On one-to-one correspondence of Gibbs distribution and reduced two-particle distribution function

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Abstract

In this article it is shown that in an equilibrium classical canonical ensemble of molecules with two-body interaction and external field full Gibbs distribution can be uniquely expressed in terms of a reduced two-particle distribution function. This means that while a number of particles $N$ and a volume $V$ are fixed the reduced two-particle distribution function contains as much information about the equilibrium system as the whole canonical distribution. The latter is represented as an absolutely convergent power series relative to the reduced two-particle distribution function. As an example a linear term of this expansion is calculated. It is also shown that Gibbs distribution function can be expressed in terms of reduced distribution function of the first order and pair correlation function. That is the later two functions contain the whole information about system under consideration.

1 Introduction

In classical statistical mechanics an equilibrium system of $N$ molecules in a volume $V$ is described by canonical distribution function $F_N(q,p)$, where $(q,p)$ is a set of phase variables: coordinates $q_i$ and momenta $p_i$ of molecules. If interaction of molecules is additive, reduced distribution functions are introduced [1, 2]. They are used for evaluation of thermodynamic characteristics of this molecular system. It’s usually accepted that reduced distribution functions contain information about a molecular system less than the initial canonical distribution function. It’s also supposed that the lower an order of a reduced distribution function is, the less information it contains. But there does not exist a proof of this statement in scientific literature.

On the other hand, it is known that for an equilibrium canonical ensemble of non-interacting particles a canonical distribution function $F_N(q,p)$ is decomposed into a product of reduced one-particle distribution functions $F_1(q,p)$ [1, 2]. This means that all information about such system is contained in the reduced one-particle distribution function.

In the article [3] it was proved that for a system with pair interaction and without external field a reduced two-particle distribution function defined in terms of nonnormalized Gibbs distribution (without configurational integral) contains the whole information about such system. In [4] that result was obtained for normalized Gibbs distribution and

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respective reduced distribution function. This results we re obtained for a system which is not subjected to influence of external field.

In this paper it’s proved that for such system placed into ext ernal field one-to-one correspondence between full canonical distribution funct ion and a reduced two-particle distribution function exists. Moreover it’s shown that one -to-one correspondence between a full canonical Gibbs distribution and a set of reduced distribution function of the first order together with pair correlation function exists too. This means that the reduced two-particle distribution function as well as mentioned set contain the total information about system under consideration.

We consider an equilibrium system of \( N \) particles contained in the volume \( V \) under the temperature \( T \). Potential energy of system is supposed to have the form

\[
U_N(q_1, \ldots, q_N) = \sum_{i=1}^{N} u_1(q_i) + \sum_{1 \leq j < k \leq N} u_2(q_j, q_k),
\]

where \( u_1(q) \) is an external field and \( u_2(q, q') \) is a two-body interaction energy of particles. Probability distribution function of equilibrium system is the canonical Gibbs distribution which is decomposed into a product of a momentum distribution function and a configurational one \[1, 2\]. The former is expressed as a product of one-particle Maxwell distributions, the latter has the form

\[
D_N(q_1, \ldots, q_N) = Q_N^{-1} \exp\{-\beta U_N(q_1, \ldots, q_N)\},
\]

where \( \beta = 1/kT \), \( k \) is the Boltzmann constant and \( Q_N \) is the configuration integral

\[
Q_N = \int \exp\{-\beta U_N(q_1, \ldots, q_N)\} dq_1 \cdots dq_N.
\]

Here and below integrating with respect to every configurational variable is carried out over the volume \( V \). For a system having interaction of form \[1\] reduced distribution functions are introduced by expressions \[2\]

\[
F_l(q_1, \ldots, q_l) = \frac{N!}{(N-l)!} \int D_N(q_1, \ldots, q_N) dq_{l+1} \cdots dq_N, \quad l = 1, 2, \ldots.
\]

These functions are used instead of full canonical distribution \[2\] to calculate various characteristics of the molecular system. Let us investigate properties of the reduced two-particle distribution function.

Potential energy \[1\] can be written as

\[
U_N(q_1, \ldots, q_N) = \sum_{1 \leq j < k \leq N} \phi(q_j, q_k),
\]

where

\[
\phi(q, q') = u_2(q, q') + \frac{u_1(q) + u_1(q')}{N - 1}.
\]

Introduce a function \( h(q, q') \) by the relation

\[
\exp\{-\beta \phi(q, q')\} = \sigma \{1 + h(q, q')\},
\]
where
\[ \sigma = \frac{1}{V^2} \int \exp\{-\beta \phi(q, q')\} \, dq \, dq'. \] (8)

The canonical Gibbs distribution (2) takes the form
\[ D_N(q_1, \ldots, q_N) = Q_N^{-1} \prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] \] (9)

with
\[ Q_N = \int \prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] \, dq_1 \cdots dq_N. \] (10)

From (9) and (10) it follows that statistical properties of system under consideration
are completely determined by the specifying single function of two configurational vari-
able \( h(q, q') \) and two external parameters \( N \) and \( V \). Gibbs distribution (9) has the same
form as for system without external field. Therefore we may suppose that results of article
[4] can be proved for system considered in this article too.

In section 2 we state a mathematical problem for our molecular system and formulate
conditions for existence and uniqueness of its solution. In section 3 feasibility of these
conditions for considered physical system are proved. In section 4 an expression for
function \( h(q, q') \) in terms of \( F_2(q, q') \) is calculated. In section 5 an expression for the
canonical distribution in terms of reduced reduced two-particle distribution function is
produced. In section 6 it is shown that a set of first reduced distribution function and pair
correlation function contains the whole information as well as two-particle distribution
function and canonical Gibbs distribution.

2 Mathematical formulation of problem

Let us introduce function \( f(q, q') \) by the relation
\[ F_2(q, q') = \frac{N!}{(N-2)!V^2} [1 + f(q, q')]. \] (11)

Both the function \( f(q, q') \) and the function \( h(q, q') \) satisfy the conditions
\[ \int f(q, q') \, dq \, dq' = 0, \quad \int h(q, q') \, dq \, dq' = 0. \] (12)

From expressions (4), (9), and (11) it follows that
\[ 1 + f(q_1, q_2) = \frac{V^2}{Q_N} \int \prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] \, dq_3 \cdots dq_N. \] (13)

This relation defines the transformation \( \{h \rightarrow f\} \) and can be considered as a nonlinear
equation relative to \( h(q, q') \). If there exists a solution \( h(q, q'; [f]) \) of this equation then
a function \( D_N(q_1, \ldots, q_N) \) becomes an operator function of \( f \). It means that both the
canonical Gibbs distribution \( D_N \) and all reduced distribution functions \( F_l \) are expressed
in terms of a single reduced distribution function \( F_2 \). Thus we have to prove that equation
(13) has a unique solution and therefore the transformation \( h \to f \) has inverse one \( f \to h \).

Multiplying equation (13) by \( Q_NV^{-N} \) and using (10) we rewrite it in the form

\[
[1 + f(q, q')] \frac{1}{V_N} \int \prod_{1 \leq j < k \leq N} [1 + h(p_j, p_k)] dp_1 \cdots dp_N
- \frac{1}{V_{N-2}} \int \prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] dq_3 \cdots dq_N = 0.
\] (14)

The left-hand side of (14) is a polynomial operator of degree \( N = N(N - 1)/2 \) relative to \( h \) and of degree one relative to \( f \). Denote this operator by \( F(h, f) \). Equation (14) can be written in a symbolic form

\[
F(h, f) = 0.
\] (15)

To solve this equation it is necessary to specify an additional condition

\[
F(h^{(0)}, f^{(0)}) = 0,
\] (16)

where \( f^{(0)}(q, q') \) and \( h^{(0)}(q, q') \) are assigned functions.

We can easily determine these functions for our physical system. If the external field and interaction between particles are absent, i.e., potentials \( u_1 \) and \( u_2 \) are constant, then the function \( h(q, q') \) vanishes. Under this condition \( Q_N = Q_N^{(0)} = V^N, D_N(q_1, \ldots, q_N) = D_N^{(0)} = V^{-N}, \) and \( f(q, q') = 0. \) Therefore we can take \( h^{(0)} = 0 \) and \( f^{(0)} = 0 \) in (16).

Equation (15) and additional condition (16) form a problem on implicit function. In functional analysis there is a number of theorems on implicit function for operators of various smoothness classes. We use the theorem for analytic operator in Banach space in the form given in the book [5].

**Theorem.** (On implicit function). Let \( F(h, f) \) be an analytic operator in \( D_r(h^{(0)}, E_1) \times D_r(f^{(0)}, E) \) with values in \( E_2 \). Let an operator \( B \) be \( -\partial F(h^{(0)}, f^{(0)})/\partial h \) have a bounded inverse one. Then there are positive numbers \( r_1 \) and \( r_2 \) such that a unique solution \( h = \chi(f) \) of the equation \( F(h, f) = 0 \) with the additional condition \( F(h^{(0)}, f^{(0)}) = 0 \) exists in a solid sphere \( D_r(h^{(0)}, E_1) \). This solution is defined in a solid sphere \( D_{r_1}(f^{(0)}, E) \), is analytic there, and satisfies the condition \( h^{(0)} = \chi(f^{(0)}) \).

Here \( D_r(x_0, \mathcal{E}) \) denotes a solid sphere of radius \( r \) in a neighborhood of the element \( x_0 \) in a normalized space \( \mathcal{E} \), the symbol \( \times \) denotes the Cartesian product of sets, \( \partial F/\partial h \) is Fréchet derivative [5, 6] of the operator \( F \), \( h^{(0)} \) and \( f^{(0)} \) are assigned elements of the respective spaces \( E_1 \) and \( E \). If the functions \( h(q, q') \) and \( f(q, q') \) satisfy this theorem conditions, the former is a single valued operator function of the later.

To prove an existence and uniqueness of the solution of problem (15), (16) we have to show that conditions of the above theorem are satisfied.

### 3 Proof of feasibility of the theorem conditions

First we define spaces \( E_1, E, \) and \( E_2 \) mentioned in the theorem for functions describing the physical system under consideration.
3.1 Functional spaces of problem

Potentials $u_1(q)$ and $u_2(q, q')$ are real symmetric functions. Suppose they are bounded below for almost all $\{q, q'\} \in V$. All physically significant potentials possess this property. Under this condition integral (8) exists and $h(q, q')$ is a real symmetric function bounded for almost all $\{q, q'\} \in V$.

A set of functions bounded nearly everywhere forms a complete linear normalized space (Banach space) with respect to the norm $\|h\| = \text{vrai sup}_{(q, q') \in V} |h(q, q')|$, (17)

where "vrai sup" denotes an essential upper bound of the function on the indicated set and $V(2) \overset{\text{def}}{=} V \times V$ is Cartesian product of $V$ by itself. It is called the space of essentially bounded functions and is denoted by $L_{\infty}(V(2))$. In addition $h(q, q')$ satisfies condition (12). The set of such functions is a subspace of $L_{\infty}(V(2))$. It is easy to show that this subspace is a complete space relative to norm (17). Therefore we can take the Banach space of symmetric essentially bounded functions satisfying condition (12) as $E_1$.

Expression (13) for $f(q, q')$ includes multiple integrals of different power combinations of $h(q, q')$. Any power of essentially bounded function are integrable with respect to arbitrary set of variables $\{q_1, \ldots, q_k\}$ over $V$ [8]. Therefore all integrals in (13) and (14) that $E_2$ is the same space. Thus we define the spaces of the above theorem as $E = E_1 = E_2 = L_{\infty}(V(2))$ with property (12).

From (7) and (11) for $h(q, q')$ and $f(q, q')$ it follows that $f > -1$ and $h > -1$. Therefore we can take a manifold $\{f > -1, h > -1\}$ as a definition domain of the operator $F(h, f)$. Since the left-hand side of (14) is a polynomial, the operator $F(h, f)$ is analytical in this domain. As stated above the additional condition (16) is valid for $f^{(0)} = f^{(0)} = 0$. Thus any solid spheres of $E_1, E$ with centers at $h^{(0)} = 0, f^{(0)} = 0$ and radii $r < 1, \rho < 1$ respectively can be used as domains $D_r(h^{(0)}, E_1)$ and $D_\rho(f^{(0)}, E)$ indicated in the theorem.

Finally it is necessary to prove that the operator

$$B \overset{\text{def}}{=} -\frac{\partial F(h, f)}{\partial h} \bigg|_{h=0, f=0}$$

has a bounded inverse one.

3.2 Properties of the operator $B$

To find the inverse operator $B^{-1}$ it is necessary to solve the equation $Bh = y$, where $h \in E_1, y \in E_2$. The expression for $Bh$ is a linear relative to $h$ part in the left-hand side of relation (14) as $f = 0$. Let us introduce next notations for arbitrary function $\xi(q, q')$

$$\bar{\xi}(q) = \frac{1}{V} \int \xi(q, q')dq', \quad \bar{\xi} = \frac{1}{V^2} \int \xi(q, q')dq dq'.$$  (19)

Expanding products in (14) and keeping linear summands we obtain

$$(Bh)(q, q') = h(q, q') + (N - 2)[\bar{h}(q) + \bar{h}(q')].$$ (20)
It’s easy to estimate a norm of the operator $B$. Using definition (17) we obtain
\[ \| Bh \| \leq (2N - 3) \| h \|. \] (21)
From here we get an estimation
\[ \| B \| \leq 2N - 3. \] (22)
Thus the operator $B$ is bounded.

Using (20) we can write a nonuniform equation $Bh = f$ in the next form
\[ h(q, q') + (N - 2)[\overline{h}(q) + \overline{h}(q')] = f(q, q'). \] (23)
Taking into account the conditions (12) we get a solution of this equation
\[ h(q, q) = (B^{-1}f)(q, q) = f(q, q') - \frac{N - 2}{N - 1} [\overline{f}(q) + \overline{f}(q')]. \] (24)
From here it’s easy to estimate a norm of the inverse operator $B^{-1}$. Evaluating the norm of right-hand-side of (24) we get
\[ \| B^{-1} \| \leq \frac{\| B^{-1}f \|}{\| f \|} \leq 1 + 2 \frac{N - 2}{N - 1} = \frac{3(N - 1) - 2}{N - 1} \leq 3. \] (25)
Therefore the operator $B^{-1}$ exists and it is bounded.

So all conditions of the above theorem are valid for our physical system. Hence there exists a unique solution $h = \chi(f)$ of problem (15), (16) as a function of $f$. This solution defines an inverse transformation from the function $f$ to the function $h(q, q') = h(q, q'; [f])$.

4 Derivation of the inverse transformation $h(f)$
To obtain the transformation $f \to h$ we have to solve equation (14) relative to $h(q, q')$. Here we present less unwieldy derivation than in the work [4]. At first define an auxiliary operator function $g(h)$ by means of a relation
\[ \frac{1}{V^{N-2}} \int \prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] dq_3 \cdots dq_N = 1 + g(h). \] (26)
This operator function is a polynomial of degree $N$ relative to $h$ and depends on two configurational variables $q_1, q_2$. It can be written in the form
\[ g(h) = \sum_{l=1}^{N} g_l(h), \] (27)
where $g_l(h)$ is a uniform operator of order $l$ relative to $h$. Let us derive the expression for $g_l(h)$ from definition (20).

For the sake of abbreviation of subsequent calculations we introduce next notations. We will denote by number $K \in \{1, \ldots, N\}$ every ordered collection \{\(j, k\)\} from the set \{\(1, \ldots, N\)\}. Such one-to-one correspondence can be always made. A collection \{\(q_j, q_k\)\} is an element of manifold $\mathcal{V}^2$. We will denote this element by $X_K$. By definition put $X_1 = (q_1, q_2)$. 

\[ X_1 = (q_1, q_2). \]
Expanding the product in (26) we obtain an expression
\[ g_l(h) = \frac{1}{V_{N-s}} \int dq_3 \cdots dq_N \sum_{1 \leq K_1 < \cdots < K_l \leq N} h(X_{K_1}) \cdots h(X_{K_l}) \] (28)
for every \( l = 1, \ldots, N \). Introduced operators \( g_l(h) \) as well as \( g(h) \) are symmetrical functions of two configurational variables: \( g_l(h) = g_l(q, q'; [h]) \) and \( g(h) = g(q, q'; [h]) \). In contrast to \( h \) and \( f \) both \( g(q, q'; [h]) \) and \( g_l(q, q'; [h]) \) don’t satisfy condition (12) except for \( g_1(q, q'; [h]) \). First term of series (27) is \( g_1(h) = Bh \) and satisfies to condition (12).

Configurational integral (10) takes the form
\[ Q_N = V^N (1 + \overline{g}) = V^N [1 + \sum_{k=2}^{N} \overline{g}_k] \] (29)
Here we used notations (19).

Substituting definitions (26) and (29) into (14) we write it in the form
\[ (1 + f)[1 + \overline{g}(h)] - [1 + g(h)] = 0, \] (30)
where \( f \) and \( g(h) \) are functions of \( X_1 = (q_1, q_2) \). But value \( \overline{g} \) doesn’t depend on configurational variables, it is a functional relative \( h \). Substituting expansions (27) and (29) here we reduce this equation to the form
\[ f[1 + \sum_{l=2}^{N} \overline{g}_l(h)] + \sum_{l=2}^{N} [\overline{g}_l(h) - g_l(h)] - Bh = 0. \] (31)
Here we have taken into account that \( g_1(h) = Bh \) and \( \overline{g}_1(h) = 0 \).

For subsequent calculation we need multilinear operators
\[ G_l(y_1, \ldots, y_l) = \frac{1}{V_{N-s}} \int dq_3 \cdots dq_N \sum_{1 \leq K_1 < \cdots < K_l \leq N} y_1(X_{K_1}) \cdots y_l(X_{K_l}). \] (32)
These operators are linear with respect to any functional argument \( y_i \). We can consider the operator functions \( g_l(h) \) as generated by these multilinear operators \( G_l \)
\[ g_l(h) = G_l(h, \ldots, h). \] (33)
Operators \( G_l(y_1, \ldots, y_l) \) are functions of configurational variables \( \{q_1, q_2\} = X_1 \). In general these functions aren’t symmetrical relative to \( (q_1, q_2) \). But this isn’t important since under substituting of these operator functions into equation (31) symmetric property will be hold automatically. In the result we can rewrite equation (31) as
\[ h = B^{-1} f[1 + \sum_{l=2}^{N} \overline{G}_l(h, \ldots, h)] + B^{-1} \sum_{l=2}^{N} [\overline{G}_l(h, \ldots, h) - G_l(h, \ldots, h)]. \] (34)
We will search a solution of this equation in the form of power series
\[ h = \sum_{k=1}^{\infty} h_k(f), \] (35)
where \( h_k(f) \) are uniform operators of order \( k \) relative to \( f \). At the same time they are functions of configurational variables \( X_i \). Substituting (35) into (34) and taken into account linearity of \( G_i(y_1, \ldots, y_i) \) with respect to any argument \( y_i \) we obtain

\[
\sum_{k=1}^{\infty} h_k(f) = B^{-1} f + B^{-1} \sum_{l=2}^{N} \sum_{j_1=1}^{\infty} \cdots \sum_{j_l=1}^{\infty} \overline{G}_i(h_{j_1}, \ldots, h_{j_l}) f
\]

\[
+ B^{-1} \sum_{l=2}^{N} \sum_{k=1}^{\infty} \cdots \sum_{j_l=1}^{\infty} [G_i(h_{j_1}, \ldots, h_{j_l}) - G_i(h_{j_1}, \ldots, h_{j_l})].
\]

(36)

Transform sums over \( j_1, \ldots, j_l \) as follows

\[
\sum_{j_1=1}^{\infty} \cdots \sum_{j_l=1}^{\infty} = \sum_{k=l}^{\infty} \sum_{j_1+\cdots+j_l=k}.
\]

Then relation (36) takes the form

\[
\sum_{k=1}^{\infty} h_k(f) = B^{-1} f + B^{-1} \sum_{l=2}^{N} \sum_{k=1}^{\infty} \sum_{j_1=1}^{\infty} \cdots \sum_{j_l=1}^{\infty} \overline{G}_i(h_{j_1}, \ldots, h_{j_l}) f
\]

\[
+ B^{-1} \sum_{l=2}^{N} \sum_{k=1}^{\infty} \sum_{j_1=1}^{\infty} \cdots \sum_{j_l=1}^{\infty} [G_i(h_{j_1}, \ldots, h_{j_l}) - G_i(h_{j_1}, \ldots, h_{j_l})].
\]

(37)

Double sum \( \sum_{l=2}^{N} \sum_{k=1}^{\infty} \) is transformed as follows

\[
\sum_{l=2}^{N} \sum_{k=1}^{\infty} = \sum_{l=2}^{N-1} \sum_{k=1}^{\infty} + \sum_{l=2}^{N} \sum_{k=1}^{N} = \sum_{k=2}^{N-1} \sum_{l=2}^{N} + \sum_{k=N}^{N} \sum_{l=2}^{N}
\]

or as follows

\[
\sum_{l=2}^{N} \sum_{k=1}^{\infty} = \sum_{l=2}^{N} \sum_{k=1}^{N} + \sum_{k=N+1}^{\infty} \sum_{l=2}^{N} = \sum_{k=2}^{N} \sum_{l=2}^{N+1} + \sum_{k=N+1}^{\infty} \sum_{l=2}^{N}
\]

Substituting these expressions into (37) we get the relation

\[
\sum_{k=1}^{\infty} h_k(f) = B^{-1} f + B^{-1} \sum_{k=3}^{N} \sum_{l=2}^{k-1} \sum_{j_1+\cdots+j_l=k-1}^{\infty} \overline{G}_i(h_{j_1}, \ldots, h_{j_l}) f
\]

\[
+ B^{-1} \sum_{k=3}^{N} \sum_{l=2}^{k-1} \sum_{j_1+\cdots+j_l=k-1}^{\infty} \overline{G}_i(h_{j_1}, \ldots, h_{j_l}) f
\]

\[
+ B^{-1} \sum_{l=2}^{N} \sum_{j_1+\cdots+j_l=k}^{\infty} \sum_{k=2}^{N+1} \sum_{l=2}^{k} [G_i(h_{j_1}, \ldots, h_{j_l}) - G_i(h_{j_1}, \ldots, h_{j_l})]
\]

\[
+ B^{-1} \sum_{l=2}^{N} \sum_{j_1+\cdots+j_l=k}^{\infty} \sum_{k=N+1}^{\infty} [G_i(h_{j_1}, \ldots, h_{j_l}) - G_i(h_{j_1}, \ldots, h_{j_l})].
\]

(38)
Here in the first two sums of the right-hand side we change summation variable \( k \) to \( k+1 \).

In this relation all sums with respect to \( k \) contain expressions of order \( k \) relative to \( f \). Putting terms of the same order being equal in accordance with the theorem on uniqueness of analytical operators \([9]\) we obtain the next recurrent system for the functions \( h_k(f) \)

\[
\begin{align*}
h_1(f) &= B^{-1}f, \\ h_2(f) &= B^{-1}[G_2(h_1, h_1) - G_2(h_1, h_1)], \\ h_k(f) &= B^{-1} \sum_{l=2}^{k-1} \sum_{j_1 + \ldots + j_l = k-1} G_l(h_{j_1}, \ldots, h_{j_l})f + B^{-1} \sum_{l=2}^{k} \sum_{j_1 + \ldots + j_l = k-1} \left[ G_l(h_{j_1}, \ldots, h_{j_l}) - G_l(h_{j_1}, \ldots, h_{j_l}) \right], \\
&\quad 3 \leq k \leq N, \\
&\quad k \geq N + 1.
\end{align*}
\]

All terms of series \( (35) \) are calculated from this system. So the solution of the equation \( (15) \) is founded. It satisfies additional condition \( (16) \). Convergence of the series \( (35) \) with \( h_k(f) \) being the solutions of system \( (39)-(42) \) is proved by Cauchy-Goursat method presented in the book \([5]\).

As soon as \( h_k \) are expressed in terms of \( f \) we can get the canonical distribution \( (9) \) in terms of \( F_2 \) since \( f \) and \( F_2 \) are uniquely bounded by relation \( (11) \).

### 5 Calculation procedure for the canonical distribution in terms of \( f \)

Since canonical distribution \( (9) \) is a ratio of two polynomials with respect to \( h \), we see that \( D_N \) is an analytical operator function of \( h \). We have just proved that \( h \) is an analytical operator function of \( f \). Therefore \( D_N \) is an analytical operator function of \( f \) and it can be expanded into an absolutely convergent series relative to \( f \)

\[
D_N = V^{-N} \left[ 1 + \sum_{k=1}^{\infty} \varphi_k(f) \right],
\]

where \( \varphi_k(f) \) is a uniform operator of order \( k \) transforming function \( f(q, q') \) to function \( \varphi_k(q_1, \ldots, q_N; [f]) \). Taking into account definitions of the reduced distribution functions \( (4) \) and the function \( f(q, q') \) \( (11) \) we can get relations for \( \varphi_k \)

\[
\begin{align*}
\frac{1}{V^{N-k}} \int dq_3 \cdots dq_N \varphi_1(q_1, \ldots, q_N; [f]) &= f(q_1, q_2), \\
\int dq_3 \cdots dq_N \varphi_k(q_1, \ldots, q_N; [f]) &= 0, \quad k = 2, 3, \ldots
\end{align*}
\]
Below we construct a procedure for calculation of functions \( \varphi_1(q_1, \ldots, q_N; [f]) \) in terms of \( f \).

We introduce a nonlinear operator function \( \lambda(h) \) by the relation
\[
\prod_{1 \leq j < k \leq N} [1 + h(q_j, q_k)] = 1 + \lambda(h).
\]
(46)

This operator function is a polynomial of degree \( N \) relative to \( h \). It can be written in the form
\[
\lambda(h) = \sum_{l=1}^{N} \lambda_l(h),
\]
(47)
where \( \lambda_k(h) \) are defined by relations
\[
\lambda_l(q_1, \ldots, q_N; [h]) = \sum_{1 \leq K_1 < \ldots < K_l \leq N} h(X_{K_1}) \cdots h(X_{K_l}).
\]
(48)

Introduce also multilinear operators
\[
\Lambda_l(y_1, \ldots, y_l) \equiv \sum_{1 \leq K_1 < \ldots < K_l \leq N} y_1(X_{K_1}) \cdots y_l(X_{K_l}).
\]
(49)

It's evident that
\[
\lambda_l(h) = \Lambda_l(h, \ldots, h).
\]
(50)

The operators introduced here are connected with the operators \( g(h) \), \( g_k(h) \), and \( G_k(h_1, \ldots, h_k) \) by the relations
\[
\frac{1}{V_{N-2}} \int dq_3 \cdots dq_N \lambda(q_1, \ldots, q_N; [h]) = g(q_1, q_2; [h]),
\]
(51)
\[
\frac{1}{V_{N-2}} \int dq_3 \cdots dq_N \lambda_k(q_1, \ldots, q_N; [h]) = g_k(q_1, q_2; [h]),
\]
(52)
\[
\frac{1}{V_{N-s}} \int dq_{s+1} \cdots dq_N \Lambda_k(q_1, \ldots, q_N; [h_1, \ldots, h_k]) = G_k(q_1, \ldots, q_s; [h_1, \ldots, h_k]).
\]
(53)

In particular for \( k = 1 \)
\[
\frac{1}{V_{N-2}} \int dq_3 \cdots dq_N \Lambda_1(q_1, \ldots, q_N; [h]) = G_1(q_1, q_2; [h]) = g_1(q_1, q_2; [h]) = (Bh)(q_1, q_2).
\]
(54)

Taking into account the expression (29) for \( Q_N \) we can write
\[
D_N = V^{-N} \frac{1 + \lambda(h)}{1 + \mathcal{g}(h)}.
\]
(55)

Comparing it with (43) we get the relation
\[
\sum_{k=1}^{\infty} \varphi_k(f) = \frac{\lambda(h) - \mathcal{g}(h)}{1 + \mathcal{g}(h)},
\]
(56)
where \( h \) is the operator function of \( f \) calculated in previous section. Using here the expressions for \( \lambda(h), \overline{\varphi}(h) \) and \( h(f) \) we can transform the right-hand side of (56) to series with respect to \( f \) and thus obtain expressions for \( \varphi_k(f) \). But less awkward transformations are obtained if we construct a recurrent system for \( \varphi_k(f) \).

Multiplying (56) by \( 1 + \overline{\varphi}(h) \) and using (33) and (50) we obtain

\[
\{1 + \sum_{k=2}^N \overline{G}_k(h, \ldots, h)\} \sum_{l=1}^\infty \varphi_l(f) = \sum_{k=1}^N \Lambda_k(h, \ldots, h) - \sum_{k=2}^{N} \overline{G}_k(h, \ldots, h). \tag{57}
\]

Substitution of the expansion (33) here gives

\[
\{1 + \sum_{k=2}^N \sum_{j_1=1}^\infty \cdots \sum_{j_k=1}^\infty G_k^{(0)}(h_{j_1}, \ldots, h_{j_k})\} \sum_{l=1}^\infty \varphi_l(f)
= \sum_{k=1}^N \sum_{j_1=1}^\infty \cdots \sum_{j_k=1}^\infty \Lambda_k(h_{j_1}, \ldots, h_{j_k}) - \sum_{k=2}^N \sum_{j_1=1}^\infty \cdots \sum_{j_k=1}^\infty G_k^{(0)}(h_{j_1}, \ldots, h_{j_k}). \tag{58}
\]

Further calculation is carried out in the same way as in the previous section. We won’t make it and write a recurrent system for \( \varphi_k(f) \) straight away

\[
\varphi_1(f) = \Lambda_1(h_1), \tag{59}
\]

\[
\varphi_2(f) = \Lambda_1(h_2) + \Lambda_2(h_1, h_1) - \overline{G}_2(h_1, h_1), \tag{60}
\]

\[
\varphi_k(f) = \Lambda_1(h_k) + \sum_{l=2}^k \sum_{j_1+\cdots+j_l=k} \left\{ \Lambda_l(h_{j_1}, \ldots, h_{j_l}) - \overline{G}_l(h_{j_1}, \ldots, h_{j_l}) \right\}
- \sum_{l=3}^k \sum_{j_1+\cdots+j_l=k} \overline{G}_{l-1}(h_{j_1}, \ldots, h_{j_{l-1}})\varphi_{j_l}(f), \quad 3 \leq k \leq N, \tag{61}
\]

\[
\varphi_k(f) = \Lambda_1(h_k) + \sum_{l=2}^N \sum_{j_1+\cdots+j_l=k} \left\{ \Lambda_l(h_{j_1}, \ldots, h_{j_l}) - \overline{G}_l(h_{j_1}, \ldots, h_{j_l}) \right\}
- \sum_{l=3}^{N+1} \sum_{j_1+\cdots+j_l=k} \overline{G}_{l-1}(h_{j_1}, \ldots, h_{j_{l-1}})\varphi_{j_l}(f), \quad k \geq N + 1. \tag{62}
\]

In this relations we have to use the expressions for \( h_r(f) \) derived from the recurrent system (39)–(42).

For example an expression for \( \varphi_1(f) \) is

\[
\varphi_1(q_1, \ldots, q_N; [f]) = \sum_{1 \leq j < k \leq N} f(q_j, q_k) - (N - 2) \sum_{i=1}^N \overline{f}(q_i). \tag{63}
\]

This expression coincides nominally with \( \varphi_1(q_1, \ldots, q_N; [f]) \) derived in the paper [4]. However in this formula the function \( f(q, q') \) depends on both the interaction potential \( u_2(q, q') \) and the external field \( u_1(q) \) whereas in [4] the latter is absent. It is easy to show that expressions (59)–(62) and (63) satisfy conditions (44), (45).

\[
\]
6 Set of irreducible functions containing the whole information about system under consideration

The program presented here can’t be realized for the reduced one-particle distribution function because not all the theorem conditions are held in this case. Namely the operator $B_1 = \partial F_1/\partial h(q, q')$ has a nontrivial space of zeroes. This space consists of all functions $h(q, q') \in E_1$ satisfying a condition

$$\int h(q, q') dq' = 0. \quad (64)$$

Such operator $B$ might not have an inverse one. And the reduced one-particle distribution function doesn’t contain the whole information about system under consideration.

At the same time there is a set of irreducible functions which is equivalent to the reduced two-particle distribution function. This set includes the reduced one-particle distribution function and a pair correlation function $\kappa(q, q') = F_2(q, q') - F_1(q)F_1(q')F_1(q)F_1(q')$. (65)

The function $F_1(q)$ can’t be expressed in terms of $\kappa(q, q')$ and vice versa.

Taken together they form the set which describes the system under consideration completely because there is a one-to-one correspondence $F_2(q, q') \longleftrightarrow \{F_1(q), \kappa(q, q')\}$. Really on the one hand $F_2(q, q')$ is expressed in terms of mentioned set of functions by relation (65). On the other hand $F_1(q)$ is expressed as an integral of $F_2(q, q')$ with respect to $q'$. And $\kappa(q, q')$ is defined by relation (65) in which $F_1(q)$ is presented in terms of $F_2(q, q')$.

So the function $f(q, q')$ can be expressed in terms of the set $\{F_1(q), \kappa(q, q')\}$. Therefore the canonical Gibbs distribution can be expressed in terms of this set of irreducible functions with the help of the relations (62)–(63) in which functions $h_l(q, q'; [f])$ must be expressed in terms of $\{F_1(q) and \kappa(q, q')\}$. Therefore this set of irreducible functions contains the whole information about the system under consideration.

7 Conclusion

Using the theorem on implicit functions in this article it is shown that the reduced distribution function of order two plays a specific role for the canonical ensemble of $N$ particles with two-body interaction and external field. The canonical Gibbs distribution $D_N(q_1, \ldots, q_N)$ can be expressed uniquely in terms of this function $F_2(q, q')$. From here we easily conclude that there is a one-to-one correspondence between these two functions. This means that the reduced distribution function $F_2$ contains information about the system under consideration as much as the whole canonical distribution $D_N$. Reduced distribution functions of all orders can be expressed in terms of this single function $F_2$.

The one-particle reduced distribution functions don’t satisfy the theorem conditions. So it is impossible to express the canonical distribution in terms of this function $F_1$. To all appearance it contains not all information about the system under consideration.

The set of irreducible functions $\{F_1(q), \kappa(q, q')\}$ as well as $F_2(q, q')$ contains the whole information about the system under consideration.
Considered theorem provides sufficient conditions for existence and uniqueness of inverse transformation \( \{f \to h\} \). Results obtained here are valid in some neighbourhood of \( h^{(0)} = 0, f^{(0)} = 0 \). The question about size of this neighbourhood demands special investigation.

References

[1] N.N. Bogolyubov. *Questions of dynamical theory in statistical physics*. Selected works, Vol. 2. Kiev: Naukova Dumka, 1970, p. 99

[2] R. Balescu. Equilibrium and Nonequilibrium Statistical Mechanics. New York-London, A Wiley Interscience Publication, 1975.

[3] M.I. Kalinin. *On the completeness of describing an equilibrium canonical ensemble using a pair distribution function*. arXiv: cond-mat/0405256.

[4] M.I. Kalinin. *Completeness of the description of an equilibrium canonical ensemble by a two-particle partition function*. Theor. Math. Phys., 2005, Vol. 145, p. 1474.

[5] M.M. Vainberg and V.A. Trenogin Theory of Branching of Solutions of Non-Linear Equations. Moscow, Nauka, 1969.

[6] N. Dunford and J.T. Schwartz. Linear Operators Part I General Theory. New York-London, Interscience Publishers, 1958.

[7] L.V. Kantorovich and G.P. Akilov. Functional Analysis. Moscow, Nauka, 1977.

[8] B.Z. Vulikh. A brief course in the theory of functions of real variables (An introduction to the theory of integral). (Moscow, Mir, 1976.

[9] E. Hille and R.S. Phillips. Functional Analysis and Semi-Groups. Providence, American Mathematical Society, 1957.