molecular diagram  in the ISF for a two-site problem which are dropped in the RISM approximation. Diagrams marked with an asterisk have only one distinct labelling (refer to text, § 3).

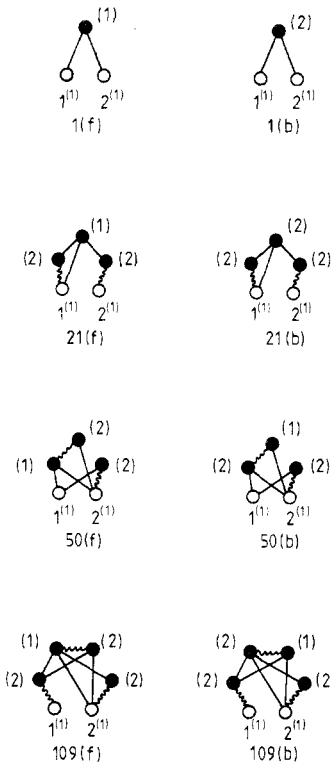


Figure 7. Examples of forward (f) and backward (b) labelling of the diagrams in figures 5 and 6. The labelling is done as follows: since $s^{2/2}$ -bonds have different sites at each end, the black circles at the end of an $s^{2/2}$ -bond which is rooted to a $1^{(1)}$ or $2^{(1)}$ white circle are labelled (2). The diagram is then traversed clockwise starting at the $1^{(1)}$ white circle, labelling the unlabelled black circles in a *forward* fashion ((1)(2)) or *backwards* ((2)(1)).

Hence $P(r) = -p(r)$ for all r , since $P(r)$ will also be zero wherever $p(r)$ is zero. The $f_{1\alpha}$ and the convolution of $s_{1\alpha}$ with $f_{\alpha\beta}$ both satisfy criterion (36). Hence we have the following diagrammatic results:

$$\begin{array}{c}
 \begin{array}{c} (1) \\ \bullet \\ / \quad \backslash \\ \circ \quad \circ \\ (1) \quad (\alpha) \end{array} = \begin{array}{c} - \\ \circ \quad \circ \\ (1) \quad (\alpha) \end{array} \quad (40)
 \end{array}$$

$$\begin{array}{c}
 \begin{array}{c} (\alpha) \quad (1) \\ \bullet \quad \bullet \\ / \quad \backslash \\ \circ \quad \circ \\ (1) \quad (\beta) \end{array} = - \begin{array}{c} (\alpha) \\ \bullet \\ / \quad \backslash \\ \circ \quad \circ \\ (1) \quad (\beta) \end{array} \quad (40b)
 \end{array}$$

Using similar arguments, it is easily shown that

$$\begin{array}{c}
 \begin{array}{c} (1) \quad (1) \\ \bullet \quad \bullet \\ / \quad \backslash \\ \circ \quad \circ \\ (\alpha) \quad (\beta) \end{array} = \begin{array}{c} - \\ \circ \quad \circ \\ (\alpha) \quad (\beta) \end{array} \quad (40c)
 \end{array}$$

Table 2. Cancellation between pairs of site–site ISF diagrams generated by the molecular diagram (34) as given in figures 5 and 6. Diagrams retained in the RISM approximation are underlined. The diagrams in boxes are labelling-direction independent (cf figure 6).

| | | | |
|-----------------|------------------|-------------------|---------------------|
| 1(b), 6(b) | 23(b), 74(b) | 46(f), 104(f) | 82(f), 85(f) |
| 2(f), 5(f) | 25(f), 60(f) | 47(f), 108(b) | 86(f), 88(f) |
| 2(b), 19(f) | 26(f), 62(f) | 47(b), 48(b) | 86(b), 91(b) |
| 3(f), 6(f) | 27(f), 64(b) | 48(f), 109(b) | 87(f), 90(f) |
| 3(b), 7(b) | 27(b), 28(b) | 50(f), 52(f) | 87(b), 92(b) |
| 4(f), 8(f) | 28(f), <u>65</u> | 51(f), 53(f) | 88(b), 93(b) |
| 4(b), 18(b) | 29(f), 30(f) | 52(b), 55(b) | 89(b), 94(b) |
| 5(b), 50(b) | 29(b), 34(b) | <u>54</u> , 56(b) | 90(b), 95(b) |
| 7(f), <u>49</u> | 30(b), 32(b) | 55(f), 57(f) | 91(f), 93(f) |
| 8(b), 24(b) | 31(f), 33(f) | 56(f), <u>58</u> | 92(f), 95(f) |
| 9(f), 12(f) | 31(b), 69(b) | 59(f), 61(f) | 96(f), 101(b) |
| 9(b), 16(b) | 32(f), 34(f) | 59(b), 60(b) | 96(b), 98(f) |
| 10(f), 17(f) | 33(b), 71(b) | 61(b), 62(b) | 97(f), 100(f) |
| 10(b), 70(b) | 35(f), 38(f) | 63(f), 64(f) | 97(b), 102(b) |
| 11(f), 18(f) | 35(b), 37(b) | 63(b), 66(b) | 98(b), 103(b) |
| 11(b), 25(b) | 36(f), 39(f) | 66(f), <u>67</u> | 99(b), 104(b) |
| 12(b), 14(b) | 36(b), 73(b) | 68(f), 70(f) | 100(b), 105(b) |
| 13(f), 15(f) | 37(f), 40(f) | 69(f), 71(f) | 101(f), 103(f) |
| 13(b), 51(b) | 38(b), 40(b) | 72(f), 74(f) | 102(f), 105(f) |
| 14(f), 16(f) | 39(b), 75(b) | 73(f), 75(f) | <u>106</u> , 107(b) |
| 15(b), 53(b) | 41(f), 79(f) | 76(f), 78(f) | 107(f), <u>110</u> |
| 17(b), 68(b) | 41(b), 42(b) | 76(b), 81(b) | 108(f), 109(f) |
| 19(b), 20(b) | 42(f), 84(f) | 77(f), 80(f) | 111(f), 114(b) |
| 20(f), 57(b) | 43(f), 99(f) | 77(b), 82(b) | 111(b), 113(f) |
| 21(f), 23(f) | 43(b), 46(b) | 78(b), 83(b) | <u>112</u> , 115(f) |
| 21(b), 72(b) | 44(f), 94(f) | 79(b), 84(b) | 113(b), 116(b) |
| 22(f), 24(f) | 44(b), 45(b) | 80(b), 85(b) | 114(f), 116(f) |
| 22(b), 26(b) | 45(f), 89(f) | 81(f), 83(f) | 115(b), <u>117</u> |

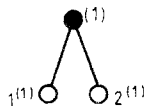
Thus the diagram (35) is easily seen to have the value

$$\begin{array}{c}
 \begin{array}{c}
 \text{(1)} \\
 \bullet \\
 \diagup \quad \diagdown \\
 \text{(2)} \bullet \quad \bullet \text{(2)} \\
 \diagdown \quad \diagup \\
 \circ \text{(1)} \quad \circ \text{(1)}
 \end{array} \\
 -
 \end{array}
 \tag{41}$$

and hence will cancel with 25(f). The key feature of 25(f) that enabled a cancelling disallowed diagram to be found is the presence of an external f_{12} -bond, which in turn allowed the addition of an appropriate diagrammatic segment so that the result (40a) could be employed. Clearly, then, this same procedure can be used for the diagrams 7(f), 23(b), 25(f), 26(f), 27(f), 28(f), 31(b), 33(b), 36(b), 46(f), 47(f) and 48(f), which are also retained in RISM and have in common with 25(f) an external f_{12} -bond.

Other diagrams retained in RISM, e.g. 5(b) and 10(b), have in common the absence of an external f_{12} -bond. However, cancelling diagrams can be found by adding diagrammatic segments so that result (40c) can be employed. Hence, we have found a scheme which allows cancellation of the allowed diagrams retained in RISM, and which will work at every order in density. We have not, however, been able to establish that the remaining disallowed diagrams which are summed in RISM are self-cancelling, although inspection of these diagrams suggests that they are indeed self-cancelling in a similar

manner to that displayed at order $\rho^{(0)}$. At this point we must now accept that this cancellation is complete, i.e. that the net result of all these cancellations for the molecular diagram (34) is the single diagram



which occurs in the expansion for $h^{PV}(r)$ for hard spheres.

The final conclusion, then, is that RISM shows the correct physical result—i.e. no dependence on the auxiliary site for the present case—somewhat fortuitously: it is *not* because the particular choice of auxiliary site problem (that of a sphere with an auxiliary site) ensures that the contribution due to neglected graphs is trivially zero and the extra, infinite class of disallowed graphs is also trivially zero. RISM only manages to obtain the correct answer in the present circumstances by a fortuitous cancellation of the effect of neglected, allowed diagrams and the infinite class of disallowed diagrams.

There is an important consequence which follows from the analysis of this section, which is that it should be possible to concoct higher-order auxiliary site problems (e.g. for diatomics) where for particular sizes of auxiliary sites RISM shows no dependence on the auxiliary site. Since RISM shows no dependence on an auxiliary site contained within a sphere, and we have shown that this results from a cancellation between diagrams which in turn comes about because of the relationship between the $\sigma_{\alpha\beta}$ and σ_{11} implied by the geometry of the sphere with auxiliary site, it is tempting to suggest that such a cancellation will persist in higher-order problems when the diameter of the auxiliary site is such that the auxiliary site is completely enclosed in the interior of all the fused hard spheres comprising the molecule. For example, in the case of a diatomic molecule, it would be conjectured that provided the auxiliary site lies entirely within the intersection (co-sphere) of the two hard spheres comprising the diatomic, then there would be no dependence on the auxiliary site. Such a conjecture is verified in the following section.

4. Symmetric diatomic molecule with a single auxiliary site

For convenience, in this section we consider a symmetric diatomic molecule with two real sites (sites 1 and 2) of diameter σ and l_{12} (simply denoted l) equal to $\sigma/2$. The auxiliary site (site 3) will be placed at the centre of the molecule (hence $l_{13} = l_{12}/2 = \sigma/4$). The only distinguishable correlation functions will thus be $h_{11} = h_{12} = h_{21} = h_{22}$ (denoted $h_{ss}(r)$, the site–site correlation function), h_{33} (denoted h_{cc} , the centre–centre correlation function) and $h_{13} = h_{31}$ (denoted h_{sc} , the site–centre correlation function). In the absence of an auxiliary site, $h_{ss}(r)$ is simply $h_{ss}^{(d)}(r)$, the correlation function for a symmetric diatomic molecule. In all the calculations reported in this section, the Lowden programs (1975) have been used in an unmodified form.

It has already been noted in § 2 that $h_{ss}(r)$ exhibits no dependence on the auxiliary site for

$$\sigma_{13} = \sigma_{33} = 0 \quad (42)$$

since, in this limit, the RISM OZ equation reduces to the OZ-like equation for a symmetric

diatomic molecule plus the following relations for $h_{sc}(k)$ and $h_{cc}(k)$ (after rearrangement):

$$h_{sc}(k) = \frac{2\omega_{13}(k)}{1 + \omega_{12}(k)} h_{ss}(k), \quad (43)$$

$$h_{cc}(k) = \frac{2\omega_{13}(k)}{1 + \omega_{12}(k)} \left(h_{sc}(k) + \frac{(1 - \omega_{13}(k))h_{ss}(k)}{(1 + \omega_{12}(k) + 2\rho h_{ss}(k))} \right). \quad (43b)$$

Further, the conjecture contained at the end of § 3 suggests that

$$h_{ss}(r) = h_{ss}^{(d)}(r) \quad (44)$$

when $\sigma_{33} < \sigma/2$. This corresponds to the auxiliary site being enclosed in the co-sphere of the two hard spheres of diameter σ . It is not clear, however, for what values of σ_{13} equation (44) is satisfied. For convenience, we will assume that there is a critical value of σ_{13} , σ_{13}^* , for which $\sigma_{13} < \sigma_{13}^*$ in conjunction with $\sigma_{33} < \sigma/2$ ensures that (44) is satisfied. Hence our conjecture is as follows:

$$h_{ss}(r) = h_{ss}^{(d)}(r) \quad \text{whenever } \sigma_{33} \leq \sigma/2, \sigma_{13} \leq \sigma_{13}^*. \quad (45)$$

Making use of the Lowden programs, we have found that $\sigma_{13}^* = \sigma/2$, i.e. we have found that

$$h_{ss}(r) = h_{ss}^{(d)}(r) \quad \text{whenever } \sigma_{33} \leq \sigma/2, \sigma_{13} \leq \sigma/2. \quad (46)$$

Hence the important point in RISM is not the presence or absence of an auxiliary site, but rather the *size* and *position* of the auxiliary site. The dependence on auxiliary sites reported by Hsu *et al* (1976) should, therefore, be properly regarded as dependence on auxiliary sites of sufficiently large size.

In discussing the results for a diatomic with auxiliary sites, it is convenient to define five particular sets of values of σ_{13} and σ_{33} (denoted SET1 to SET5) which satisfy the inequalities (21). These are given in table 3. SET3 corresponds to the assumption that σ_{33} satisfies the upper limit given in (44), and the diameters of the auxiliary site are considered to be additive; SET4 corresponds to the largest value of σ_{33} for which the third site is contained inside the symmetric diatomic, while σ_{13} comes from assuming that the diameters are additive; SET5 represents the upper limit given in (21). In the latter case, the third (auxiliary) site projects beyond the molecule.

Table 3. Sets of values for σ_{13} and σ_{33} used in the discussion given in § 4.

| | |
|------|---|
| SET1 | $\sigma_{33} = \sigma_{13} = 0$ |
| SET2 | $\sigma_{33} = \sigma_{13} = 0.5$ |
| SET3 | $\sigma_{33} = 0.5, \sigma_{13} = 0.75$ |
| SET4 | $\sigma_{33} = (3/2)^{1/2}, \sigma_{13} = (2 + \sqrt{3})/4$ |
| SET5 | $\sigma_{33} = (7/8)^{1/2}, \sigma_{13} = (15/16)^{1/2}$ |

In verifying (46) we consider the RISM approximation for a symmetric diatomic molecule at density $\rho\sigma^3 = 0.5$. In figure 8 the site-site radial distribution function ($g_{ss}(r)$) is shown for various values of σ_{13} and σ_{33} . The symmetric diatomic result ($g_{ss}^{(d)}(r) = h_{ss}^{(d)}(r) + 1$) and the results for SET1 and SET2 are all the same function, shown by the solid line. The results for SET3, SET4 and SET5 are also shown. The

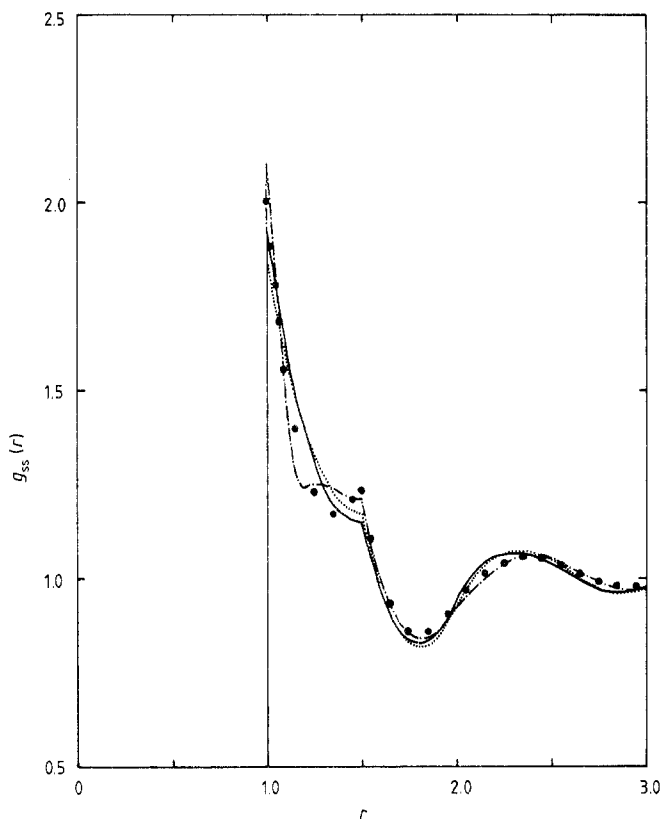


Figure 8. The site-site correlation function calculated in the RISM approximation at density $\rho\sigma^3 = 0.3$; the symmetric diatomic result ($g_{ss}^{(d)}(r)$), SET1 and SET2 (all indistinguishable) (—); SET3 (····); SET4 and SET5 (- · -); Monte Carlo (MC) results (●) (G P Morriss 1980, private communication).

SET4 result for $g_{ss}(r)$ is indistinguishable from the result for SET5 on the scale of this graph. The result for SET3 shows intermediate dependence on the auxiliary site.

In figure 9, the centre-centre correlation functions are shown. Their main feature is that except for SET5, they are unphysical, having regions where $g_{cc}(r) < 0$ inside the physical core. By including an auxiliary site with interaction distances set by the upper limits of (21) (i.e. SET5), the centre-centre correlation functions are of course made to be physical. Since this is a clear improvement over the case of a diatomic molecule without auxiliary sites (the SET1 curve yields this centre-centre correlation function), it might be suggested that a corresponding improvement might be found in $g_{ss}(r)$, as suggested by Hazoumé (1978) based on the results of Chandler *et al* (1977).

Examining figure 8, we see that this indeed appears to be the case: $g_{ss}(r)$ for a molecule with an auxiliary site with interaction distances given by SET5 appears to show the following improvements over $g_{ss}^{(d)}(r)$: the height of the peak at $r = 1.0\sigma$ is greater, in closer agreement with the Monte Carlo (MC) results (G P Morriss 1980, private communication); the cusp at $r = 1.5\sigma$ is higher, again in closer agreement with the MC results; at $r > 1.5\sigma$, the phase of $g_{ss}(r)$ is in better agreement with the MC result. However, for $1.2\sigma < r < 1.5\sigma$ there is a curious secondary minimum in $g_{ss}(r)$ which is

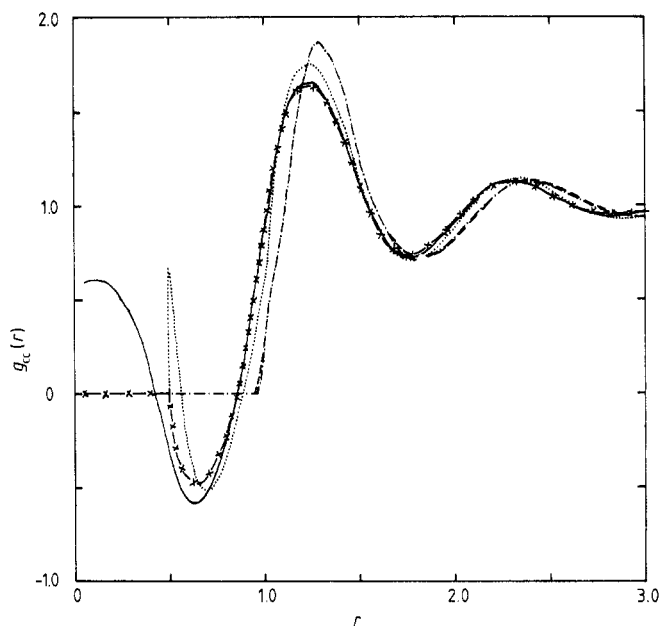


Figure 9. The centre-centre correlation function in the RISM approximation at density $\rho\sigma^3 = 0.5$; SET1 (—); SET2 (-×-); SET3 (···); SET4 (---); SET5 (- - -).

not present in the MC results, which tends to detract a little from the overall conclusion of Hazoumé (1978) that $g_{ss}(r)$ with σ_{13}, σ_{33} given by SET5 is an apparent improvement over $g_{ss}^{(d)}(r)$.

However this improvement is, to a certain extent, illusory, as is demonstrated by examining the symmetric diatomic with an auxiliary site (σ_{13}, σ_{33} given by SET5) at lower densities, as shown in figures 10–13 at densities $\rho\sigma^3 = 0.2, 0.3, 0.4$ and 0.6 respectively. A common feature in the lower density graphs ($\rho\sigma^3 < 0.4$) is a qualitatively and quantitatively incorrect peak at $r = 1.0\sigma$. Since this peak has no physical origin (being absent from the MC data) we are forced to attribute this behaviour solely to the way in which the RISM approximation deals with auxiliary sites.

The second common feature in these figures is that there is, for all values of ρ , better agreement between the MC values and $g_{ss}(r)$ for the diatomic with an auxiliary site for $r > 1.5\sigma$.

Thus we conclude that the inclusion of an auxiliary site causes the site-site radial distribution function ($g_{ss}(r)$) to be both qualitatively and quantitatively incorrect at small separations, although it is clearly a significant improvement at larger separations. One consequence of this is that we must regard the improved peak height at $r = 1.0\sigma$ for $\rho\sigma^3 = 0.5$ and 0.6 (figures 8 and 13) as having its origin in physically wrong effects in RISM, and hence it should not be regarded as an improvement (at this range) over the result for a symmetric diatomic without an auxiliary site.

A possible explanation for the observed trends (i.e. worse agreement at small r , better agreement at large r) now follows, although it must be stressed that this explanation remains a conjecture whose verification would be difficult. A major difference between a RISM treatment and an ISF treatment for $g_{ss}(r)$ for a diatomic with an auxiliary site is the absence of three-site intramolecular correlations in RISM. This is

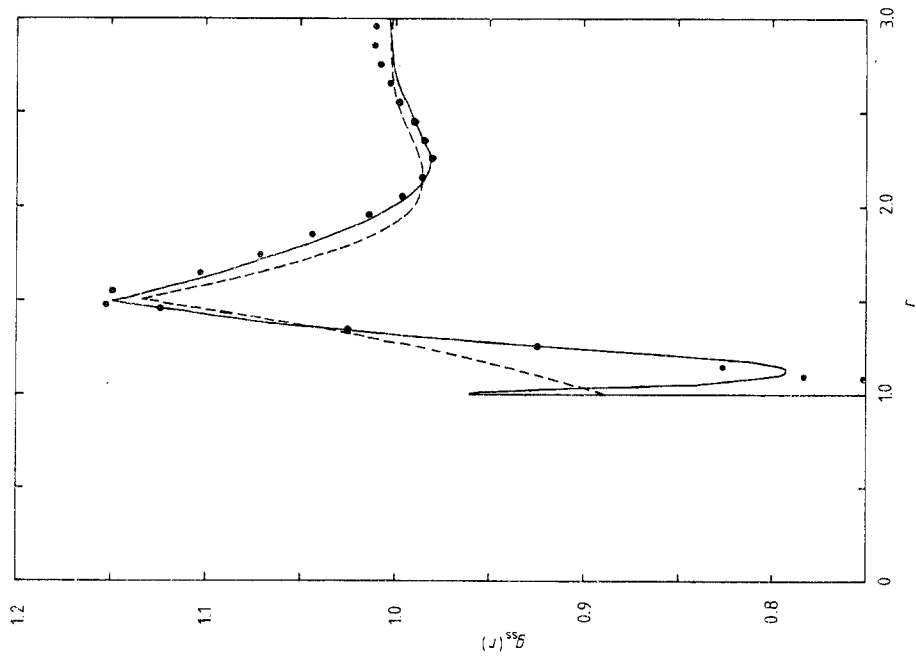


Figure 10. Site-site correlation function at density $\rho\sigma^3 = 0.2$; no auxiliary site (---); auxiliary site with values for $\sigma_{1,3}, \sigma_{3,3}$ given by SETS (---); MC results (●) (G P Morriss 1980, private communication).

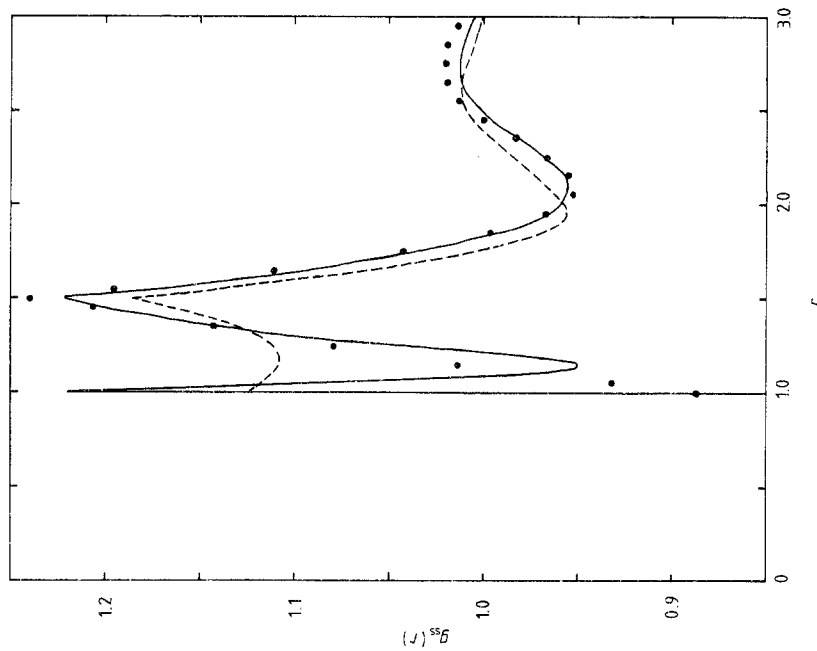


Figure 11. As for figure 10, density $\rho\sigma^3 = 0.3$.

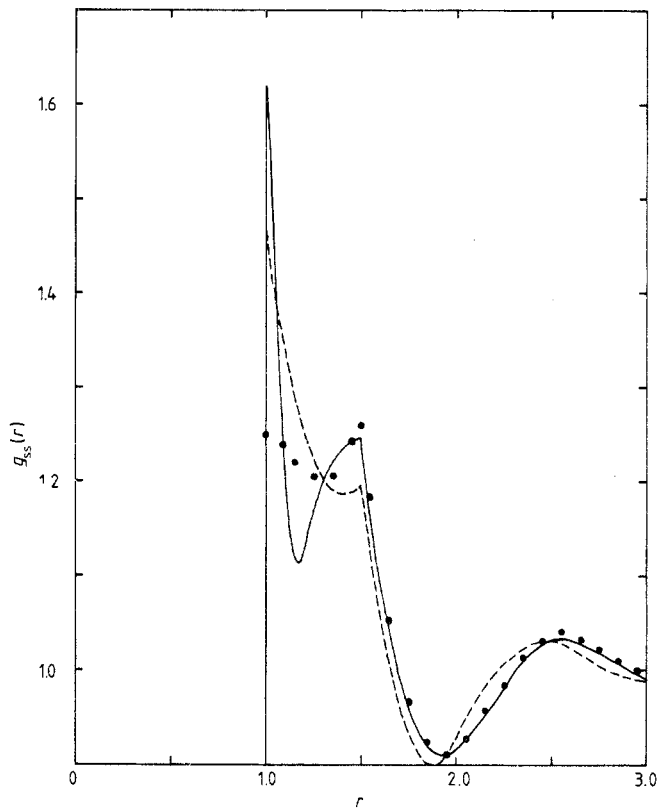


Figure 12. As for figure 10, density $\rho\sigma^3 = 0.4$.

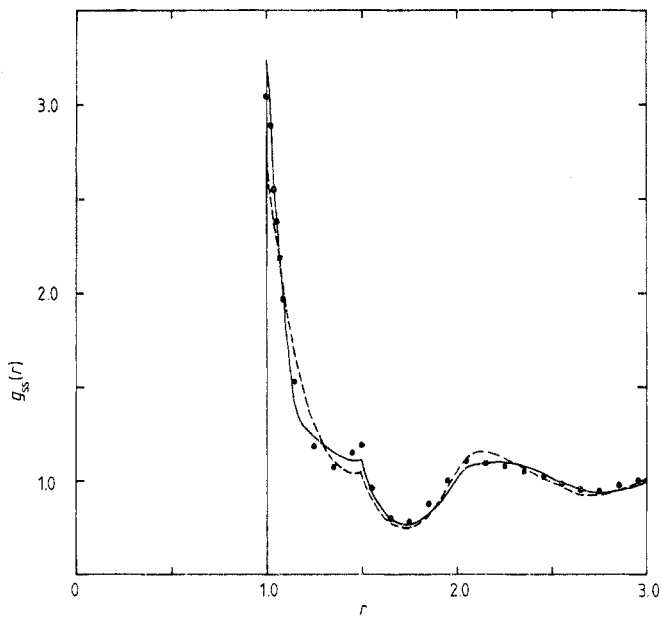


Figure 13. As for figure 10, density $\rho\sigma^3 = 0.6$.

a crucial deficiency, since in the ISF the translation from a two-site to a three-site (auxiliary site) formalism for the same diatomic molecule involves the introduction of further diagrams involving $s_{\alpha\beta}^{2/3}$ -bonds (like those in figures 4–6) as well as diagrams involving $s_{\alpha\beta\gamma}^{3/3}$ -bonds. Since the net value of the expansion for $h_{ss}(r)$ is unchanged in going from the two-site expansion to the three-site expansion (provided the third site is auxiliary), the extra set of diagrams generated must be self-cancelling. Since the distances $\sigma_{\alpha\beta}$ involved do not satisfy the simple linear geometrical relationships satisfied in the case of the sphere with embedded sites (§ 3), the cancellation involved here can be expected to be of a more subtle type than that encountered in § 3. In particular, it is easy to envision cancellation between diagrams involving $s_{\alpha\beta}^{2/3}$ -bonds and diagrams involving $s_{\alpha\beta\gamma}^{3/3}$ -bonds. This latter class of diagrams is absent from the RISM approximation for $h_{ss}(r)$; hence it is possible that the RISM approximation sums, in many instances, one half of a self-cancelling pair. The point to note, however, is that $s_{\alpha\beta}^{2/3}$ -bond diagrams which cancel with $s_{\alpha\beta\gamma}^{3/3}$ -diagrams in the ISF are likely to be quite short-ranged, in view of the fact that $s_{\alpha\beta\gamma}^{3/3}$ -bond diagrams involve three-site intramolecular correlations, and that each of the three sites must be f -bonded to sites in other molecule(s), limiting to a certain extent the regions over which such diagrams are

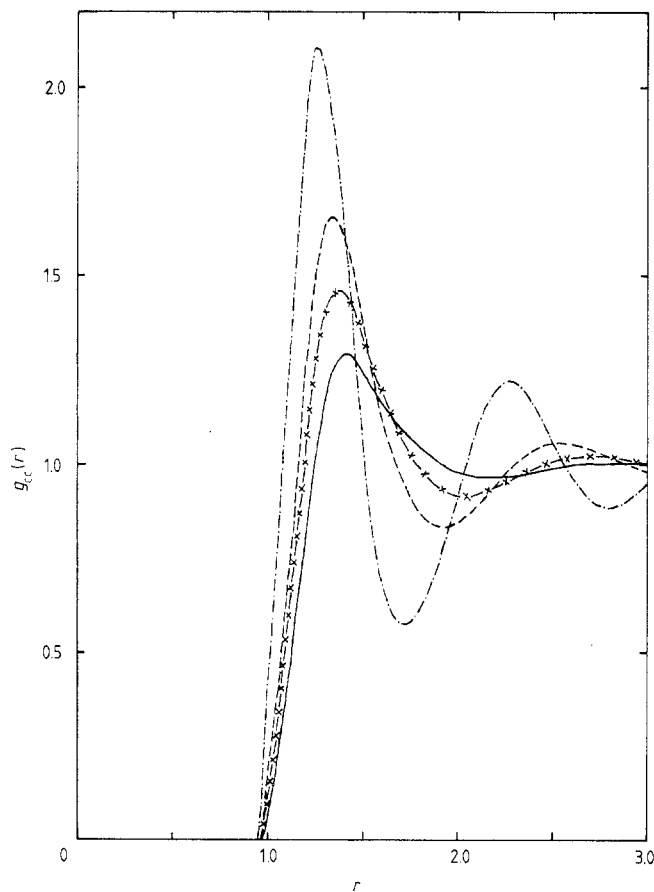


Figure 14. Centre-centre correlation function calculated for σ_{13}, σ_{33} given by SET5 at $\rho\sigma^3 = 0.2$ (—), 0.3 (-x-x-), 0.4 (---) and 0.6 (-·-).

non-zero. Thus a possible explanation for the apparent improvement at large separations combined with worse behaviour at small separations is that RISM sums short-ranged contributions which would be cancelled in the exact ISF.

In figure 14 we have displayed the $g_{cc}(r)$ which arise in RISM when σ_{13}, σ_{33} given by SET5 are used at various densities.

In conclusion, then, it is clear that the inclusion of an auxiliary site with physical distances of closest approach (the upper limits of (21), SET5) has a mixed effect on $g_{ss}(r)$ and $g_{cc}(r)$. On the one hand, $g_{ss}(r)$ is improved at large r and $g_{cc}(r)$ is made to be physical. On the other hand, $g_{ss}(r)$ is found to be qualitatively and quantitatively wrong at small separations.

Acknowledgments

We gratefully acknowledge NSERC (Canada) for financial support of this research. We thank Robin Barker for performing the numerical calculations.

Appendix. Graphical expansions in ISF and RISM

In this Appendix, we quote the results for the diagrammatic expansions for $h_{\alpha\beta}(r)$ in the ISF and its RISM approximation, and note the differences between them. The ISF results are taken from Ladanyi and Chandler (1975), who give a complete account of the reduction of the full molecular cluster series for $h(12)$ to the site-site cluster series for $h_{\alpha\beta}(r, r')$. The RISM results are taken from Chandler (1976).

We begin by noting the Mayer cluster expansion for $h(12)$ which, in the standard graph terminology (Stell 1964), is given by

$h(12)$ = the sum of all connected diagrams involving f -bonds with two white one-circles (labelled 1 and 2), any number of black ρ -circles (molecular field points), at most one f -bond connecting any two circles directly, and no articulation circles. (A1)

An articulation circle is a circle whose removal leaves a disconnected diagram, one or more of the disconnected parts containing white diagrams. Some of the diagrams in $h(12)$ are exhibited in figure 15.

The f -bonds referred to in the expansion (A1) represent $f(ij)$ functions in the integrals represented by the diagram. The function $f(ij)$ is the full, angular Mayer f -function defined by

$$f(12) = \exp[-u(12)/k_B T] - 1 \tag{A2}$$

where $u(12)$ is given by (1), k_B is Boltzmann's constant and T is the absolute temperature. With $u(12)$ written in terms of the site-site potentials $u_{\alpha\beta}(r_{\alpha\beta})$, $f(12)$ can be written as a finite sum of terms involving site-site Mayer f -functions, defined by

$$f_{\alpha\beta}(r) = \exp[-u_{\alpha\beta}(r)/k_B T] - 1 \tag{A3}$$

as (Ladanyi and Chandler 1975)

$$f(12) = \sum_{\alpha\beta=1}^m f_{\alpha\beta}(r_{\alpha\beta}) + \sum_{\substack{\alpha\beta \quad \gamma\delta \\ (\alpha\beta) \neq (\gamma\delta)}}^m f_{\alpha\beta}(r_{\alpha\beta}) f_{\gamma\delta}(r_{\gamma\delta}) + \dots \tag{A4}$$

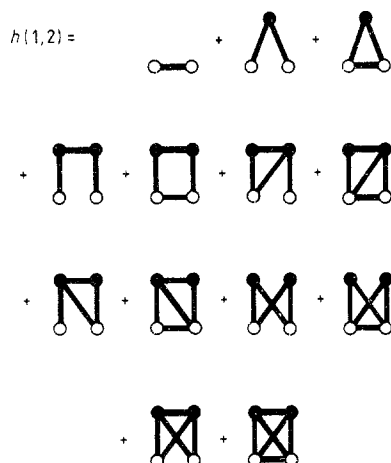


Figure 15. The first few terms (through to $O(\rho^2)$) in the molecular cluster series for $h(12)$. The bonds are $f(ij)$ bonds. Refer to (A1).

Taking the diagrammatic expansion (A1) for $h(12)$, replacing the $f(ij)$ -bonds by sums of site-site terms given in (A4) and using the definition of $h_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in terms of $h(12)$ given in (3), Ladanyi and Chandler derive the following graphical expansion for $h_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$:

$h_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ = the sum of all allowed interaction site diagrams with two white-circles labelled $1^{(\alpha)}$ and $2^{(\beta)}$, any number of black circles, one or more f -bonds and zero or more s -bonds. (A5)

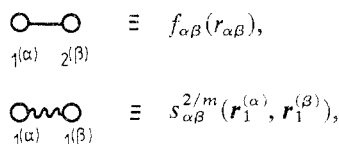
In this expansion, 'f-bonds' and 's-bonds' denote sets of $f_{\gamma\delta}$ and $s_{\nu\delta\dots\eta}^{n/m}$ bonds and the black circles represent sums over sites as well as integration over the positions of those sites. The $s_{\nu\delta\dots\eta}^{n/m}$ bonds represent the function (Ladanyi and Chandler 1975)

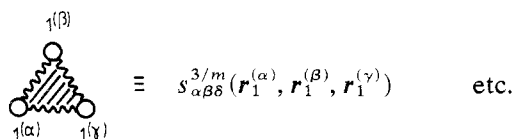
$$\begin{aligned}
 S_{\alpha_1\alpha_2\dots\alpha_n}^{n/m}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \\
 = \left(\prod_{i>j}^n (1 - \delta_{\alpha_i\alpha_j}) \right) \int d\mathbf{R} \Omega^{-1} \int d\Omega \prod_{i=1}^n \delta(\mathbf{R} + l^{(\alpha_i)}(\Omega) - \mathbf{x}_i)
 \end{aligned} \quad (\text{A6})$$

and are called the n -site intramolecular correlation functions for an m -site ISF problem. They arise naturally through the use of (3) and in essence fix the relative positions of n sites $(\alpha_1, \alpha_2, \dots, \alpha_n)$ within a single molecule. An important particular case is $s^{2/m}(x_1, x_2)$ which is given by

$$\begin{aligned}
 s_{\alpha\beta}^{2/m}(\mathbf{x}_1, \mathbf{x}_2) &= s_{\alpha\beta}^{2/m}(|\mathbf{x}_1 - \mathbf{x}_2|) \\
 &= (1/4\pi l_{\alpha\beta}^2) \delta(|\mathbf{x}_1 - \mathbf{x}_2| - l_{\alpha\beta}).
 \end{aligned} \quad (\text{A7})$$

In representing pictorially the expansion (A5) the convention of Ladanyi and Chandler (1975) is followed: i.e.

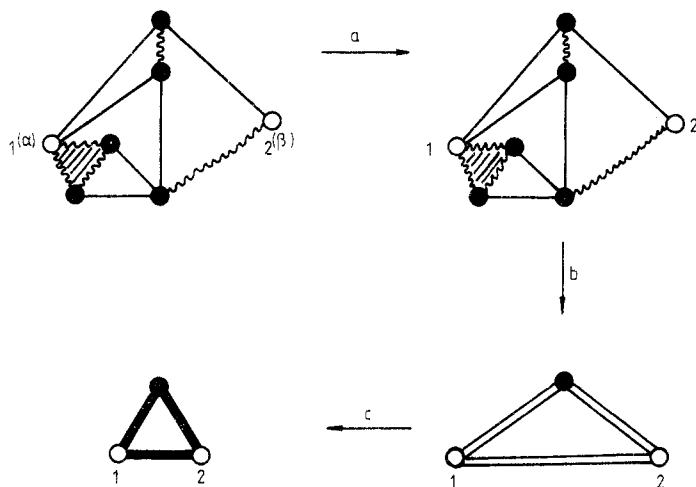





A diagram in the expansion (A5) is ‘allowed’ (Ladanyi and Chandler 1975) if: it is connected; any two circles are joined directly by at most one bond; the two white circles are joined directly by a single *f*-bond, if at all; all black circles must be intersected by at least one *f*-bond; any circle is intersected by at most one *s*-bond; and there are no articulation circles nor any articulation *s*-bonds.

Ladanyi and Chandler (1975) discuss the symmetry numbers to be associated with the allowed diagrams; we do not concern ourselves with that problem here. The other factor which must be associated with each diagram—that is, the appropriate power in density—is found by tracing back from the site-site diagram to the molecular diagram from which it has its origin, and finding the power of density associated with the original molecular diagram. This process is a well defined algorithm of three steps as follows.

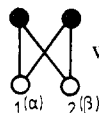
- (a) Relabel the white $1^{(\alpha)}$ and $2^{(\beta)}$ circles as 1 and 2 respectively.
 - (b) Compress all *s*-bonds onto the associated black circle(s). (It is convenient to think of the *s*-bonds as springs in this regard.)
 - (c) Between any two of the resulting circles connected by one or more ‘*f*-bonds’, place a single, heavy line to represent an *f*(*ij*)-bond.
- For example, consider the following diagram:



Hence the original diagram is $O(\rho)$, since its molecular origin has a single ρ -circle. In figure 2 we present all 15 site-site diagrams generated by the first diagram in the molecular expansion (A5) in the case of the simplest molecular fluid, the diatomic fluid ($m = 2$). For a molecule with $m > 2$, clearly there will be a further large number of diagrams generated containing $s^{(3/m)}$, $s^{(4/m)}$, etc bonds. Note that, even for the simple


case ($m = 2$) of a diatomic, the next diagram in figure 15 (i.e. ) , generates 117 topologically distinct site-site diagrams. These are shown in figures 5 and 6.


other diagrams it will generate the site-site diagram



which is present in the ISF

expansion for $h_{\alpha\beta}(r)$ but is absent from the expansion for $[h_{\alpha\beta}(r)]_{\text{RISM}}$ (equation (A9)). The graph G is a member of the class of diagrams dropped in the PY approximation for $h(12)$ (Stell 1964): in fact, the PY-like topology of the diagrams in the expansion for $h_{\alpha\beta}(r)$ (Chandler 1976) means that none of the diagrams which are dropped in the PY expansion for $h(12)$ can be the molecular origin of any site-site diagrams summed in $[h_{\alpha\beta}(r)]_{\text{RISM}}$. Hence, it is straightforward to see that *the RISM theory has, as its starting point at the molecular level, the PY approximation for $h(12)$ rather than the exact series.* This approximation will be denoted by API.

(ii) In addition to the PY approximation at the molecular cluster expansion level, there are two additional ‘approximations’ made by RISM in the translation to a site-site formalism. The first of these is: *a large number of the diagrams generated by molecular diagrams in the PY approximation for $h(12)$ are dropped in $[h_{\alpha\beta}(r)]_{\text{RISM}}$ (APII).* For example in figure 4 the diagrams generated by the molecular graph  are shown for the ISF; diagrams 12, 13, 14, 15 are dropped in the RISM approximation.

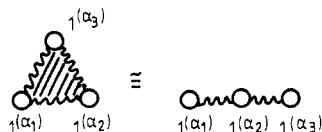
In figures 5 and 6, the site-site diagrams generated by the molecular graph  in the

ISF for a diatomic ($m = 2$) molecule are shown. Of these 117 graphs, 69 graphs (those shown in figure 6) are dropped in the RISM approximation: i.e. even at order ρ^1 , RISM is dropping more than half of the expected site-site diagrams. At higher orders of density, and for more complex diagrams in the PY approximation for $h(12)$, the fraction of graphs retained by the RISM approximation grows diminishingly small. In addition, RISM drops all the diagrams derived from the PY approximation for $h(12)$ involving $s^{n/m}$ -bonds which arise whenever the number of sites $m > 3$. Further discussion of this point follows below.

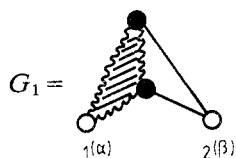
(iii) Up to this point the approximations made by RISM (API, APII) have followed the familiar pattern of integral equation approximations, such as the PY approximation for hard spheres (cf the Introduction), in that the approximation has involved *dropping* diagrams from the exact expansion for $h_{\alpha\beta}(r, r')$ (equation (A5)). However, as pointed out by Chandler (1976), *the RISM approximation also involves, at each order in density, summing an infinite set of diagrams disallowed in the rigorous theory (APIII).* Examples of such disallowed diagrams are shown in figure 5 of Chandler (1976). Some explanation for the inclusion of the disallowed diagrams has been given by Hazoum  (1978) who demonstrated that the n -site intramolecular correlation functions, $s_{\alpha\beta\dots\gamma}^{n/m}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n)$, could be expanded as follows:

$$s_{\alpha_1\alpha_2\dots\alpha_n}^{n/m}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \left(\prod_{i=2}^n s_{\alpha_{i-1}\alpha_i}^{2/m}(|\mathbf{x}_{i-1} - \mathbf{x}_i|) \right) (1 + S_\infty)$$

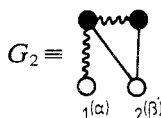
where S_∞ is a sum of an infinite number of terms involving functions of the angles between the vectors $l_{\alpha_i\alpha_j}$. Hence, to a first approximation, an $s^{n/m}$ function may be replaced by a chain of $s^{2/m}$ bonds: e.g., for $n = 3$,



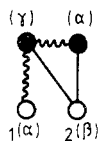
Hence the diagram



appearing in the exact cluster series (A5) for an m -site problem ($m > 3$) could be approximated by



This diagram appears in the expansion of $[h_{\alpha\beta}(r)]_{\text{RISM}}$ (equation (A9)). Hazoumé goes on to indicate that, as a consequence, RISM is applicable in an exact sense only to molecules with an infinite number of interaction sites, since there occur terms in $[h_{\alpha\beta}(r)]_{\text{RISM}}$ which, in the Hazoumé interpretation, correspond to approximations for $s^{n/m}$ where n and m are arbitrarily large. Such an explanation appears plausible only until it is noted that a diagram such as G_2 corresponds to a sum of diagrams, one of which includes the site labelling



Such a labelling does not arise in any rigorously allowed diagrams such as G_1 . Unfortunately, then, we cannot regard RISM as a formally 'correct' theory for molecules with an infinite number of sites which loses accuracy when applied to problems involving a finite number of sites.

The cause of the present problem (APIII) can be traced to the inadequacy of the closure (8b). We do this by considering the form of $c_{\alpha\beta}(r)$ in an exact theory as predicted by the RISM OZ equation (5). For simplicity, we consider the case of a two-site molecule at zero density, since this illustrates the key point regarding closure. At zero density, the RISM OZ equation (5) yields

$$\mathbf{h}(k) = \boldsymbol{\omega}(k)\mathbf{c}(k)\boldsymbol{\omega}(k) \quad (\text{A13})$$

where, for a two-site ($m = 2$) problem, $\boldsymbol{\omega}(k)$ can be written as

$$\boldsymbol{\omega}(k) = \begin{pmatrix} 1 & w \\ w & 1 \end{pmatrix}. \quad (\text{A14})$$

Here $w = \omega_{12}$ is given by

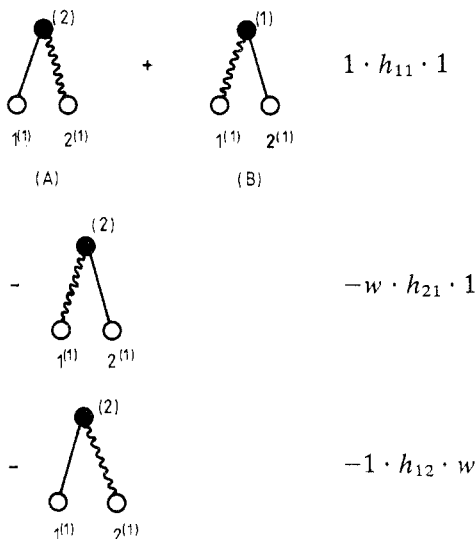
$$w(k) = (\sin kl_{12})/kl_{12}. \quad (\text{A15})$$

Inverting (A13) and expanding $\omega(k)^{-1}$ in powers of w , one obtains for $c_{11}(k)$

$$\begin{aligned}
 c_{11}(k) = & (1 + w^2 + w^4 + \dots)h_{11}(1 + w^2 + w^4 + \dots) \\
 & - (w + w^3 + w^5 + \dots)h_{21}(1 + w^2 + w^4 + \dots) \\
 & - (1 + w^2 + w^4 + \dots)h_{12}(w + w^3 + w^5 + \dots) \\
 & + (w + w^3 + w^5 + \dots)h_{22}(w + w^3 + w^5 + \dots).
 \end{aligned}
 \tag{A16}$$

By considering the ISF (exact) expansions for $h_{\alpha\beta}$ at zero density, and substituting these into (A16), we obtain an expansion for $c_{11}(r)$ which contains an infinite class of diagrams. The subtracted terms ensure the removal of diagrams having only a single path between the white circles. For example, consider the following diagrams; the origin of each diagram in (A16) is indicated—they arise from considering diagrams in $h_{\alpha\beta}$ in the ISF (A5).

Diagrams Origin in equation (A16)



Hence the diagrams A and B, which incidentally are not present in the expansion for $[c_{11}(r)]_{\text{RISM}}$, will not be present in the expansion for an exact $c_{11}(r)$. Consideration of further terms in (A16) leads to the conclusion that an expansion for the exact $c_{11}(r)$ would contain an infinite set of diagrams at order ρ^0 and hence, by iteration through the RISM OZ equation, at higher orders in density as well.

The important point to note, however, is that in the exact theory the use of the exact expansion for $c_{\alpha\beta}(r)$, even though it contains an infinite number of diagrams at each order in density, will yield via the exact closure relationship between $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$ (i.e. the independent, exact closure to the RISM OZ which at present is unknown) expansions for $h_{\alpha\beta}(r)$ containing a *finite* number of terms at each order in density. Use of the RISM PY-like closure (equations (A9) and (A11)), however, causes the expansion for $[h_{\alpha\beta}(r)]_{\text{RISM}}$ to have an *infinite* number of diagrams at each order in density.

Hence it can be seen that the use of the RISM approximation for $c_{\alpha\beta}(r)$ (and the implied closure relation to the RISM OZ given in (A8)–(A12)) represents an approximation having greater repercussions for molecular fluids than the similar PY approximation has for the atomic hard sphere fluid. It is very important, especially from the point of

view of the deficiencies of the RISM approximation noted in the Introduction, that more appropriate closures to the RISM OZ be developed. From the failure of RISM to predict the parameters G_l correctly (cf § 1), it can be conjectured that, in some cases, $c_{\alpha\beta}(r)$ will be long-ranged. Certainly one aspect of the RISM closure to the RISM OZ which will certainly require attention in any improved closure is that, at present, the closure relates $c_{\alpha\beta}$ to $y_{\alpha\beta}(r)$ only; obviously there should be some relationship between $c_{\alpha\beta}(r)$ and the y -functions for other site pairs, just as there is in the RISM OZ itself.

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