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TRIPLET CORRELATIONS IN FLUIDS

Six schemes for calculating the triplet correlation function of a fluid are considered. Four are based upon density expansions and their resummation. The other two approximations are based upon considering one or more of the particles to be the source of an inhomogeneity in the fluid and then using the formalism of the theory of inhomogeneous fluids. In contrast to the other approximations, the two approximations based on the theory of inhomogeneous fluids are inherently asymmetric, although they can be symmetrized easily. A few thoughts about the relative merits of the six schemes are given.

1. Introduction

Interest in the theory of fluids centers on the thermodynamic properties of the fluid and its structure, as described by the h-body correlation functions, $g_{1\ldots h} = g(\mathbf{r}_1\ldots\mathbf{r}_h)$, where $\mathbf{r}_1\ldots\mathbf{r}_h$ are the positions of the h molecules. The greater the value of h, the greater the computational difficulty and the greater the difficulty in comprehending the results, if numerical, because of the increasing number of arguments of $g_{1\ldots h}$ as h increases. For central forces, g_{12} is a function of one spatial variable while g_{123} and g_{1234} are functions of three and six variables, respectively. To this one must add the thermodynamic variables. If the forces are noncentral, the number of variables is even greater. For this reason, interest is usually restricted to $h = 2$ or 3, and, occasionally, $h = 4$. Our interest in this note will be similarly restricted . .

2. Density expansions

The pair and triplet correlation functions, g_{12} and g_{123}, can be expanded in power of the density, $\rho = N/V$ (N is the number of molecules and V is the volume). The result is

$$g_{12} = e_{12}\left\{1 + c2_{12} + \rho^2\left(d3_{12} + 2d4_{12} + \frac{1}{2}(c2_{12})^2 + \frac{1}{2}d5_{12}\right) + \cdots\right\} \tag{1}$$

and

$$g_{123} = g_{12}g_{13}g_{23}\left\{1 + \rho\delta 3_{123} + \rho^2(\varepsilon 4_{123} + \varepsilon 4_{231} + \varepsilon 4_{312} + \varepsilon 5\alpha_{123} + \varepsilon 5\alpha_{231} + \right.$$

$$+ \varepsilon 5\alpha_{312} + \varepsilon 5\beta_{123} + \varepsilon 5\beta_{231} + \varepsilon 5\beta_{312} + \varepsilon 6_{123} + \varepsilon 6_{231} + \varepsilon 6_{312} + \frac{1}{2}(\delta 3_{123})^2 +$$

$$\left. + \frac{1}{2}(\varepsilon 7_{123}) + \cdots\right\}, \tag{2}$$

where

$$c2_{12} = \int f_{13}f_{23}dr_3, \tag{3}$$

$$d3_{12} = \int f_{13}f_{24}f_{34}dr_3dr_4, \tag{4}$$

$$d4_{12} = \int f_{13}f_{14}f_{24}f_{34}dr_3dr_4, \tag{5}$$

$$d5_{12} = \int f_{13}f_{14}f_{23}f_{24}f_{34}dr_3dr_4 \tag{6}$$

and

$$\delta 3_{123} = \int f_{14}f_{24}f_{34}dr_4, \tag{7}$$

$$\varepsilon 4_{123} = \int f_{14}f_{24}f_{35}f_{45}dr_4dr_5, \tag{8}$$

$$\varepsilon 5\alpha_{123} = \int f_{14}f_{24}f_{34}f_{35}f_{45}dr_4dr_5, \tag{9}$$

$$\varepsilon 5\beta_{123} = \int f_{14}f_{15}f_{24}f_{35}f_{45}dr_4dr_5, \tag{10}$$

$$\varepsilon 6_{123} = \int f_{14}f_{15}f_{24}f_{25}f_{35}f_{45}dr_4dr_5, \tag{11}$$

and

$$\varepsilon 7_{123} = \int f_{14}f_{15}f_{24}f_{25}f_{34}f_{35}f_{45}dr_4dr_5. \tag{12}$$

In Eqs (1) — (12)

$$e_{ij} = \exp\{-\beta u(R_{ij})\}, \tag{13}$$

$u(R_{ij})$ is the pair interaction energy between molecules i and j,

$$R_{ij} = |r_i - r_j|, \tag{14}$$

$$f_{ij} = e_{ij} - 1, \tag{15}$$

and $\beta = 1/kT$ (k is Boltzmann's constant and T is the temperature). Equations (1) to (12) are based on the assumption of pairwise addivity.

3. Calculation of the pair correlation function

The above expansion of g_{12} can be summed through the use of the Ornstein — Zernike (OZ) relation

$$h_{12} = c_{12} + \rho\int h_{13}c_{23}dr_3,$$

where

$$h_{12} = g_{12} - 1 \tag{17}$$

is called the total correlation function and c_{12} is called the direct correlation function. The OZ relation is just a definition of c_{12}. However, an approximation, such as the Percus — Yevick (PY) approximation,

$$h_{12} - c_{12} = y_{12} - 1 \tag{18}$$

or the hypernetted chain (HNC) approximation,

$$h_{12} - c_{12} = \ln y_{12}, \tag{19}$$

where

$$y_{12} = g_{12}/e_{12}, \tag{20}$$

gives, when coupled with the OZ relation, an integral equation for g_{12} and provides an approximate summation of Eq. (2).

4. Superposition approximation and generalizations

In contrast to the situation for g_{12}, there is no agreed procedure for the calculation of g_{123}. In the remainder of this note, some schemes will be considered.

The simplest scheme is that of Kirkwood [1] who suggested that all the terms beyond unity in Eq. (2) be neglected. Thus

$$g_{123} = g_{12}g_{13}g_{23}. \tag{21}$$

This is the superposition approximation.

If we observe that the density expansion of h_{12} is

$$h_{12} = f_{12} + \cdots \tag{22}$$

we may introduce the renormalized expansion

$$g_{123} = g_{12}g_{13}g_{23}\{1 + \rho\delta 3'_{123}\}, \tag{23}$$

where

$$\delta 3'_{123} = \int h_{14}h_{24}h_{34}dr_4. \tag{24}$$

That is, $\delta 3'_{123}$ is a renormalized $\delta 3_{123}$ with the f_{ij} replaced by h_{ij}. Equations (23) and (24) have been proposed by several authors. To the author's knowledge the earliest authors are Verlet [2], Stell [3], and Blood [4]. Substitution of (1) and (17) into (23) yields

$$g_{123} = g_{12}g_{13}g_{23}\{1 + \rho\delta 3_{123} + \rho^2(\varepsilon 4_{123} + \varepsilon 4_{231} + \varepsilon 4_{312} + \\ + \varepsilon 5\alpha_{123} + \varepsilon 5\alpha_{231} + \varepsilon 5\alpha_{312}) + \cdots\}. \tag{25}$$

Equation (23) yields some, but not all, of the diagrams of order ρ^2.

The next step, which is still computationally straightforward, is to include a few more renormalized h-bond diagrams. For example, Henderson [5] has proposed

$$g_{123} = g_{12}g_{13}g_{23}\{1 + \rho\delta 3'_{123} + \rho^2(\varepsilon 5\beta'_{123} + \varepsilon 6'_{123} + \\ + \text{terms obtained by cyclic permutation of } 123)\}, \tag{26}$$

where again the prime means that renormalized integrals involving h bonds are used. Substitution of (1) and (17) into (26) yields (2) with all but the last two terms. Only the last term is difficult to compute. As will be discussed later, the squared term can be included without problem. Generally speaking, the more highly connected the integral, the smaller its value. Hopefully, the last term, at least, should be small enough to be neglected safely.

5. Approximations for the triplet correlation function based on the theory of inhomogeneous fluids

Recently, Lozada — Cassou [6] and Attard [7] have investigated the calculation of g_{123} using the formalism of inhomogeneous fluids. The pair correlation function of an inhomogeneous fluid can be calculated from the inhomogeneous OZ equation

$$h_{12} = c_{12} + \int \rho_3 h_{13} c_{23} d\boldsymbol{r}_3. \tag{27}$$

Equation (27) must be supplemented by a relation between the pair and singlet functions. One convenient relation is that of Lovett et al [8] and Wertheim [9]

$$\frac{\partial \ln \rho_1}{\partial r_1} = \int \frac{\partial \rho_2}{\partial r_2} c_{12} d\boldsymbol{r}_2. \tag{28}$$

Equations (27) and (28) must be further supplemented by some approximation, such as the PY or HNC approximation.

Most applications of Eqs (27) and (28) involve inhomogeneities in the presence of large spheres. However, Lozada — Cassou and Attard have considered the source of the inhomogeneity to be one or more of the fluid molecules. This permits the calculation of the triplet correlation function using a formalism developed originally for pairs.

In Lozada — Cassou's method, $g_{1/23}$, the singlet function in the presence of a pair of molecules is calculated whereas in Attard's method $g_{12/3}$, the pair function in the presence of a third molecule, is calculated. Holovko et al[10] have also considered these types of approaches. The method is quite general and can be applied to calculate higher-order correlation functions. For example, g_{1234} could be calculated from $g_{12/34}$, $g_{123/4}$, or $g_{1/234}$. In Lozada — Cassou's method

$$g_{123} = g_{23} g_{1/23} \tag{29}$$

while in Attard's method

$$g_{123} = g_{13} g_{23} g_{12/3}. \tag{30}$$

If we employ Attard's method, using the PY approximation for sake of explicitness, we obtain the expansion

$$g_{12/3} = e_{12} \Big\{ 1 + \int \rho_4 f_{14} f_{24} d\boldsymbol{r}_4 + \int \rho_4 \rho_5 f_{14} f_{25} f_{45} d\boldsymbol{r}_4 d\boldsymbol{r}_5 + \\ + 2 \int \rho_4 \rho_5 f_{14} f_{15} f_{25} f_{45} d\boldsymbol{r}_4 d\boldsymbol{r}_5 + \cdots \Big\}. \tag{31}$$

Substitution of

$$\rho(4) = \rho + \rho f_{34} + \rho^2 \{ (1 + f_{34}) \int f_{35} f_{45} d\boldsymbol{r}_5 + \cdots \}, \tag{32}$$

which results from (28), yields the f-bond expansion

$$g_{123} = g_{12} g_{13} g_{23} [1 + \rho \delta_{123} + \rho^2 (\varepsilon 4_{123} + \varepsilon 5\alpha_{123} + \varepsilon 5\beta_{123} + \\ + \text{terms obtained by cyclic permutation of } 123 + \varepsilon 6_{123} + \\ + \varepsilon 6_{312} - c2_{12} \delta 3_{123}) + \cdots]. \tag{33}$$

Thus, g_{123}, in this scheme, is symmetric in 1 and 2 but not in 3. The approximation replaces last three terms in Eq. (2) by a spurious product of c_{12} and $\delta 3_{123}$. Attard, of course, was aware of the asymmetry and suggested symmetrizing

$$g_{123} = \frac{1}{3} (g_{13} g_{23} g_{12/3} + g_{12} g_{23} g_{31/2} + g_{12} g_{13} g_{23/1}). \tag{34}$$

This results in a symmetric triplet correlation functions but the weights of $\varepsilon 6_{ijk}$ are now incorrect and there are now three spurious terms.

Proceeding in a similar manner, Lozada — Cassou's scheme yields

$$g_{123} = g_{12}g_{13}g_{23}[1 + \rho\delta3_{123} + \rho^2(\varepsilon4_{123} + \varepsilon5\alpha_{123} + \text{terms obtained by cyclic permutation} + \varepsilon5\beta_{312} + \varepsilon5\beta_{231} + \varepsilon6_{231} - c2_{12}\delta3_{123} - c2_{13}\delta3_{123}) + \cdots]. \tag{35}$$

As known to Lozada — Cassou, this scheme is symmetric in 2 and 3 but not in 1. It too can be symmetrized by an equation analogous to (34). Comparing Attard's and Lozada — Cassou's schemes, Attard's scheme includes more diagrams and fewer spurious diameters. Which approximation is more accurate in practice is, of course, not known at present.

The lack of symmetry in g_{123} is similar to the lack of symmetry in the earlier prescription of Verlet [11]. In fact, Verlet's equation for g_{123} is the same as that of Lozada — Cassou. If g_{123} is used only to calculate g_{12}, as was a vocated by Verlet and as was done in some of the papers of Attard, the asymmetry is no problem. It is also no difficulty in applications to problems which are inherently asymmetric, such as inhomogeneities in the presence of one or two large spheres. In any case, as we have indicated, the problem is removed by symmetrization.

6. A new approximation

One interesting thought is to use Eq. (23) and (24) but with bonds composed of $h_{ij/k} = g_{ij/k} - 1$ instead of h_{ij}. For example,

$$g_{123} = g_{12}g_{13}g_{23}\left[1 + \rho\int\left(\frac{g_{134}}{g_{13}g_{14}} - 1\right)\left(\frac{g_{234}}{g_{23}g_{34}} - 1\right) \times \right.$$
$$\left. \times \left(\frac{g_{124}}{g_{12}g_{24}} - 1\right) dr_4 + \cdots\right]. \tag{36}$$

If the superposition approximation is used, Eq. (36) becomes Eq. (23). Whether Eq. (36) is computationally convenient has not been investigated.

Equation (36) could be used with the $g_{ij/k}$ in the integral given by any of the above approximations or full self consistency could be demanded. In any case, to order ρ^2, Eq. (36), using any of the earlier schemes to calculate $g_{ij/k}$, yields Eq. (2) with only the last two terms missing and with no spurious integrals.

7. Some thoughts about the accuracy of the various approximations

Even without numerical calculations, some thoughts can be given with reasonable reliability. First the superposition approximation is too crude. It is correct only at very low densities. Equation (23) is an improvement but still includes too few diagrams. Equation (26) is no harder computationally than Eq. (23) and, on expansion in powers of density, yields the approximation for the ρ^2 term

$$(\delta3_{123})^2 + \varepsilon7_{123} = \int f_{14}f_{15}f_{24}f_{25}f_{35}(1 + f_{45})\, dr_4 dr_5 = 0. \tag{37}$$

Equation (36) leads to the same approximation for the ρ^2 term but is more difficult computationally. Equation (37) is rather like the equivalent PY approximation

$$(c2_{12})^2 + d5_{12} = 0. \tag{38}$$

Based on our experience with the PY approximation for g_{12}, one might expect Eq. (37) to be quite accurate for hard spheres, but less useful for other systems.

The Attard prescription involves (37) and the further approximation

$$\varepsilon6_{123} + c2_{12}\delta3_{123} = \int f_{14}f_{15}f_{24}f_{25}f_{35}(1 + f_{45})\, dr_4 dr_5 = 0. \tag{39}$$

This too may be a reasonable approximation, at least for hard spheres. In Lozada-Cassou's scheme there are 5 missing integrals and 2 spurious integrals. As a result it is difficult to pair terms and simple minded arguments, such as that given above, are probably not informative.

8. Summary

Six approximation for g_{123} have been considered. The superposition approximation and Eq. (23) are too simple, the Lozada — Cassou and Attard approximations are more sophisticated but more difficult computationally. Equation (36) is even more demanding computationally. Equation (26) may be the best compromise between sophistication and ease of use.

All of the approximations which we have considered neglect $(\delta 3_{123})^2$. There is no difficulty in including this integral. Each approximation can be cast in a HNC version, rather than the PY version considered here, by considering $\ln g_{123}$ rather than g_{123}. Probably the PY version would be best for hard spheres but the HNC version might be preferable for other systems.

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INTEGRAL EQUATIONS FOR THE CORRELATION FUNCTIONS OF FLUIDS NEAR WALLS

An integral equations for the correlation functions of fluids near impenetrable wall are considered within the singlet and pair theory. The main attention is paid to the treatment of the long-range Coulomb interparticle and particle-wall interactions.

1. Introduction

Despite recent progress in the description of the electrode — electrolyte interface the theory of electric double layer is still not complete. Integral equations form a basis for studies in this area and a wide set of models within different approximate schemes has been investigated.

In this article we have two goals. First, we should like to present a brief but consistent general route of the integral equations application for the electrolyte/wall problem. On the other hand we shall introduce some important supplements which are helpful methodologically as well as necessary for the numerical treatment. The singlet theory which provides the density profiles