Pair Correlation Functions of a Quantum-Mechanical Many-Body System with Several Components

M. P. KAWATRA*
Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received 21 May 1964)

The three pair distribution functions have been calculated for a quantum-mechanical mixture of interacting gases obeying Bose-Einstein or Fermi-Dirac statistics in terms of the respective fugacity series expansions, the coefficients of which are temperature-dependent. The case of a mixture of two kinds ofh ard-sphere bosons has been explicitly studied and the results have been expressed up to first order in interaction parameters.

1. INTRODUCTION

IT is of great physical interest to study the equilibrium properties of a mixture consisting of two different kinds of components.[1] The main feature of such a program lies in the fact that the study of such properties leads us to a clear understanding of the interactions operating between the particles of different kinds. In this, one invariably starts with an assumed law of interaction and then compares the conclusions with the experiment to revise the interacting potential between the particles. If the interparticle potential is assumed to be pairwise additive, one can readily show that the equilibrium properties of the system are determined by the two-body pair correlation functions. It may also be noted here that in some of the recent work on transport phenomena in fluids the importance of the pair correlation functions has been duly emphasized with particular regard to the calculations of various transport coefficients. If the system consists of one type of particles, all the thermodynamical properties can be expressed in terms of one-pair correlation functions $g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$ of London[2] and Placzek[3] (and through recent work of Colin and Peretti[4]). But in, say, a binary mixture there are three correlation functions, two "pure" and one "mixed," which need be specified separately and calculated. In this paper an attempt has been made in this direction. We have here essentially followed the binary-collision-expansion method of Lee and Yang[5] which was generalized by Pathria and the author[6] (PK) to embrace the systems having more than one component. We have started with a system of two bosons and as in PK, the method can easily be generalized to include the effects of particles obeying arbitrary statistics and having any spins. Starting with such a system, calculations for the three pair correlation functions have been done up to first order in interaction parameters. It may be added that the three pair correlation functions, $g^{(20)}$, $g^{(02)}$, and $g^{(11)}$, two "pure" and one "mixed," respectively, are related to the respective three distribution functions, $\rho^{(20)}$, $\rho^{(02)}$, and $\rho^{(11)}$, through the relations: $\rho^2 g^{(20)}=\rho^{(20)}$; $\rho^{*2}g^{(02)}=\rho^{(02)}$; and $\rho\rho^* g^{(11)}=\rho^{(11)}$, where ρ is the density of the one of the components (the unstarred) and ρ^* is that of the other (the starred one) in a binary mixture.

The discussion can be readily generalized to embrace systems having more than two components. In an M-component system we would have M pure correlation functions and $M(M-1)/2$ mixed ones, and up to the first order in interaction parameters, the above starred and unstarred symbols in the two-component system would then span all the components. The generalization being straightforward the present calculations are given only for a two-component system.

2. FORMULATION OF THREE DISTRIBUTION FUNCTIONS IN A BINARY MIXTURE

We consider a two-component system consisting of N particles of one kind (the unstarred) and N^* particles belonging to the other (the starred type), all confined in a cubic box of dimensions $L\times L\times L$ (volume $L^3=\Omega$, which would, in turn, be let to go to infinity with the respective densities of the components being maintained constant). Also, it is assumed the system is subjected to (that is, the motions of the constituent particles conform to) periodic boundary conditions. The partition function Z_{NN^*} of such a system can straightaway be written as[7]

$$Z_{NN^*}=\frac{1}{N!N^*!}\int\langle 1,2,\cdots N;1^*,2^*,\cdots N^*|\times W_{NN^*}{}^q|1,2,\cdots N;1^*,2^*,\cdots N^*\rangle d^{3N}r d^{3N^*}r^*. \quad (1)$$

Here, the quantum-mechanical (probability) operator $W_{NN^*}{}^q$ is defined by

$$W_{NN^*}{}^q\equiv N!N^*!\exp(-\beta H_{NN^*}), \quad (2)$$

* On leave of absence from Department af Physics, University of Delhi, Delhi, India. Present address: Courant Institute of Mathematical Sciences, New York University, New York, New York.

[1] E. G. D. Cohen and J. M. J. Van Leeuwen, Physica **26**, 1171 (1960); **27**, 1157 (1961).

[2] F. London, J. Chem. Phys. **11**, 203 (1943).

[3] G. Placzek, in *Proceedings of the Second Berkeley Symposium on Mathematical Statistics and Probability, 1950* (University of California Press, Berkeley and Los Angeles, 1951), p. 581.

[4] L. S. Garcia-Colin and J. Peretti, J. Math. Phys. **1**, 97 (1960).

[5] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).

[6] R. K. Pathria and M. P. Kawatra, Phys. Rev. **129**, 944 (1963), hereafter referred to as PK in the text.

[7] The variables $1, 2, \cdots; 1^*, 2^*, \cdots$ in the state vectors are really the position vectors $\mathbf{r}_1, \mathbf{r}_2, \cdots; \mathbf{r}_1^*, \mathbf{r}_2^*, \cdots$ of the particles labeled by $1, 2, \cdots$, etc. It may also be mentioned here that if one chooses to work in momentum representation, these variables will stand for the particle momenta.

where H_{NN^*} is the total Hamiltonian of the system given by

$$H_{NN^*}=-\frac{1}{2m}\sum_{i=1}^{N}\nabla_i^2-\frac{1}{2m^*}\sum_{i^*=1}^{N^*}\nabla_{i^*}^2+V, \quad (3)$$

with m and m^* being the respective masses of the two types of particles, while V is the potential energy operator which consists of a sum over all pairs of particles constituting the system,[8] and

$$\beta=1/k_BT. \quad (4)$$

Here, and throughout the present investigation, we shall use $\hbar=1$.

While studying the thermodynamic properties of a system one goes through the generalized Mayer-Kahn-Uhlenbeck[9] scheme of cluster integrals for imperfect gases:

$$U^{\text{cl}}\rightarrow W^{\text{cl}}\rightarrow W^q\rightarrow U^q, \quad (5)$$

and a generalization of the above for a mixture of several components has been achieved by Pathria and the author.[6] We shall, in the present analysis, follow the same scheme in deriving the explicit expressions for the various distribution functions.

The three, two "pure" and one "mixed," distribution functions in the system of our interest are respectively defined by the following relations:

$$\rho_{NN^*}^{(i,j)}=\frac{1}{Z_{NN^*}}\frac{1}{(N-i)!(N^*-j)!}\times\int\langle 1,2,\cdots,\mathbf{N};1^*,2^*,\cdots,\mathbf{N}^*|W_{NN^*}^q|\times|1,2,\cdots\mathbf{N};1^*,2^*,\cdots,\mathbf{N}^*\rangle\times d^3r_{1+i}\cdots d^3r_Nd^3r_{(1+j)^*}\cdots d^3r_{N^*}, \quad (6)$$

where (i,j) takes the values (2,0), (0,2), and (1,1) for the two pure distribution functions, $\rho^{(20)}(\mathbf{r}_1,\mathbf{r}_2)$ and $\rho^{(02)}(\mathbf{r}_{1^*},\mathbf{r}_{2^*})$, and for the mixed one $\rho^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$, respectively.

The above definitions correspond to considerations with regard to a canonical ensemble and to go over to a grand canonical ensemble what one does is to write as follows:

$$\rho^{(i,j)}=\sum_{N=i}^{\infty}\sum_{N^*=j}^{\infty}\rho_{NN^*}^{(i,j)}\frac{z^Nz^{*N^*}}{\Xi}Z_{NN^*}, \quad (7)$$

where Ξ, the grand partition function, is defined as

$$\Xi=\sum_{N=0}^{\infty}\sum_{N^*=0}^{\infty}z^Nz^{*N^*}Z_{NN^*}, \quad (8)$$

and z and z^* are the respective fugacities of the two components.

3. EVALUATION OF THE "PURE" DISTRIBUTION FUNCTIONS $\rho^{(20)}$ AND $\rho^{(02)}$

To evaluate $\rho^{(20)}(\mathbf{r}_1,\mathbf{r}_2)$ and $\rho^{(02)}(\mathbf{r}_{1^*},\mathbf{r}_{2^*})$, one follows the rule set out in PK[10] and writes $W_{NN^*}^q$ through the classification of the entire ensemble into clusters keeping the particles 1 and 2 fixed. It is easy to see that there are only two possibilities of breaking up of the ensemble into clusters: (1) the particles 1 and 2 are in different clusters, and (2) the particles 1 and 2 fall in the same cluster. Once we pick up the clusters containing the particles 1 and 2, the system can be thought of as compartmentalized, one part containing these two fixed particles and the other without them. We then see that $W_{NN^*}^q$ can be written as:

$$W_{NN^*}^q=\sum_{\substack{p,q=0\\p+q\leqslant N-2}}^{N-2}\sum_{\substack{p^*,q^*=0\\p^*+q^*\leqslant N^*}}^{N^*}\sum_{\{p\},\{q\}}{}'\sum_{\{p^*\},\{q^*\}}{}''U_{p+1,p^*}[1,\{p\};\{p^*\}]U_{q+1,q^*}[2,\{q\};\{q^*\}]\times W^q_{N-p-q-2,N^*-p^*-q^*}\gamma^{P_p+P_q}\gamma^{*P_{p^*}+P_{q^*}}+\sum_{p=0}^{N-2}\sum_{p^*=0}^{N^*}\sum_{\{p\}}{}'\sum_{\{p^*\}}{}''U_{p+2,p^*}[1,2,\{p\};\{p^*\}]W^q_{N-p-2,N^*-p^*}\gamma^{P_p}\gamma^{*P_{p^*}}, \quad (9)$$

where

$$U_{p+1,p^*}[1,\{p\};\{p^*\}]=\langle 1,P(2,\cdots\mathbf{p}+1);P^*(1^*,\cdots\mathbf{p}^*)|U_{p+1,p^*}|1,2,\cdots\mathbf{p}+1;1^*,\cdots\mathbf{p}^*\rangle \quad (10)$$

and

$$U_{p+2,p^*}[1,2,\{p\};\{p^*\}]=\langle 1,2,P(3,\cdots\mathbf{p}+2);P^*(1^*,\cdots\mathbf{p}^*)|U_{p+2,p^*}|1,2,3,\cdots\mathbf{p}+2;1^*,\cdots\mathbf{p}^*\rangle. \quad (11)$$

The summation $\sum_{\{p\}}'$ is over all possible permutations P of the p particles of unstarred type and $\sum_{\{p^*\}}''$ over all possible permutations P^* of the p^* starred particles, γ and γ^* are either $+1$ or -1 depending upon whether the respective component is of boson or fermion type. In the following analysis we shall consider the system to be made up to two types of spinless bosons for sake of convenience of calculations and the effects of the particles obeying

[8] We shall restrict ourselves, in the present analysis, to only two-body interactions and will not consider those of higher orders.

[9] J. E. Mayer, J. Chem. Phys. 5, 67 (1937); J. E. Mayer and P. G. Ackermann, *ibid.* 5, 74 (1937); J. E. Mayer and S. F. Harrison, *ibid.* 6, 87, 101 (1938); B. Kahn and G. E. Uhlenbeck, Physica 5, 99 (1938).

[10] See also the classification of the ensemble into clusters in a one-component system, L. Colin and J. Peretti, Compt. Rend. 248, 1625 (1959).

arbitrary statistics and having any spin can be, as stated earlier, inserted at the end following, essentially, the method of Lee and Yang[11] and PK. Substituting $W_{NN^{*}q}$ from (9) into (6) we find

$$Z_{NN^*}\rho_{NN^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\substack{p,q=0\\ p+q\leqslant N-2}}^{N-2}\sum_{\substack{p^*,q^*=0\\ p^*+q^*\leqslant N^*}}^{N^*} A_{pp^*}^{(10)}(\mathbf{r}_1)A_{qq^*}^{(10)}(\mathbf{r}_2)Z_{N-p-q-2,N^*-p^*-q^*} + \sum_{p=0}^{N-2}\sum_{p^*=0}^{N^*} A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)Z_{N-p-2,N^*-p^*}, \quad (12)$$

where the generalized cluster integrals $A_{pp^*}^{(10)}$ and $A_{pp^*}^{(20)}$ are:

$$A_{pp^*}^{(10)}(\mathbf{r}_1)=\frac{1}{p!p^*!}\int\langle 1,\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_p;\mathbf{y}_1^*,\cdots\mathbf{y}_{p^*}|U_{p+1,p^*}|1,\mathbf{x}_1,\mathbf{x}_2\cdots\mathbf{x}_p;\mathbf{y}_1^*,\cdots\mathbf{y}_{p^*}\rangle d^{3p}xd^{3p^*}y$$

$$=(p+1)b_{p+1,p^*}\ (\text{in the limit } \Omega\to\infty) \quad (13)$$

and

$$A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{p!p^*!}\int\langle 1,2,\mathbf{x}_1,\cdots\mathbf{x}_p;\mathbf{y}_1^*,\cdots\mathbf{y}_{p^*}|U_{p+2,p^*}|1,2,\mathbf{x}_1,\cdots\mathbf{x}_p;\mathbf{y}_1^*,\cdots\mathbf{y}_{p^*}\rangle d^{3p}xd^{3p^*}y, \quad (14)$$

while b_{p+1,p^*} is Mayer's cluster integral. Thus we have

$$\rho^{(20)}(\mathbf{r}_1,\mathbf{r}_2)=\Big[\sum_{p=0}^{\infty}\sum_{p^*=0}^{\infty}A_{pp^*}^{(10)}(\mathbf{r}_1)z^{p+1}z^{*p^*}\Big]^2 + \sum_{p=0}^{\infty}\sum_{p^*=0}^{\infty}A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)z^{p+2}z^{*p^*}$$
$$=\rho^2+F^{(20)}(\mathbf{r}_1,\mathbf{r}_2), \quad (15)$$

where ρ is the density of the unstarred component of the system given by

$$\rho=\left(\frac{m}{2\pi\beta}\right)^{3/2}\left[g_{5/2}(z)-2a\left(\frac{m}{2\pi\beta}\right)^{1/2}\{g_{3/2}(z)\}^2\right] - a_{11^*}\frac{(mm^*)^{1/2}(m+m^*)}{(2\pi\beta)^2}g_{3/2}(z)g_{3/2}(z^*), \quad (16)$$

up to first order in interaction parameters. Here,

$$g_n(z)=\sum_{l=1}^{\infty}\frac{z^l}{l^n}. \quad (17)$$

To evaluate $F^{(20)}(\mathbf{r}_1,\mathbf{r}_2)$, we decompose the sums in two parts and write

$$\sum_{p=0}^{\infty}\sum_{p^*=0}^{\infty}A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)z^{p+2}z^{*p^*} = \sum_{p=0}^{\infty}A_{p0}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)z^{p+2} + \sum_{p=0}^{\infty}\sum_{p^*=1}^{\infty}A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)z^{p+2}z^{*p^*}. \quad (18)$$

The first sum in the above equation (18) can easily be recognized as the contribution if the system had only one component. This has been computed by Colin and Peretti, through a mixed approach of the binary-collision expansion method of Lee and Yang and that of torons[12] and is, up to first order in interaction parameters,

$$\sum_{p=0}^{\infty}A_{p0}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)z^{p+2}=\left(\frac{m}{2\pi\beta}\right)^3\left[\{g_{3/2}(z,s)\}^2\left(1-\frac{8a}{r}\right) - 8a\left(\frac{m}{2\pi\beta}\right)^{1/2}g_{3/2}(z)g_{1/2}(z,s)g_{3/2}(z,s)\right], \quad (19)$$

where

$$s=(m/2\beta)^{1/2}r, \quad (20)$$

$$r=|\mathbf{r}_1-\mathbf{r}_2|, \quad (21)$$

and

$$g_n(z,s)=\sum_{l=1}^{\infty}(z^l/l^n)\exp(-s^2/l). \quad (22)$$

Here, a has been used for the hard sphere diameter of the unstarred particles. It may be added here that the corresponding quantity for the starred particles will be referred to as a^*. Also, a_{11^*} will be used for the corresponding parameter in the case of interaction between the unlike particles. In the present case of hard spheres $a_{11^*}=\frac{1}{2}(a+a^*)$, however, we shall retain here the independent parameter a_{11^*} especially keeping in view the extension of the present treatment to cases involving more realistic interactions.

Now we shall evaluate the second sum in Eq. (18). To do so we shall follow essentially the same toron method generalized to embrace different types of components present in the system and keep in mind that the coordinates of the particles 1 and 2 are to be kept fixed. The generalized cluster integral $A_{pp^*}^{(20)}$ can be

[11] T. D. Lee and C. N. Yang, Phys. Rev. **116**, 25 (1959).

[12] E. W. Montroll and J. C. Ward, Phys. Fluids **1**, 55 (1958).

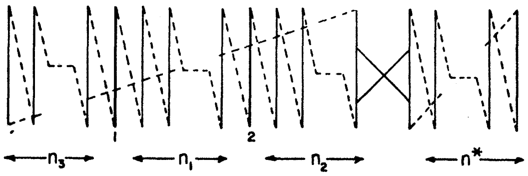

FIG. 1. A typical schematic sketch of $\{(p+2),p^*\}$ cluster with n_1, n_2, n_3, and n^* as the number of particles of respective groups as indicated· for details see the text.

diagrammatically represented as in Fig. 1. This diagram represents a typical set up of the cluster of $p+2$ particles of the unstarred and p^* of the starred type. Keeping the particles 1 and 2 fixed, we let n_1 be the number of particles between 1 and 2, n_2 as the number between 2 and the particle (including this one) providing the link between the starred and unstarred group of particles, and n_3 is the number of particles between this linking particle and the 1, also similarly n^* is the number of particles in the starred group excluding the one providing the link between the groups. Thus

$$n_1+n_2+n_3+2=p+2 \quad \text{and} \quad n^*+1=p^*. \tag{23}$$

To evaluate the integral it is convenient to work in the momentum representation, and the transformation from the coordinate to momentum space can be carried out through

$$\langle \mathbf{k}_1',\cdots|U|\mathbf{k}_1,\cdots\rangle = \int \exp[-i(\mathbf{k}_1'\cdot\mathbf{r}_1'+\cdots)+i(\mathbf{k}_1\cdot\mathbf{r}_1+\cdots)] \times\langle \mathbf{r}_1',\cdots|U|\mathbf{r}_1,\cdots\rangle d^3r_1'\cdots d^3r_1\cdots. \tag{24}$$

The corresponding diagram for the generalized cluster integral is the momentum representation is given in Fig. 2. Here, the momenta of particles 1 and 2 are to be kept fixed and the interacting pair has the initial momenta $\mathbf{k}_3$ and $\mathbf{k}_1^*$ and the final as $\mathbf{k}_4$ and $\mathbf{k}_2^*$ and integration is to be carried over all momenta except for those of 1 and 2. The evaluation of such an integral can be carried out following the general procedure laid in PK. The integral corresponding to the typical set up in Fig. 2 can be written as

$$\begin{aligned} I(\mathbf{k}_1,\mathbf{k}_2) &= \int \exp\left\{-\beta\left(\frac{n_3k_1^2+n_2k_2^2}{2m}+\frac{n^*k_{1^*}^2}{2m^*}\right)\right\} \\ &\quad\times\langle \mathbf{k}_4,\mathbf{k}_{2^*}|U_{11}|\mathbf{k}_3,\mathbf{k}_{1^*}\rangle\delta^3(\mathbf{k}_1-\mathbf{k}_4)\delta^3(\mathbf{k}_2-\mathbf{k}_3) \\ &\quad\times\delta^3(\mathbf{k}_{1^*}-\mathbf{k}_{2^*})d^3k_3d^3k_4d^3k_{1^*}d^3k_{2^*} \\ &= \exp\left\{-\beta\left(\frac{n_3k_1^2+n_2k_2^2}{2m}\right)\right\}\int \exp\left(-\beta\frac{n^*k_{1^*}^2}{2m^*}\right) \\ &\quad\times\langle \mathbf{k}_1,\mathbf{k}_{1^*}|U_{11}|\mathbf{k}_2,\mathbf{k}_{1^*}\rangle d^3k_{1^*}. \end{aligned} \tag{25}$$

We know from Eq. (29) of PK

$$\langle \mathbf{k}_1,\mathbf{k}_{1^*}|U_{11}|\mathbf{k}_2,\mathbf{k}_{1^*}\rangle = \frac{a_{11^*}}{2\pi^2}\frac{\exp(-\beta E'')-\exp(-\beta E)}{k''^2-k^2}\delta^3(\mathbf{k}_1-\mathbf{k}_2), \tag{26}$$

where

$$E=k_1^2/2m+k_{1^*}^2/2m^*, \tag{27}$$

$$E''=k_2^2/2m+k_{1^*}^2/2m^*, \tag{28}$$

$$\mathbf{k}=\mu(\mathbf{k}_1/m-\mathbf{k}_{1^*}/m^*), \tag{29}$$

$$\mathbf{k}''=\mu(\mathbf{k}_2/m-\mathbf{k}_{1^*}/m^*), \tag{30}$$

and μ is the reduced mass. Thus we have

$$\begin{aligned} I(\mathbf{k}_1,\mathbf{k}_2) &= \frac{a_{11^*}}{2\pi^2}\delta^3(\mathbf{k}_1-\mathbf{k}_2)\exp\left\{-\beta\frac{n_3k_1^2+n_2k_2^2}{2m}\right\} \\ &\quad\times\int \exp\left\{-\beta\frac{n^*k_{1^*}^2}{2m^*}\right\}\frac{\exp(-\beta E'')-\exp(-\beta E)}{k''^2-k^2}d^3k_{1^*}, \end{aligned} \tag{31}$$

and now going back to the configuration space we have

$$I(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{8\pi^3}\int I(\mathbf{k}_1,\mathbf{k}_2)\exp(i\mathbf{k}_1\cdot\mathbf{r}_1-i\mathbf{k}_2\cdot\mathbf{r}_2)d^3k_1d^3k_2. \tag{32}$$

Substituting (32) in (31) and changing the vaiiables to total and relative momenta, and keeping in mind the rotational symmetry, the integral yields

$$I(r)=\frac{c_1}{p^{*3/2}}\frac{1}{(p-n_1+1)^{3/2}}\exp\left\{-\frac{mr^2}{2(p-n_1+1)\beta}\right\}, \tag{33}$$

where

$$c_1=-\frac{a_{11^*}m^{1/2}m^{*1/2}(m+m^*)}{(2\pi\beta)^2}. \tag{34}$$

But in the above we have not considered the contribution of the loops formed by n_1 particles between the particles 1 and 2, and this would result in a multiplica-

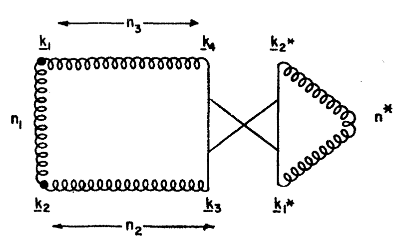

FIG. 2. Schematic toron structure corresponding to Fig. 1 in momentum representation.

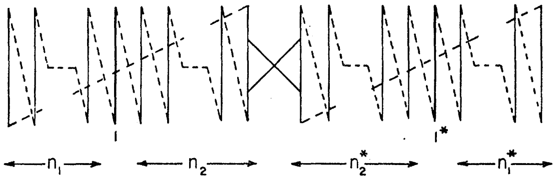

FIG. 3. A typical schematic sketch of $\{(p+1),(p^*+1)\}$ cluster.

tion factor of

$$\left(\frac{m}{2\pi\beta}\right)^{3/2}\frac{1}{(n_1+1)^{3/2}}\exp\left\{-\frac{mr^2}{2(n_1+1)\beta}\right\}. \quad (35)$$

Therefore,

$$I(n_1,n_2,n_3;p^*;r) = c_1\left(\frac{m}{2\pi\beta}\right)^{3/2}\frac{1}{p^{*3/2}}\frac{1}{\{(p-n_1+1)(n_1+1)\}^{3/2}} \times\exp\left\{-\frac{m(p+2)r^2}{2(p-n_1+1)(n_1+1)\beta}\right\}. \quad (36)$$

Now we have to sum over all possible combinations of n_1, n_2 and n_3 subject to the conditions

$$n_1+n_2+n_3=p;\quad 0\leqslant n_1\leqslant p;\quad 0\leqslant n_2\leqslant p;\quad 0\leqslant n_3\leqslant p. \quad (37)$$

It is quite easy to see there would be $p!p^*!$ possible orientations of such diagrams. Thus the contribution from this generalized cluster integral $A_{pp^*}^{(20)}(\mathbf{r}_1,\mathbf{r}_2)$ to the pair distribution function is given by

$$\sum_{p=0}^{\infty}\sum_{p^*=1}^{\infty}\sum_{\{n_1\},\{n_2\},\{n_3\}} I(n_1,n_2,n_3;p^*;r)z^{p+2}z^{*p^*} =C_1 g_{3/2}(z^*)\{g_{3/2}(z,s)\}^2, \quad (38)$$

where

$$C_1=-\frac{a_{11}{}^*m^2m^{*1/2}(m+m^*)}{(2\pi\beta)^{7/2}}. \quad (39)$$

Thus we have from (15), (16), (19), and (38)

$$\rho^{(20)}(r)=\rho^2+\left(\frac{m}{2\pi\beta}\right)^3\left[\{g_{3/2}(z,s)\}^2\left(1-\frac{8a}{r}\right)-8a\left(\frac{m}{2\pi\beta}\right)^{1/2}g_{3/2}(z)g_{1/2}(z,s)g_{3/2}(z,s) -\frac{a_{11}{}^*m^{-1}m^{*1/2}(m+m^*)}{(2\pi\beta)^{1/2}}\{g_{3/2}(z,s)\}^2g_{3/2}(z^*)\right], \quad (40)$$

and from a similar consideration as above we may evaluate the other pure pair distribution function $\rho^{(02)}(r^*)$ for the starred particles and it is quite evident that it can straightaway be written by interchanging the role of starred and unstarred variables in the above equation (40).

4. THE "MIXED" PAIR DISTRIBUTION FUNCTION $\rho^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$

In this section we shall evaluate the mixed distribution function which would measure the correlation between the two types of particles in the system. In the present context we may imagine the cluster formation such that either the unstarred and starred fixed particles 1 and 1* are in different clusters or they may be in the same one, and for this purpose we can write

$$W_{NN^*}{}^q=\sum_{\substack{p,q=0\\p+q\leqslant N-1}}^{N-1}\sum_{\substack{p^*,q^*=0\\p^*+q^*\leqslant N^*-1}}^{N^*-1}\sum_{\{p\},\{q\}}{}'\sum_{\{p^*\},\{q^*\}}{}'' U_{p+1,p^*}[1,\{p\};\{p^*\}]U_{q,q^*+1}[\{q\};1^*,\{q^*\}]W^q{}_{N-p-q-1,N^*-p^*-q^*-1} +\sum_{p=0}^{N-1}\sum_{p^*=0}^{N^*-1}\sum_{\{p\}}{}'\sum_{\{p^*\}}{}'' U_{p+1,p^*+1}[1,\{p\};1^*,\{p^*\}]W^q{}_{N-p-1,N^*-p^*-1} \quad (41)$$

and

$$Z_{NN^*}\rho_{NN^*}{}^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})=\sum_{\substack{p,q=0\\p+q\leqslant N-1}}^{N-1}\sum_{\substack{p^*,q^*=0\\p^*+q^*\leqslant N^*-1}}^{N^*-1} A_{pp^*}{}^{(10)}(\mathbf{r}_1)A_{qq^*}{}^{(01)}(\mathbf{r}_{1^*})Z_{N-p-q-1,N^*-p^*-q^*-1} +\sum_{p=0}^{N-1}\sum_{p^*=0}^{N^*-1}A_{pp^*}{}^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})Z_{N-p-1,N^*-p^*-1}. \quad (42)$$

Therefore,

$$\rho^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})=\rho\rho^*+F^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*}), \quad (43)$$

where

$$F^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})=\sum_{p=0}^{\infty}\sum_{p^*=0}^{\infty}A_{pp^*}{}^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})z^{p+1}z^{*p^*+1}. \quad (44)$$

To evaluate $A_{pp^*}^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$, and then $F^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$, we consider a typical orientation of a $\{(p+1),(p^*+1)\}$ cluster schematically shown in Fig. 3. In this diagram we have considered, in the unstarred group, n_1 as the number of particles between the particle 1 (keeping in mind that this particle and also 1* are to be kept fixed) and the one providing the link between the unstarred and the starred groups, and n_2 as the number between the link particle and the 1 going round the cluster. n_1^* and n_2^* are the corresponding numbers in the starred particles group. Figure 4 represents the same scheme in the momentum representation and the corresponding integral is given by

$$I=\int \exp\left\{-\beta\left(\frac{n_1k_1^2+n_2k_1'^2}{2m}+\frac{n_1^*k_{1^*}^2+n_2^*k_{1^*}'^2}{2m^*}\right)\right\}$$
$$\times\langle\mathbf{k}_4,\mathbf{k}_{4^*}|U_{11}|\mathbf{k}_3,\mathbf{k}_{3^*}\rangle$$
$$\times\delta^3(\mathbf{k}_1-\mathbf{k}_3)\delta^3(\mathbf{k}_1'-\mathbf{k}_4)\delta^3(\mathbf{k}_{1^*}-\mathbf{k}_{3^*})$$
$$\times\delta^3(\mathbf{k}_{1^*}'-\mathbf{k}_{4^*})d^3k_3d^3k_4d^3k_{3^*}d^3k_{4^*} \quad (45)$$

and U_{11}, here, is given by

$$\langle\mathbf{k}_1',\mathbf{k}_{1^*}'|U_{11}|\mathbf{k}_1,\mathbf{k}_{1^*}\rangle=\frac{a_{11^*}}{2\pi^2}\delta^3(\mathbf{k}_1'+\mathbf{k}_{1^*}'-\mathbf{k}_1-\mathbf{k}_{1^*})$$
$$\times\frac{\exp(-\beta E')-\exp(-\beta E)}{k'^2-k^2}, \quad (46)$$

where

$$E'=k_1'^2/2m+k_{1^*}'^2/2m^*, \quad (47)$$

$$\mathbf{k}'=\mu(\mathbf{k}_1'/m-\mathbf{k}_{1^*}'/m^*), \quad (48)$$

and E and $\mathbf{k}$ are given by (27) and (29), respectively. Substituting (46) in (45) and going over the spatial configuration we can evaluate the contribution of the cluster considered above. One, then, first sums over all such orientations and afterwards over all values of p and p^* to get the expression for $F^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$. These calculations aıe given in the Appendix wherein one arrives at

$$F^{(11)}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)$$
$$=-2\frac{a_{11^*}}{|\mathbf{r}_1-\mathbf{r}_{1^*}|}\frac{(mm^*)^{3/2}}{(2\pi\beta)^3}g_{3/2}\left(z,\frac{\mu(|\mathbf{r}_1-\mathbf{r}_{1^*}|)}{(m\beta)^{1/2}}\right)$$
$$\times g_{3/2}\left(z^*,\frac{\mu(|\mathbf{r}_1-\mathbf{r}_{1^*}|)}{(m^*\beta)^{1/2}}\right), \quad (49)$$

where the various symbols have their usual meaning.

5. GENERAL DISCUSSION

We observe that the results obtained in the previous sections have the series of the type $g_n(x)$ and $g_n(x,s)$ appearing, and these series converge only for values of $x<1$ irrespective of the value of the index n, thus restricting the validity of the results only to low-density (gaseous) systems. Also, the calculations have been carried out only up to first order in the interaction parameters, thereby limiting ourselves to comparatively large interparticle distances. For short distances, however, higher order terms have to be considered where the contribution from multiparticle scattering also becomes quite significant.

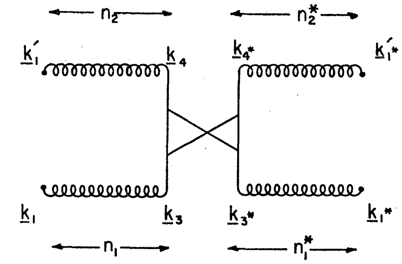

FIG. 4. Schematic toron structure of $\{(p+1),(p^*+1)\}$ cluster of Fig. 3 in momentum representation.

It is not difficult to see that the foregoing treatment can be generalized to the case where the particles constituting the system have arbitrary spin. While doing so it is naturally necessary to keep in mind the statistics followed by individual particles. Taking the representation where all the spins are quantized along the z direction and noting that the particle spin remains conserved, it is easy to see that the foregoing formalism requires only formal changes, e.g., the integrations over various momenta have to be augmented by summations over the respective spins. Also since the hard sphere interaction, considered in this paper, is spin-independent, the introduction of spin in the analysis only brings in certain multiplication factors depending upon the spin of the individual components. These factors can straightaway be calculated following the rule of Lee and Yang,[11] later generalized by Pathria and the author.[6]

Next, it may be remarked here that the treatment given in the foregoing sections should be capable of generalization to the system with more realistic interactions than the simple hard sphere interactions. This can be achieved in a quite straightforward manner provided the potential is such that there are no bound states, but at the same time the relative kinetic energy is smaller than the attractive potential energy between the particles, the conditions which in ıeality are quite compatible to each other. One expects then that in the foregoing analysis, one needs to replace everywhere the hard-sphere diameter by the respective scattering length.[13] In this connection it may be noted that the calculation of some of the thermodynamical quantities of a fluid from the pair correlation functions is quite sensitive to the relative position of the minimum of the potential and the first peak in the correlation function. This problem in the one-component system has been dealt by Lowry, Davis, and Rice in their recent paper.[14]

[13] This statement is made here in view of the results of an earlier investigation into a single-component system by Pathria and the author; R. K. Pathria and M. P. Kawatra, Progr. Theoret. Phys. (Kyoto) **27**, 1085 (1962).

[14] B. A. Lowry, H. T. Davis, and S. A. Rice, Phys. Fluids **7**, 402 (1964).

APPENDIX

In this appendix we shall evaluate $F^{(11)}(\mathbf{r}_1,\mathbf{r}_{1^*})$. We have after substituting (46) in (45) and carrying out the integrations over $\mathbf{k}_3$, $\mathbf{k}_4$, $\mathbf{k}_{3^*}$ and $\mathbf{k}_{4^*}$:

$$I(n_1,n_2;n_1^*,n_2^*;\mathbf{k}_1',\mathbf{k}_1,\mathbf{k}_{1^*}',\mathbf{k}_{1^*})$$

$$=\frac{a_{11^*}}{2\pi^2}\delta^3(\mathbf{k}_1'+\mathbf{k}_{1^*}'-\mathbf{k}_1-\mathbf{k}_{1^*})\exp\left[-\beta\left(\frac{n_1k_1^2+n_2k_1'^2}{2m}+\frac{n_1^*k_{1^*}^2+n_2^*k_{1^*}'^2}{2m^*}\right)\right]\frac{\exp(-\beta E')-\exp(-\beta E)}{k'^2-k^2}. \quad (50)$$

We then go over the spatial configurations and write

$$I(n_1,n_2;n_1^*,n_2^*;\mathbf{r}_1,\mathbf{r}_{1^*})$$

$$=\frac{1}{64\pi^6}\int I(n_1,n_2;n_1^*,n_2^*;\mathbf{k}_1',\mathbf{k}_1,\mathbf{k}_{1^*}',\mathbf{k}_{1^*})\exp[i(\mathbf{k}_1'\cdot\mathbf{r}_1+\mathbf{k}_{1^*}'\cdot\mathbf{r}_{1^*}-\mathbf{k}_1\cdot\mathbf{r}_1-\mathbf{k}_{1^*}\cdot\mathbf{r}_{1^*})]d^3k_1'd^3k_1d^3k_{1^*}'d^3k_{1^*}. \quad (51)$$

Making a change of variables from $\mathbf{k}_1'$, $\mathbf{k}_1$, $\mathbf{k}_{1*}'$, $\mathbf{k}_{1*}$ to $\mathbf{K}'$ and $\mathbf{K}$, given by

$$\mathbf{K}'=\mathbf{k}_1'+\mathbf{k}_{1^*}' \quad \text{and} \quad \mathbf{K}=\mathbf{k}_1+\mathbf{k}_{1^*}, \quad (52)$$

and $\mathbf{k}'$ and $\mathbf{k}$ given by (48) and (29), respectively, and integrating first over $\mathbf{K}'$ and then over $\mathbf{K}$ one gets:

$$I(n_1,n_2;n_1^*,n_2^*;\mathbf{r}_1,\mathbf{r}_{1^*})$$

$$=\frac{c_2}{(mp+m^*p^*+M)^{3/2}}\int\frac{\exp(-\beta k'^2/2\mu)-\exp(-\beta k^2/2\mu)}{k'^2-k^2}\exp[-(Ak^2+Bk'^2+C\mathbf{k}'\cdot\mathbf{k})]$$
$$\times\exp[-i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}_1-\mathbf{r}_{1^*})]d^3k'd^3k, \quad (53)$$

where

$$A=\frac{(mp+m^*p^*+M)(m^*n_1+mn_1^*)-mm^*(n_1-n_1^*)^2}{2(mp+m^*p^*+M)mm^*}\beta, \quad (54)$$

$$B=\frac{(mp+m^*p^*+M)(m^*n_2+mn_2^*)-mm^*(n_2-n_2^*)^2}{2(mp+m^*p^*+M)mm^*}\beta, \quad (55)$$

$$C=-\frac{(n_1-n_1^*)(n_2-n_2^*)}{(mp+m^*p^*+M)}\beta, \quad (56)$$

and

$$c_2=\frac{a_{11^*}}{16\pi^5}\frac{M^3}{(2\pi\beta)^{3/2}}. \quad (57)$$

The integral (53) can be evaluated in a similar fashion as in Ref. 4. Since the integrand remains finite when $\mathbf{k}'\to\mathbf{k}$, we shall replace $(k'^2-k^2)^{-1}$ by its principal value

$$P\left(\frac{1}{k'^2-k^2}\right)=\frac{1}{2i}\int_0^\infty\exp[i(k'^2-k^2)\xi]d\xi-\frac{1}{2i}\int_{-\infty}^0\exp[i(k'^2-k^2)\xi]d\xi. \quad (58)$$

Substituting the above in (53) we see that the integral breaks up into four different parts, picking up one of them

$$I_1=\frac{1}{2i}\int d^3k'd^3k\int_0^\infty d\xi\exp\left[i(k'^2-k^2)\xi-\beta\frac{k^2}{2\mu}-(Ak^2+Bk'^2+C\mathbf{k}\cdot\mathbf{k}')-i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{r}_1-\mathbf{r}_{1^*})\right]. \quad (59)$$

Integrating over $\mathbf{k}'$ and $\mathbf{k}$ and keeping in mind the rotational symmetry, we get

$$I_1=\frac{1}{2i}\int_{-u}^{\infty-u}\frac{2d\eta}{(\eta^2+v^2-4C^2)^{3/2}}\exp\left[-\frac{2(v+2C)}{\eta^2+v^2-4C^2}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)^2\right], \quad (60)$$

where

$$u=i(2A-2B+\beta/\mu) \tag{61}$$

and

$$v=2A+2B+\beta/\mu\,, \tag{62}$$

and similarly other parts can be evaluated. Combining these pairwise and after a little algebra one arrives at:

$$I(n_1,n_2;\,n_1^*n_2^*;\,|\mathbf{r}_1-\mathbf{r}_{1^*}|)=-2(2\pi)^3c_2[Y(n_1+1,\,n_2;\,n_1^*+1,\,n_2^*)-Y(n_1,\,n_2+1;\,n_1^*,\,n_2^*+1)]\,, \tag{63}$$

where

$$Y(n_1,n_2;\,n_1^*,n_2^*)=\int_0^{a-b}\frac{dt}{[(a-b)^2-4c^2-t^2]^{3/2}}\exp\left[-\frac{2(a+b+2c)}{(a+b)^2-4c^2-t^2}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)^2\right], \tag{64}$$

with

$$a=\frac{(mp+m^*p^*)(m^*n_1+mn_1^*)-mm^*(n_1-n_1^*)^2}{mm^*(mp+m^*p^*)}\beta\,, \tag{65}$$

$$b=\frac{(mp+m^*p^*)(m^*n_2+mn_2^*)-mm^*(n_2-n_2^*)^2}{mm^*(mp+m^*p^*)}\beta\,, \tag{66}$$

and

$$c=-\frac{(n_1-n_1^*)(n_2-n_2^*)}{mp+m^*p^*}\beta\,. \tag{67}$$

There are $p!p^*!$ various diffeient orientations of the set up as in Fig. 3 with the given value of n_1, n_2, n_1^*, and n_2^* and while evaluating $F^{(11)}$ we allow each one of the n's to vary from zero to infinity. Thus

$$F^{(11)}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)=-2(2\pi)^3c_2\sum_{\substack{n_1,n_2,\\ n_1^*,n_2^*=0}}^{\infty}\frac{z^{n_1+n_2+1}z^{*n_1^*+n_2^*+1}}{(mp+m^*p^*+M)^{3/2}}[Y(n_1+1,\,n_2;\,n_1^*+1,\,n_2^*)-Y(n_1,\,n_2+1;\,n_1,\,n_2^*+1)]$$

$$=-2(2\pi)^3c_2\left[\sum_{n_2,n_2^*=0}^{\infty}\frac{z^{n_2}z^{*n_2^*}}{(mn_2+m^*n_2^*)^{3/2}}Y(0,n_2;\,0,n_2^*)-\sum_{n_1,n_1^*=0}^{\infty}\frac{z^{n_1}z^{*n_1^*}}{(mn_1+m^*n_1^*)^{3/2}}Y(n_1,0;\,n_1^*,0)\right]. \tag{68}$$

The function Y can be evaluated with the help of the following standard formula:

$$\int_0^{\alpha}\frac{dy}{(x^2-y^2)^{3/2}}\exp\left(-\frac{s^2}{x^2-y^2}\right)=\frac{1}{x|s|}\exp\left(-\frac{s^2}{x^2}\right)\mathrm{erf}\left[\frac{|s|\alpha}{x(x^2-\alpha^2)^{1/2}}\right]. \tag{69}$$

Noting that the erf is $-\pi^{1/2}/2$ when α is negative, we can write

$$F^{(11)}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)=-2\frac{(2\pi)^3c_2\pi^{1/2}}{\sqrt{2}(|\mathbf{r}_1-\mathbf{r}_{1^*}|)}\left(\frac{mm^*}{M}\right)^{3/2}\sum_{n,n^*=0}^{\infty}\frac{z^nz^{*n^*}}{(nn^*)^{3/2}}\exp\left[-\frac{2\mu^2}{\beta}\left(\frac{1}{mn}+\frac{1}{m^*n^*}\right)(|\mathbf{r}_1-\mathbf{r}_{1^*}|)^2\right]$$

$$=-2\left\{\frac{mm^*}{(2\pi\beta)^2}\right\}^{3/2}\frac{a_{11^*}}{|\mathbf{r}_1-\mathbf{r}_{1^*}|}g_{3/2}\left(z,\frac{\mu|\mathbf{r}_1-\mathbf{r}_{1^*}|}{(m\beta)^{1/2}}\right)g_{3/2}\left(z^*,\frac{\mu|\mathbf{r}_1-\mathbf{r}_{1^*}|}{(m^*\beta)^{1/2}}\right). \tag{70}$$