UNIVERSAL EXPANSION OF THREE-PARTICLE DISTRIBUTION FUNCTION

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A universal, i.e., not dependent on the Hamiltonian of the two-particle interaction, expansion of the equilibrium three-particle distribution function with respect to the two-particle correlation functions is constructed. A diagram technique that permits systematic calculation of the coefficients of this expansion is proposed. In particular, it is established that allowance for the first four orders in the absence of long-range correlations gives the Kirkwood approximation. Corrections to the Kirkwood approximation both in the presence and absence of long-range correlations are found.

1. Introduction

One of the central problems in statistical mechanics is that of finding closed equations for the partial distribution functions. Two approaches can be distinguished (for more details, see, for example, [1–3]). The first is based on closure of the equilibrium BBGKY hierarchy and reduces to approximation of the partial distribution functions (usually the three- or four-particle functions) by an expression that contains the partial distribution functions of lower order. In particular, Born–Green theory, which is based on the Kirkwood superposition approximation for the three-particle distribution function, is obtained in this manner.

The second approach is based on the Ornstein–Zernike equation and various forms of virial expansion.

It has often been noted [1,2] that the Kirkwood approximation (and also more complicated forms of closure) has not yet been established from first principles; its domain of applicability has also not been established.

In this paper, we consider classical systems with two-body interaction and obtain a universal (independent of the Hamiltonian) expansion of the three-particle distribution function with respect to the two-particle correlation functions. In particular, we establish that allowance for the first few orders of the expansion in the absence of long-range correlations leads to the Kirkwood approximation. We find the first corrections to the Kirkwood approximation both in the presence and the absence of long-range correlations. Our point of departure is the construction of a quasi-equilibrium ensemble for given two-particle distribution function [4].

2. Reduced Distribution Functions and Variational Principle

We consider a system consisting of N identical structureless classical particles in a macroscopic volume V. A complete statistical description is determined by the N-particle distribution function $F_N(x_1, \ldots, x_N)$, where $x_i = (r_i, p_i)$ are the phase variables of particle i: the radius vector r_i and momentum vector p_i. We denote by B_V^1 the range of allowed values of x_i. The function F_N is non-negative for all x_i in B_V^1, is symmetric with respect to all permutations of the arguments $x_1, \ldots, x_N$, and satisfies the normalization condition

$$\int\limits_{B_V^N} F_N(x_1, \ldots, x_N)\, dx_1 \ldots dx_N = 1. \tag{1}$$

Here and in what follows, B_V^k is the Cartesian product of k regions B_V^1, $dx_i = d^3r_i d^3p_i$. We define the s-particle distribution functions $F_{s(N)}(x_1, \ldots, x_s)$, $s = 1, \ldots, N-1$:

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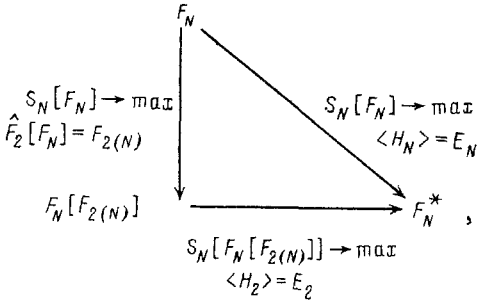
$$F_{s(N)} = (N!/(N-s)!) \int\limits_{B_V^{N-s}} F_N(x_1, \ldots, x_N)\, dx_{s+1} \ldots dx_N. \tag{2}$$

The subscript N means that we consider a system of a finite number N of particles. The passage to the thermodynamic limit $N \to \infty$, $V \to \infty$, $N/V = n = \text{const}$ is made at the end of the calculations, and the subscript N is omitted in the limiting expressions.

We consider the N-particle entropy $S_N[F_N]$:

$$S_N[F_N] = -k_B \int\limits_{B_V^N} F_N \ln F_N\, dx_1 \ldots dx_N, \tag{3}$$

where k_B is Boltzmann's constant; in (3) we have omitted a constant that is unimportant for what follows. In accordance with Gibbs's variational principle [5], the canonical distribution function F_N^* realizes a conditional maximum of the entropy (3) for given mean value of the Hamiltonian and the normalization (1). For systems with two-body interaction, the equilibrium F_N^* can be determined in two stages; we first find the quasi-equilibrium distribution $F_N[F_{2(N)}]$ that realizes the maximum of $S_N[F_N]$ for given two-particle distribution function $F_{2(N)}$ and the normalization (1), and we then determine the equilibrium distribution that maximizes the quasi-equilibrium entropy $S_N[F_N[F_{2(N)}]]$ for given mean energy of a pair of particles. The two paths for the determination of F_N^* can be represented schematically in the form of the diagram



(4)

where H_2 and H_N are the Hamiltonians of the two particles and the N particles, and E_2 and E_N are the corresponding mean energies (the normalization condition is omitted). For particles with two-body interaction, the diagram (4) is commutative — successive transition along the vertical and horizontal sides of the triangle in the direction of the arrows is equivalent to transition along the hypotenuse. We shall consider systems with two-body interaction. The problem of constructing the quasi-equilibrium distribution $F_N[F_{2(N)}]$ can be solved separately. Its solution establishes a universal (independent of the Hamiltonian) connection between the s-particle ($s \geq 3$) distribution functions and the two-particle functions.

Our argument shows that the result of the universal expression $F_3[F_2]$ can indeed be used to close the equilibrium BBGKY hierarchy with two-body interaction and motivates the proposed approach. Different forms of the method of quasi-equilibrium ensembles are often used in statistical physics [6-8]. It was used in [9] to construct Zubarev's nonequilibrium statistical operator.

On the basis of what we have said, we have the following extremal problem (in place of the entropy (3), we use the H function $H_N[F_N] = -k_B^{-1} S_N[F_N]$):

$$\begin{aligned} &H_N[F_N] \to \min \text{ for } \int\limits_{B_V^N} F_N(x_1, \ldots, x_N)\, dx_1 \ldots dx_N = 1, \\ &N(N-1) \int\limits_{B_V^{N-2}} F_N(x_1, \ldots, x_N)\, dx_3 \ldots dx_N = F_{2(N)}(x_1, x_2). \end{aligned} \tag{5}$$

Note that $F_{2(N)}$ in (5) is an arbitrary parameter.

3. Expansion in the Neighborhood of an Uncorrelated State

Solving the problem (5) by using Lagrangian multipliers, we find $F_N[F_{2(N)}]$ in the form

$$F_N[F_{2(N)}]=a_{(N)}\Phi_{(N)}(x_1,\ldots,x_N),\quad \Phi_{(N)}=\prod_{i<j}\varphi_{(N)}(x_i,x_j), \tag{6}$$

where the unknowns $a_{(N)}$, $\varphi_{(N)}(x_i, x_j)$ are determined from the system of equations

$$\begin{aligned} a_{(N)} &\int\limits_{B_V^N} \Phi_{(N)}(x_1,\ldots,x_N)\,dx_1\ldots dx_N=1,\\ a_{(N)}N(N-1) &\int\limits_{B_V^{N-2}} \Phi_{(N)}(x_1,\ldots,x_N)\,dx_3\ldots dx_N=F_{2(N)}(x_1,x_2). \end{aligned} \tag{7}$$

In the absence of correlations, $F_{2(N)}$ has the form

$$F_{2(N)}(x_i,x_j)=N^{-1}(N-1)F_{1(N)}(x_i)F_{1(N)}(x_j), \tag{8}$$

where $F_{1(N)}(x_i)$ is the single-particle distribution function. In this case, the solution of the system (7) is readily found:

$$\varphi_{(N)}(x_i,x_j)=c_{(N)}(F_{1(N)}(x_i)F_{1(N)}(x_j))^{1/(N-1)},\quad a_{(N)}N^N c_{(N)}^{N(N-1)/2}=1. \tag{9}$$

The coresponding expression for $F_N[F_{2(N)}]$ (6) has the form

$$F_N(x_1,\ldots,x_N)=N^{-N}\prod_{i=1}^{N}F_{1(N)}(x_i). \tag{10}$$

In the general case, we represent $F_{2(N)}$ identically in the form

$$F_{2(N)}(x_i,x_j)=N^{-1}(N-1)F_{1(N)}(x_i)F_{1(N)}(x_j)+f_{(N)}(x_i,x_j). \tag{11}$$

It follows from the definition (2) that

$$\int\limits_{B_V^1} f_{(N)}(x,y)\,dx=\int\limits_{B_V^1} f_{(N)}(x,y)\,dy=0 \tag{12}$$

for all N ≥ 2.

We introduce the formal parameter ε > 0 in front of $f_{(N)}$ in (11) and seek the solution $\varphi_{(N)}(x, y)$ in the form

$$\varphi_{(N)}(x,y)=\sum_{k=0}^{\infty}\varepsilon^k\varphi_{(N)}^{(k)}(x,y). \tag{13}$$

Such a representation generates an expansion of the nonlinear integral operators (7) in Taylor series in the neighborhood of the point (8). The resulting series of linear inhomogeneous integral equations can be solved recursively [4].

We emphasize that ε is a formal, but not small, expansion parameter. Variation of ε from zero to unity corresponds formally to the "switching on" of the two-body correlation. Therefore, only the value ε = 1 has meaning. As will be seen from what follows, the expansion in powers of ε is actually an expansion with respect to the number of pairs of correlating particles. The question of the convergence of the obtained formal series goes beyond the framework of this paper. We note that for finite N and V there are grounds for assuming that the expansion converges for all ε since they are obtained by finding the extremum of the convex analytic functional H under linear constraints. Therefore, difficulties in the proof of the convergence may arise only in the thermodynamic limit. The device of "switching on the coupling" is often used. For example, the Born-Green equation is derived in [10] by the method of formal "switching on of the two-body interaction."

Substituting (13) in $\Phi_{(N)}$ (6), we obtain

$$\begin{aligned} &\Phi_{(N)}=\sum_{k=0}^{\infty}\varepsilon^k\Phi_{(N)}^{(k)},\quad \Phi_N^{(0)}=c_{(N)}^{N(N-1)/2}\prod_{i=1}^{N}F_{1(N)}(x_i),\\ &\Phi_N^{(k)}=c_{(N)}^{\frac{N(N-1)}{2}-1}\sum_{i<j}\psi_N^{(k)}(x_i,x_j)\prod_{s\neq i,\,j}F_{1(N)}(x_s)+Z_{(N)}^{(k)},\quad k\geqslant 1, \end{aligned} \tag{14}$$

$$Z_N^{(k)} = \sum_{\substack{(j_1,\ldots,j_q)\\ 0<j_i<k}} c_{(N)}^{\frac{N(N-1)}{2}-\sum_{i=1}^{l} j_i} \psi_{(N)}^{(j_1)}(x_{m_1}, x_{n_1}) \ldots \psi_{(N)}^{(j_l)}(x_{m_l}, x_{n_l}) \prod_{j=1}^{N} (F_{1(N)}(x_p))^{-q_{j_1,\ldots,j_l}+1},$$

where in place of the functions $\varphi_{(N)}^{(k)}$ (13) we have used the functions $\psi_{(N)}^{(k)}$:

$$\psi_{(N)}^{(k)}(x_i, x_j) = (F_{1(N)}(x_i) F_{1(N)}(x_j))^{(N-2)/(N-1)} \varphi_{(N)}^{(k)}(x_i, x_j). \tag{15}$$

In $Z_{(N)}^{(k)}$ (14) it is assumed that no pair of arguments (x_{m_i}, x_{n_i}) is encountered twice; the number $q_{j_1,\ldots,j_l}$ is equal to the number of times the variable x_p is encountered among the arguments in the product $\psi_{(N)}^{(j_1)}(x_{m_1}, x_{n_1}) \ldots \psi_{(N)}^{(j_l)}(x_{m_l}, x_{n_l})$. In what follows, we shall assume that N is sufficiently large for all the encountered expressions to be well defined.

Substituting (9)–(15) in (7) and equating the terms of the same order in ε, we obtain the required recursive system for $\psi_{(N)}^{(k)}$. In the first approximation, we have

$$\psi_{(N)}^{(1)}(x_i, x_j) = c_{(N)} \frac{N}{N-1} f_{(N)}(x_i, x_j). \tag{16}$$

For $k \geq 2$ the recursive solution has the form (details of the calculations are given in [4])

$$\psi_{(N)}^{(k)}(x_i, x_j) = -c_{(N)} (N^2 P_{(N)}^{(k)}(x_i, x_j) - \frac{N-2}{N-1} (F_{1(N)}(x_i) R_{(N)}^{(k)}(x_j) + F_{1(N)}(x_j) R_{(N)}^{(k)}(x_i)) + N^{-1}(N-1) F_{1(N)}(x_i) F_{1(N)}(x_j) T_{(N)}^{(k)}), \tag{17}$$

where $P_N^{(k)}$, $R_{(N)}^{(k)}$, $T_{(N)}^{(k)}$ are expressed in terms of $\psi_N^{(n)}$ with $n < k$:

$$P_N^{(k)}(x_i, x_j) = a_{(N)} \int_{B_V^{N-2}} Z_N^{(k)}(x_1, \ldots, x_N) \prod_{s \neq i, j} dx_s,$$
$$R_N^{(k)}(x) = \int_{B_V^1} P_{(N)}^{(k)}(x, y)\, dy, \quad T_{(N)}^{(k)} = \int_{B_V^1} R_{(N)}^{(k)}(x)\, dx. \tag{18}$$

All the s-particle distribution functions can be represented as expansions in powers of ε. In particular, for $F_{3(N)}(x_1, x_2, x_3) = \sum_{k=0}^{\infty} \varepsilon^k F_{3(N)}^{(k)}(x_1, x_2, x_3)$ the coefficients $F_{3(N)}^{(k)}$ have the form

$$F_{3(N)}^{(0)} = (N-1)(N-2) N^{-2} F_{1(N)}(x_1) F_{1(N)}(x_2) F_{1(N)}(x_3), \tag{19}$$

$$F_{3(N)}^{(1)} = N^{-1}(N-2) \{F_{1(N)}(x_1) f_{(N)}(x_2, x_3) + F_{1(N)}(x_2) f_{(N)}(x_1, x_3) + F_{1(N)}(x_3) f_{(N)}(x_1, x_2)\}, \tag{20}$$

$$F_{3(N)}^{(k)} = N(N-1)(N-2) \{-N^{-3} F_{1(N)}(x_1) F_{1(N)}(x_2) F_{1(N)}(x_3) T_{(N)}^{(k)} - N^{-1}(F_{1(N)}(x_1) P_{(N)}^{(k)}(x_2, x_3) + F_{1(N)}(x_2) P_{(N)}^{(k)}(x_1, x_3) + F_{1(N)}(x_3) P_{(N)}^{(k)}(x_1, x_2)) + N^{-2}(R_{(N)}^{(k)}(x_1) F_{1(N)}(x_2) F_{1(N)}(x_3) + R_{(N)}^{(k)}(x_2) F_{1(N)}(x_1) F_{1(N)}(x_3) + R_{(N)}^{(k)}(x_3) F_{1(N)}(x_1) F_{1(N)}(x_2)) + Q_{(N)}^{(k)}(x_1, x_2, x_3)\}, \quad k \geq 2, \tag{21}$$

where

$$Q_{(N)}^{(l)}(x_1, x_2, x_3) = a_{(N)} \int_{B_V^{N-3}} Z_{(N)}^{(l)}\, dx_4 \ldots dx_N. \tag{22}$$

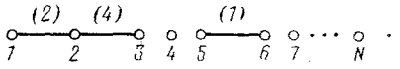
The expressions (14)–(22) enable us to calculate $F_{3(N)}^{(k)}$ for any k. We emphasize the recursive nature of the procedure for determining the coefficients $F_{3(N)}^{(k)}$: to find the k-th order, it is necessary to know the functions $\psi_{(N)}^{(m)}$ for $m = 0, \ldots, k-1$. Because of the combinatorial complexity of the calculations, it is expedient to use a diagram technique.

4. Rules for Constructing Diagrams

We shall proceed from the expression for $Z_{(N)}^{(k)}(x_1, \ldots, x_N)$ (14). From (17), it can be seen that $\psi_{(N)}^{(m)}$ are proportional to $c_{(N)}$. Further, we assume that in (16) the factor $c_{(N)}^{N(N-1)}$ is taken

in front of the summation sign and the products of functions $\chi_{(N)}^{(m)} = v_{(N)}^{-1}\psi_{(N)}^{(m)}$ are summed. With each term in $Z_{(N)}^{(k)}$ (16) we associate a diagram in accordance with the following rules. With the phase variables of particle i we associate a vertex with index i. The function $\chi_{(N)}^{(m)}(x_i, x_j)$ is associated with a line of order m connecting the vertices i and j, the order m being written next to the line. Any two vertices can be directly connected by not more than one line. With vertex i there is associated the function $[F_{1(N)}(x_i)]^{-p+1}$, $p \geqslant 0$ is the number of lines that converge at vertex i. The diagram as a whole is associated with the product of functions corresponding to the vertices and lines shown in it.

The graphical representation of a term in the sum $Z_{(N)}^{(k)}$ (16) is constructed as follows. On a plane we describe N open circles (vertices) and label them with numbers from 1 to N; we then connect the vertices whose phase variables are contained among the arguments of the functions $\chi_{(N)}^{(m)}(x_i, x_j)$ by lines of the corresponding orders. The typical term in $c_{(N)}^{N(N-1)} Z_{(N)}^{(7)}$ has the form



To it there corresponds the analytic expression

$$\frac{\chi_{(N)}^{(2)}(x_1, x_2)\chi_{(N)}^{(4)}(x_2, x_3)}{F_{1(N)}(x_2)} F_{1(N)}(x_4)\chi_{(N)}^{(1)}(x_5, x_6) \prod_{i=7}^{N} F_{1(N)}(x_i).$$

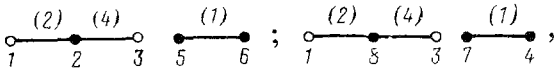
We call the sum of the orders of the lines represented in a diagram the order of the diagram. To the expression $Z_{(N)}^{(k)}$ there corresponds the set of all possible diagrams of order k for which all lines have order not higher than k − 1.

In calculating the expressions (18) and (22), we integrate $Z_{(N)}^{(k)}$ over a certain set of phase variables and then multiply the result by $a_{(N)}$. The integration of the expression $Z_{(N)}^{(k)}$ with respect to the phase variables of particle i is represented by deletion of vertex i in all diagrams corresponding to $Z_{(N)}^{(k)}$.

The diagram expansion of the expressions $P_{(N)}^{(k)}(x_i, x_j)$, $R_{(N)}^{(k)}(x_i)$, $T_{(N)}^{(k)}$ and $Q_{(N)}^{(k)}(x_i, x_j, x_k)$ is generated by the diagram expansion for $Z_{(N)}^{(k)}$. We shall say that the vertices in the diagram in $Z_{(N)}^{(k)}$ with respect to whose phase variables no integration is made are fixed and represent them by open circles. All the remaining vertices — the field vertices — are represented by black circles. The free field vertices are not shown in the diagram.

It is easy to show that the contribution from the diagram in $Z_{(N)}^{(k)}$ to the diagram expansion of the expressions (18) and (22) is equal to the integral over the phase variables of the field vertices of the product of the functions $\chi_{(N)}^{(m)}(x_i, x_j)$, and the functions $[F_{1(N)}(x_s)]^{-p+1}$ corresponding to the fixed and connected field vertices, the integral being multiplied by N^{-q}, where q is the number of fixed and connected field vertices in the diagram.

Further, the diagrams in the expansions $P_{(N)}^{(k)}(x_i, x_j)$, $R_{(N)}^{(k)}(x_i)$, $T_{(N)}^{(k)}$ and $Q_{(N)}^{(k)}(x_i, x_j, x_k)$ can be divided in the usual manner into topological equivalence classes. Diagrams that differ only in the labeling of the field vertices are assumed to be equivalent. Thus, in the example given above the same contribution to $P_{(N)}^{(7)}(x_1, x_3)$ is made by the topologically equivalent diagrams



and also all diagrams for which the fixed vertex 1 is connected to a field vertex by a line of second order; this field vertex is connected to the fixed vertex 3 by a line of fourth order, the two other field vertices are connected by lines of second order, while all the remaining field vertices are free.

The contribution from a complete set of diagrams of class D is equal to the contribution from any diagram of the class, multiplied by the number of diagrams M(D) in the class:

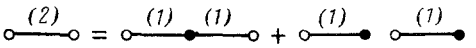
$$M(D) = P(D)S(D), \qquad P(D) = (N - r(D))![p(D)!(N - p(D) - r(D))!]^{-1},$$

where p(D) and r(D) are, respectively, the numbers of field and fixed vertices, and S(D) is the number of ways in which one can label the field vertices with numbers from 1 to p(D) without deforming the lines and without changing their orders. A class of topologically equivalent diagrams is represented by a single diagram with unlabeled field vertices.

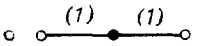
As a result, we arrive at a diagram expansion for the functions $F_{3(N)}^{(k)}$ (21). It is formed by diagram expansions: $T_{(N)}^{(k)}$ with the addition of the fixed vertices 1, 2, and 3, $R_{(N)}^{(k)}(x_i)$ with the addition of the two missing fixed vertices, $P_{(N)}^{(k)}(x_i, x_j)$ with the addition of one missing fixed vertex, and, finally, the expansion of $Q_{(N)}^{(k)}(x_1, x_2, x_3)$.

We note a particular feature of the proposed diagram technique due to the complicated recursive structure of the solution. In the graphical representation of the expansion for $F_{3(N)}^{(k)}$ (21), it is convenient to assume that all lines are independent. However, in accordance with (17) all lines of order $k \geq 2$ can be recursively expressed in terms of a line of first order. To the first-order line there corresponds the analytic expression (16), which is proportional to the binary correlation function $f_{(N)}(x_i, x_j)$, and it is the only "parameter of the theory." Therefore, when the diagrams are associated with analytic expressions and the reduction is made to the form containing only the binary correlation functions $f_{(N)}(x_i, x_j)$, it is found that some of them are proportional to each other. For example, the line of order 2

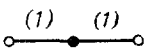
is represented graphically in the form



Therefore, in the calculation of the coefficient $F_{3(N)}^{(2)}$ proportional contributions are made, in particular, by diagrams of the form



in the expansion of $Q_{(N)}^{(2)}(x_1, x_2, x_3)$ and diagrams of the form



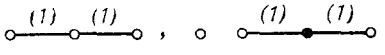
in the expansion of $P_{(N)}^{(2)}(x_i, x_j)$. A similar remark also applies to the topologically inequivalent diagrams in the expansions of $P_{(N)}^{(k)}(x_i, x_j)$, $R_{(N)}^{(k)}(x_i)$, $T_{(N)}^{(k)}$ and $Q_{(N)}^{(k)}(x_i, x_j, x_k)$. This circumstance leads to a change in the numerical factors multiplying the analytic expressions corresponding to the diagrams.

5. Kirkwood Approximation. Long-Range Correlations

We give the results of calculation of the lowest orders of the $F_3[F_2]$ expansion. Restricting ourselves to the zeroth and first approximations (19) and (20), and setting $\varepsilon = 1$, i.e., going over to the "completely switched-on binary correlation," we obtain in the thermodynamic limit

$$F_3 = -2F_1(x_1)F_1(x_2)F_1(x_3) + F_1(x_1)F_2(x_2, x_3) + F_1(x_2)F_2(x_1, x_3) + F_1(x_3)F_2(x_1, x_2), \tag{23}$$

which corresponds to the Cheng approximation (quoted from [11]). In the next order, nonvanishing contributions to $F_3^{(2)}$ are made by diagrams of the type



The corresponding analytic expression for $F_3^{(2)}$ has the form

$$f(x_1, x_2)f(x_1, x_3)F_1^{-1}(x_1) + f(x_1, x_2)f(x_2, x_3)F_1^{-1}(x_2) + f(x_1, x_3) \times$$
$$f(x_2, x_3)F_1^{-1}(x_3) - \lim_{V \to \infty}(nV)^{-1}\{F_1(x_1)G_{(N)}(x_2, x_3) + F_1(x_2)G_{(N)}(x_1, x_3) + F_1(x_3)G_{(N)}(x_1, x_2)\}, \tag{24}$$

where we have used the notation

$$G_{(N)}(x_i, x_j) = \int_{B_V^1} f_{(N)}(x_i, x) f_{(N)}(x_j, x) F_{1(N)}^{-1}(x)\, dx. \tag{25}$$

The term in (24) containing the expression (25) makes a nonvanishing contribution only in the case of long-range correlations. Going over to the Fourier transforms, we can, for sufficiently large N and V, represent the product of correlation functions in (24) and (25) at the equilibrium point in the form

$$f_{(N)}(x_i, x) f_{(N)}(x_j, x) = n^k \varphi(\mathbf{p}) \varphi(\mathbf{p}_i) \varphi(\mathbf{p}_j) \int_{R^3} \sigma_{(N)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{k}) e^{i\mathbf{kr}} d^3k,$$

where $\mathbf{k}$ is the wave vector, n is the equilibrium density, and $\varphi(\mathbf{p})$ is the Maxwell distribution function at unit density. Then the contribution from (25) to (24) has the form

$$\lim_{V\to\infty} \frac{1}{nV} F_1(x_l) G_{(N)}(x_i, x_j) = n^3 \varphi(\mathbf{p}_i) \varphi(\mathbf{p}_j) \varphi(\mathbf{p}_l) \lim_{V\to\infty} V^{-1} \sigma_{(N)}(\mathbf{r}_i, \mathbf{r}_j, 0)$$

and is nonvanishing only when the spectrum of correlations has a singularity at $\mathbf{k}=0$. In the third order, we have

$$F_3^{(3)} = f(x_1, x_2) f(x_2, x_3) f(x_1, x_3) (F_1(x_1) F_1(x_2) F_1(x_3))^{-1} +$$

$$\lim_{V\to\infty} \int_{B_V^1} f_{(N)}(x_1, x) f_{(N)}(x_2, x) f_{(N)}(x_3, x) F_{1(N)}^{-2}(x)\, dx -$$

$$\lim_{V\to\infty} \Big\{ \frac{1}{nV} (G_{(N)}(x_1, x_2) F_1^{-1}(x_1) F_1^{-1}(x_2) + G_{(N)}(x_2, x_3) F_1^{-1}(x_2) F_1^{-1}(x_3) +$$

$$G_{(N)}(x_1, x_3) F_1^{-1}(x_1) F_1^{-1}(x_3)) (F_1(x_1) f(x_2, x_3) + F_1(x_2) f(x_1, x_3) +$$

$$F_1(x_3) f(x_1, x_2)) + (nV)^{-3} F_1(x_1) F_1(x_2) F_1(x_3) J_{(N)} - 2(nV)^{-2} \times$$

$$(F_1(x_1) A_{(N)}(x_2, x_3) + F_1(x_2) A_{(N)}(x_1, x_3) + F_1(x_3) A_{(N)}(x_1, x_2)) -$$

$$(nV)^{-2} (F_1(x_1) F_1(x_2) C_{(N)}(x_3) + F_1(x_1) F_1(x_3) C_{(N)}(x_2) + F_1(x_2) F_1(x_3) C_{(N)}(x_1)) \Big\}, \tag{26}$$

where we have used the notation

$$J_{(N)} = \int_{B_V^3} \frac{f_{(N)}(x, y) f_{(N)}(y, z) f_{(N)}(x, z)}{F_{1(N)}(x) F_{1(N)}(y) F_{1(N)}(z)} dx\, dy\, dz,$$

$$A_{(N)}(x, y) = \int_{B_V^1} f_{(N)}(x, z) G_{(N)}(y, z) F_{1(N)}^{-1}(z) dz, \quad C_{(N)}(x) = \frac{A_{(N)}(x, x)}{F_{1(N)}(x)}.$$

In the absence of long-range correlations, allowance for the first four coefficients (19), (20), (22), and (26) gives the following expression for $F_3[F_2]$:

$$F_3 = F_2(x_1, x_2) F_2(x_2, x_3) F_2(x_1, x_3) F_1^{-1}(x_1) F_1^{-1}(x_2) F_1^{-1}(x_3) +$$

$$\lim_{V\to\infty} \int_{B_V^1} f_{(N)}(x_1, x) f_{(N)}(x_2, x) f_{(N)}(x_3, x) F_{1(N)}^{-2}(x) dx. \tag{27}$$

The first term in the expression (27) corresponds to the Kirkwood approximation. The second term gives the first correction to the Kirkwood approximation in the power of the density n (see the following section).

6. One-Irreducible Diagrams

As noted above, contributions from certain topologically inequivalent diagrams to (21) can compensate each other, leading to the appearance of averaging factors of the type $(nV)^{-s}$ in front of the integrals of the products of correlation functions. In the absence of long-range correlations, these contributions vanish in the thermodynamic limit. In this section, we shall give a condition on diagrams that is sufficient for their contribution to be nonvanishing in the thermodynamic limit.

Below, we consider the case when the dependences on the coordinates and momenta in F_s separate. Then in the thermodynamic limit,

$$F_1(x) = n\varphi(\mathbf{p}), \qquad F_2(x_i, x_j) = n^2 n_2(\mathbf{r}_i, \mathbf{r}_j) \varphi(\mathbf{p}_i) \varphi(\mathbf{p}_j),$$

$$f(x_i, x_j) = n^2 h(\mathbf{r}_i, \mathbf{r}_j) \varphi(\mathbf{p}_i) \varphi(\mathbf{p}_j), \qquad n_2(\mathbf{r}_i, \mathbf{r}_j) = 1 + h(\mathbf{r}_i, \mathbf{r}_j), \tag{28}$$

$$F_3(x_i, x_j, x_k)=n^3 n_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)\varphi(\mathbf{p}_i)\varphi(\mathbf{p}_j)\varphi(\mathbf{p}_k),$$

where $\varphi(\mathbf{p})$ is the Maxwell distribution function for unit density, and n is the constant density.

In each order $k \geq 2$, some of the diagrams can be obtained from diagrams in which all lines have first order by replacing some of the lines and field vertices by lines of higher order. We shall say that diagrams with lines of only first order in which such canceling is impossible are one-irreducible diagrams. It is obvious that none of the classes of diagrams can make a contribution of the same type as the one-irreducible diagrams. The contribution of the one-irreducible diagrams to $F^{(r)}_{3(N)}$ (21) is provided only by the functional $Q^{(k)}_{(N)}(x_1, x_2, x_3)$ (22).

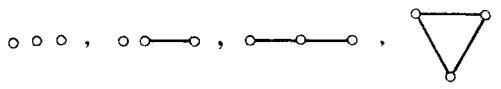
It is convenient to classify the one-irreducible diagrams in accordance with the number of field vertices. For nonvanishing number of field vertices, the one-irreducible diagrams in the expansion (22) are constructed as follows. All the field vertices are connected with each of three fixed first-order lines. Then, adding in each case one line of first order this diagram is transformed into the complete graph. The diagrams obtained during the course of the construction give all (up to the labeling of the fixed vertices) one-irreducible diagrams with the given number of field vertices.

The one-irreducible diagram with q field vertices and minimal number of lines makes the following contribution to $n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$:

$$n^q \int\limits_{R^{3q}} \prod_{i=1}^{q} h(\mathbf{r}_1, \mathbf{r}^{(i)})\, h(\mathbf{r}_2, \mathbf{r}^{(i)})\, h(\mathbf{r}_3, \mathbf{r}^{(i)})\, d^3\mathbf{r}^{(1)} \ldots d^3\mathbf{r}^{(q)}.$$

This expression is proportional to the q-th power of the density. It is readily verified that the addition of a first-order line for constant number of field vertices does not change this proportionality.

The one-irreducible diagrams without field vertices



(29)

give the Kirkwood approximation for $n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ (28):

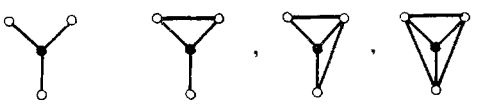
$$n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)=n_2(\mathbf{r}_1, \mathbf{r}_2)\, n_2(\mathbf{r}_2, \mathbf{r}_3)\, n_2(\mathbf{r}_1, \mathbf{r}_3).$$

In (29) and what follows, all the lines are of first order.

It is easy to show that the division of the one-irreducible diagrams into classes in accordance with the number of field vertices leads to the approximation of $n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ in the form of a series in powers of the density of the form

$$n_2(\mathbf{r}_1, \mathbf{r}_2)\, n_2(\mathbf{r}_2, \mathbf{r}_3)\, n_2(\mathbf{r}_1, \mathbf{r}_3)\left\{1+\sum_{i=1}^{\infty} n^i q_i(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\right\}.$$

The class of one-irreducible diagrams with one field vertex



(30)

gives q_1 and corresponds to the Henderson approximation [12]:

$$q_1(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)=\int\limits_{R^3} h(\mathbf{r}_1, \mathbf{r})\, h(\mathbf{r}_2, \mathbf{r})\, h(\mathbf{r}_3, \mathbf{r})\, d^3r.$$

Finally, we give the expression for q_2:

$$q_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)=q_1^2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)+\int\limits_{R^3}\int\limits_{R^3} h(\mathbf{r}_1, \mathbf{r})\, h(\mathbf{r}_2, \mathbf{r})\, h(\mathbf{r}_3, \mathbf{r})\, h(\mathbf{r}, \mathbf{r}')\, h(\mathbf{r}_1, \mathbf{r}')\, h(\mathbf{r}_3, \mathbf{r}')\, d^3\mathbf{r}\, d^3\mathbf{r}'.$$

It remains an open question whether there are further classes of diagrams that are different from the one-irreducible diagrams and make a contribution that does not vanish in the thermodynamic limit in the absence of long-range correlations in n_3. We note, however, that analysis of all diagrams in the expansion (21) to the sixth order in ε inclusively shows that only the one-irreducible diagrams make the required contribution.

Thus, the expansion (21) establishes a universal connection between the three-particle distribution function and the two-particle function. The question of the convergence of the expansion (21) in the thermodynamic limit requires a separate investigation.

The proposed method of construction of a universal quasi-equilibrium ensemble admits generalization to the case of an arbitrary s-particle interaction — instead of the second restriction in the problem (5) one must specify the s-particle distribution function. Extension to quantum and lattice models is also possible.

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