Statistical field theory for a multicomponent fluid: The collective variables approach

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Abstract

Using the collective variables (CV) method the basic relations of statistical field theory of a multicomponent non-homogeneous fluids are reconsidered. The corresponding CV action depends on two sets of scalar fields - fields $\rho_\alpha$ connected to the local density fluctuations of the $\alpha$th species of particles and fields $\omega_\alpha$ conjugated to $\rho_\alpha$. The explicit expressions for the CV field correlations and their relation to the density correlation functions are found. The perturbation theory is formulated and a mean field level (MF) of the theory is considered in detail.

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1This paper is dedicated to Professor Ivan Vakarchuk on the occasion of his 60th birthday
1 Introduction

In recent years much attention has been focused on an issue of the phase transitions in multicomponent fluid mixtures, especially in ionic fluids. In spite of significant progress in this field, such systems are far from being completely understood. The investigation of complex models is of great importance in understanding the nature of critical and phase behavior of real ionic fluids which demonstrate both the charge and size asymmetry. The powerful tools for the study of multicomponent continuous systems are those based on the functional methods. In many cases the partition function of multicomponent models (see, e.g. [1]) can be re-expressed as a functional integral after performing the Hubbard-Stratonovich transformation [2, 3], a simple device proposed in the 50ies. Nearly at the same time another method, the method of collective variables (CVs), that allows in a explicit way to construct a functional representation for many-particle interacting systems was developed [4, 5]. The method, proposed initially in the 1950s [4, 5, 6] for the description of the classical charged many particle systems and developed later for the needs of the phase transition theory [7, 8, 9, 10], was in fact one of the first successful attempts to attack the problems of statistical physics using the functional integral representation. Recently, the rigorous scalar field KSSHE (Kac-Siegert-Stratonovich-Hubbard-Edwards) theory [11, 12], which uses the Stratonovich-Hubbard transformation, was developed to describe the phase equilibria in simple and ionic fluids. As was shown [13, 14], both groups of theories are in close relation.

In [13] the CV representation of simple (one-component) fluids was reexamined from the point of view of statistical field theory. Our goal here is to derive the exact functional representation for the grand canonical partition function of a non-homogeneous multicomponent fluid. We reformulate the method of CV in real space and derive the CV action that depends on two sets of scalar fields - fields \( \{\rho_\alpha\} \) connected to the densities of the \( \alpha \)th species and fields \( \{\omega_\alpha\} \) conjugate to \( \{\rho_\alpha\} \). We study the correlations between these fields as well as their relations to the density correlations of the fluid.

The CV method is based on: (i) the concept of collective coordinates being appropriate for the physics of the system considered (see, for instance, [15]) and (ii) the integral identity allowing to derive an exact functional representation for the configurational Boltzmann factor. Being applied to the continuous system the CV method uses the idea of the reference system (RS), one of the basic ideas of the liquid state theory [16]. The idea consists in the splitting of an interparticle interaction potential in two parts: the potential of short-range repulsion which describes the mutual impenetrability of the particles and the potential describing mainly the behaviour at moderate and large distances. The equilibrium properties of the system interacting via the short-range repulsion are assumed to be known. Therefore, this system can be regarded as the “reference” system. The remainder of the interaction is described in the phase space of CVs (collective coordinates). The fluid of hard spheres is most frequently used as the RS in the liquid state theory since its thermodynamic and structural properties are well known. In this paper we derive the functional representation for the grand canonical partition function of a multicomponent fluid which includes both short-range and long-range interactions.

The paper is organized as follows. In Section 2 we obtain the exact expression for
the functional of the grand partition function of a multicomponent non-homogeneous mixture. Section 3 is devoted to the study of the correlations of CVs fields and their relation to the density correlation functions of a multicomponent fluid. In Section 4 we formulate the perturbation theory. The MF level of the theory is considered in detail.

2 The functional representation of the grand partition function

2.1 The model

Let us consider a classical \(m\)-component system consisting of \(N\) particles among which there exist \(N_1\) particles of species 1, \(N_2\) particles of species 2, \ldots and \(N_m\) particles of species \(m\). The potential energy of the system is assumed to be of the form

\[
U_{N_1 \ldots N_m} = \frac{1}{2} \sum_{\alpha, \beta} \sum_{i \neq j} U_{\alpha \beta}(r_i^\alpha, r_j^\beta) + \sum_{i=1}^N \psi_\alpha(r_i^\alpha),
\]

where \(U_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) denotes the interaction potential of two particles and the second term is the potential energy due to external forces.

We present the pair interaction potential \(U_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) as

\[
U_{\alpha \beta}(r_i^\alpha, r_j^\beta) = v_{\alpha \beta}^0(r_i^\alpha, r_j^\beta) + w_{\alpha \beta}(r_i^\alpha, r_j^\beta),
\]

where \(v_{\alpha \beta}^0(r_i^\alpha, r_j^\beta)\) is a potential of a short-range repulsion that can be chosen as an interaction between two hard spheres of respective diameters \(\sigma_\alpha\) and \(\sigma_\beta\). We call the \(m\)-component system with the interaction \(v_{\alpha \beta}^0(r_i^\alpha, r_j^\beta)\) a reference system (RS). The thermodynamic and structural properties of the RS are assumed to be known. \(w_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) is some potential which can describe both repulsion (e.g., soft repulsion) and attractive interactions. In general, \(w_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) can be presented in the form

\[
w_{\alpha \beta}(r_i^\alpha, r_j^\beta) = w_{\alpha \beta}^R(r_i^\alpha, r_j^\beta) + w_{\alpha \beta}^A(r_i^\alpha, r_j^\beta),
\]

where \(w_{\alpha \beta}^R(r_i^\alpha, r_j^\beta)\) and \(w_{\alpha \beta}^A(r_i^\alpha, r_j^\beta)\) are repulsive and attractive parts of the interaction potential \(w_{\alpha \beta}(r_i^\alpha, r_j^\beta)\). Since \(w_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) are arbitrary in the core, i.e. for \(r \leq \sigma_{\alpha \beta} \equiv (\sigma_\alpha + \sigma_\beta)/2\), we assume that the \(w_{\alpha \beta}(r_i^\alpha, r_j^\beta)\) have been regularized in such a way that their Fourier transforms \(\tilde{w}_{\alpha \beta}(k)\) are well-behaved functions of \(k\) and that \(w_{\alpha \beta}(0)\) are finite quantities. We denote by \(\Omega\) the domain of volume \(V\) occupied by particles.

We present the potential energy \(U_{N_1 \ldots N_m}\) as follows

\[
U_{N_1 \ldots N_m} = U_{N_1 \ldots N_m}^{RS} + \frac{1}{2} \left( \rho_\alpha w_{\alpha \beta}|\rho_\beta \right) + \left( \psi_\alpha | \rho_\alpha \right) - N_\alpha \nu_\alpha^S,
\]

where

\[
\rho_\alpha(r) = \sum_{i=1}^{N_\alpha} \delta(r - r_i^\alpha)
\]

(4)
is the microscopic density of the $\alpha$th species in a given configuration and $\psi_\alpha(\mathbf{r})$ is some external one-body potential acting on particles of species $\alpha$. The following notations are introduced in (3): $V_{RS}^{N_1 \ldots N_m}$ is the contribution from a $m$-component RS, $\nu^S_\alpha$ is the self-energy of the $\alpha$th species

$$\nu^S_\alpha = \frac{1}{2} w_{\alpha\alpha}(0).$$  \hfill (5)

In (3) we have also introduced Dirac’s brackets notations

$$\langle \hat{\rho}_\alpha | w_{\alpha\beta} | \hat{\rho}_\beta \rangle = \int_\Omega d^3r_1 d^3r_2 \hat{\rho}_\alpha (\mathbf{r}_1^\alpha) w_{\alpha\beta}(\mathbf{r}_1^\alpha, \mathbf{r}_2^\beta) \hat{\rho}_\beta (\mathbf{r}_2^\beta),$$

$$\langle \psi_\alpha | \hat{\rho}_\alpha \rangle = \int_\Omega d^3r_1 \psi_\alpha (\mathbf{r}_1^\alpha) \hat{\rho}_\alpha (\mathbf{r}_1^\alpha).$$

In the above formulas summation over repeated indices is meant.

The system under consideration is at equilibrium in the grand canonical (GC) ensemble, $\beta = 1/k_B T$ is the inverse temperature ($k_B$ Boltzmann constant), $\mu_\alpha$ is the chemical potential of the $\alpha$th species. Then, the GC partition function can be written as

$$\Xi[\nu_\alpha] = \sum_{N_1 \geq 0} \frac{1}{N_1!} \sum_{N_2 \geq 0} \frac{1}{N_2!} \ldots \sum_{N_m \geq 0} \frac{1}{N_m!} \int (d\Gamma) \exp \left[ -\beta V_{RS}^{N_1 \ldots N_m} - \frac{\beta}{2} \langle \hat{\rho}_\alpha | w_{\alpha\beta} | \hat{\rho}_\beta \rangle + \langle \psi_\alpha | \hat{\rho}_\alpha \rangle \right],$$  \hfill (6)

where $\mathbf{\nu}_\alpha (\mathbf{r}) = \nu_\alpha + \nu^S_\alpha - \beta \psi_\alpha (\mathbf{r})$ is the local chemical potential of the $\alpha$th species and $\nu_\alpha = \beta \mu_\alpha - 3 \ln \Lambda_\alpha$, $\Lambda_\alpha^{-1} = (2 \pi m_\alpha \beta^{-1}/h^2)^{1/2}$ is the inverse de Broglie thermal wavelength. $(d\Gamma) = \prod_\alpha d\Gamma_{N_\alpha}$, $d\Gamma_{N_\alpha} = dr_1^\alpha dr_2^\beta \ldots dr_{N_\alpha}^\alpha$ is the element of the configurational space of $N$ particles.

For a given volume $V$, $\Xi[\nu_\alpha]$ is a function of the temperature $T$ and a log-convex functional of the local chemical potentials $\nu_\alpha (\mathbf{r}^\alpha)$.

### 2.2 The collective variables representation

We introduce the collective variable $\rho_\alpha (\mathbf{r})$ which describes the field of the number particle density of the $\alpha$th species. To this end we use the identity

$$\exp \left( \frac{1}{2} \langle \hat{\rho} | w | \hat{\rho} \rangle \right) = \int \mathcal{D} \rho \delta_{\mathcal{F}} [\rho - \hat{\rho}] \exp \left( \frac{1}{2} \langle \rho | w | \rho \rangle \right).$$  \hfill (7)

In (7) the functional “delta function” $\delta_{\mathcal{F}} [\rho]$ is defined as [17]

$$\delta_{\mathcal{F}} [\rho] \equiv \int \mathcal{D} \omega \exp \left( i \langle \omega | \rho \rangle \right),$$  \hfill (8)

Using (8) we can present the Boltzmann factor which does not include the RS interaction in the form

$$\exp \left( \frac{1}{2} \langle \hat{\rho}_\alpha | w_{\alpha\beta} | \hat{\rho}_\beta \rangle \right) = \int \mathcal{D} \rho \mathcal{D} \omega \exp \left( \frac{1}{2} \langle \rho_\alpha | w_{\alpha\beta} | \rho_\beta \rangle \right. + i \langle \omega_\alpha | \{ \rho_\alpha - \hat{\rho}_\alpha \} \rangle \right),$$  \hfill (9)
Inserting equation (9) in the definition (6) of the GC partition function \( \Xi[\nu_\alpha] \) one obtains

\[
\Xi[\nu_\alpha] = \int \mathcal{D}\rho \exp \left( -\frac{\beta}{2} \langle \rho_\alpha | w_{\alpha\beta} | \rho_\beta \rangle \right) \mathcal{J}[\{\rho_\alpha, \nu_\alpha\}],
\]

(10)

where the Jacobian

\[
\mathcal{J}[\{\rho_\alpha, \nu_\alpha\}] = \int \mathcal{D}\omega \exp (i \langle \omega_\alpha | \rho_\alpha \rangle) \Xi_{RS}[\{\nu_\alpha - i \omega_\alpha\}]
\]

(11)

allows one for the passage from the microscopic variables \( r^\alpha \) (the Cartesian coordinates of particles) to the collective variables \( \rho_\alpha(r) \) (fields of the number density of particles). In (11) \( \Xi_{RS}[\{\nu_\alpha - i \omega_\alpha\}] = \Xi_{RS}[Z^*] \) is the GC partition function of a \( m \)-component RS

\[
\Xi_{RS}[Z^*] = \sum_{N_1 \geq 0} \frac{1}{N_1!} \sum_{N_2 \geq 0} \frac{1}{N_2!} \cdots \sum_{N_m \geq 0} \frac{1}{N_m!} \int (d\Gamma) \prod_i Z^* (r_i),
\]

(12)

where \( Z^*(r) = \prod_\alpha Z^*_\alpha (r) = \exp(\nu^*_\alpha (r)) \). \( Z^*_\alpha \) is the activity of the species \( \alpha \) associated with the dimensionless local chemical potential \( \nu^*_\alpha (r) = \nu_\alpha (r) - i \omega_\alpha (r) \). It should be noted that \( \mathcal{J}[\{\rho_\alpha, \nu_\alpha\}] \) does not depend on the pair interaction \( w_{\alpha\beta}(r_i, r_j) \) but only on the GC partition function of the RS \( \Xi_{RS}[Z^*] \) which is supposed to be known.

Equation (10) can also easily be recast in the form of a standard statistical field theory, i.e.

\[
\Xi[\nu_\alpha] = \int \mathcal{D}\rho \mathcal{D}\omega \exp (-\mathcal{H}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}]),
\]

(13)

where the action \( \mathcal{H}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}] \) of the CV field theory reads as

\[
\mathcal{H}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}] = \frac{\beta}{2} \langle \rho_\alpha | w_{\alpha\beta} | \rho_\beta \rangle - i \langle \omega_\alpha | \rho_\alpha \rangle - \ln \Xi_{RS}[\{\nu_\alpha - i \omega_\alpha\}].
\]

(14)

Functional integrals which enter the above-mentioned formulas can be given a precise meaning in the case where the domain \( \Omega \) is a cube of side \( L \) (\( V = L^3 \)) with periodic boundary conditions. This means that we restrict ourselves to fields \( \rho_\alpha(r) \) and \( \omega_\alpha(r) \) which can be written as Fourier series

\[
\rho_\alpha(r) = \frac{1}{L^3} \sum_{k \in \Lambda} \rho_{k,\alpha} e^{ikr},
\]

(15)

and

\[
\omega_\alpha(r) = \frac{1}{L^3} \sum_{k \in \Lambda} \omega_{k,\alpha} e^{ikr},
\]

(16)

where \( \Lambda = (2\pi/L) \mathbb{Z}^3 \) is the reciprocal cubic lattice. The reality of \( \rho_\alpha \) (and \( \omega_\alpha \)) implies that, for \( k \neq 0 \) \( \rho_{-k,\alpha} = \rho_{k,\alpha}^* \) (\( \omega_{-k,\alpha} = \omega_{k,\alpha}^* \)), where the star means complex conjugation. Then, the normalized functional measure \( \mathcal{D}\rho \) (and \( \mathcal{D}\omega \)) is defined as [18]
\[ D \rho \equiv \prod_\alpha \prod_{k \in \Lambda} \frac{d\rho_{k,\alpha}}{\sqrt{2\pi V}} \]  
(17)

\[ d\rho_{k,\alpha} d\rho_{-k,\alpha} = 2 d\Re \rho_{k,\alpha} d\Im \rho_{k,\alpha}, \quad k \neq 0. \]  
(18)

Equation (17) can be rewritten as

\[ D \rho = \prod_\alpha \frac{d\rho_{0,\alpha}}{\sqrt{2\pi V}} \prod_{q \in \Lambda^*} \frac{d\Re \omega_{q,\alpha} d\Im \omega_{q,\alpha}}{\pi V}, \]  
(19)

where the sum in the r.h.s. runs over only the half \( \Lambda^* \) of all the vectors of the reciprocal lattice \( \Lambda \). We have for \( D \omega \), respectively

\[ D \omega = \prod_\alpha \frac{d\omega_{0,\alpha}}{\sqrt{2\pi V}} \prod_{q \in \Lambda^*} \frac{d\Re \omega_{q,\alpha} d\Im \omega_{q,\alpha}}{\pi V}. \]  
(20)

Now let us present the action (14) for the isotropic interaction potential \( w_{\alpha\beta}(r) \) as follows

\[ H[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}] = \frac{1}{2} \sum_{\alpha,\beta} \sum_k \tilde{\Phi}_{\alpha\beta}(k) \rho_{k,\alpha} \rho_{-k,\beta} - i \sum_\alpha \sum_k \omega_{k,\alpha} \rho_{k,\alpha} - \ln \Xi_{\text{RS}}[\{\nu_\alpha - i\omega_\alpha\}], \]  
(21)

Here \( CV_{\rho_{k,\alpha}} \) describes the \( k \)th mode of number density fluctuations of the \( \alpha \)th species. \( \tilde{\Phi}_{\alpha\beta}(k) = \frac{\beta}{V} \tilde{w}_{\alpha\beta}(k) \), where \( \tilde{w}_{\alpha\beta}(k) \) is the Fourier transform of the interaction potential \( w_{\alpha\beta}(r) \).

In order to obtain another equivalent representation of the action \( H[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}] \) we first distinguish the chemical potential \( \nu_0^\alpha \) of the particle of the species \( \alpha \) in the RS. To this end we put

\[ \nu_\alpha - i\omega_\alpha(r) = \nu_0^\alpha - i\omega'_\alpha(r) \]  
(22)

and obtain

\[ i\omega_\alpha(r) = \Delta \nu_\alpha + i\omega'_\alpha(r) \]

with \( \Delta \nu_\alpha = \nu_\alpha - \nu_0^\alpha \). As a result, the action (or the Hamiltonian) (21) can be written as

\[ H[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}] = -\sum_\alpha \Delta \nu_\alpha \rho_{k=0,\alpha} + \frac{1}{2} \sum_{\alpha,\beta} \sum_k \tilde{\Phi}_{\alpha\beta}(k) \rho_{k,\alpha} \rho_{-k,\beta} - i \sum_\alpha \sum_k \omega'_{k,\alpha} \rho_{k,\alpha} - \ln \Xi_{\text{RS}}[\{\nu_0^\alpha - i\omega'_\alpha\}]. \]  
(23)

We have obtained the exact representations of the grand partition function of a multicomponent system (eqs. (13)- (14), (21) and (23)) in terms of CVs \( \rho_\alpha(r) \), which are number density fields of the \( \alpha \)th species particles (or fluctuation modes of the \( \alpha \)th species number density) We also stress that \( \rho_\alpha(r) \) and \( \omega_\alpha(r) \) are two real scalar fields and that eqs. (13)- (14) (as well as eqs. (21) and (23)) are valid for repulsive, attractive as well as arbitrary pair interactions.
Besides the usual GC average \( \langle A \rangle_{GC} \) of a dynamic variable we introduce statistical field averages of the type

\[
\langle A [\{\rho_\alpha, \omega_\alpha\}] \rangle_{CV} = \Xi [\{\nu_\alpha\}]^{-1} \int \mathcal{D}\rho\mathcal{D}\omega \ A [\{\rho_\alpha, \omega_\alpha\}] \exp (-\mathcal{H} [\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}]),
\]

where \( A [\{\rho_\alpha, \omega_\alpha\}] \) is a functional of the two CV fields \( \rho_\alpha \) and \( \omega_\alpha \).

3 Correlation functions

3.1 General relations

Let us write some important relations. First, according to \[20, 21\] we introduce the ordinary and truncated (or connected) density correlation functions

\[
G^{(n)}_{\alpha_1...\alpha_n} [\{\nu_\alpha\}] (1, \ldots, n) = \left< \prod_{i=1}^{n} \hat{\rho}_{\alpha_i} (i) \right>_{GC} = \frac{1}{\Xi [\{\nu_\alpha\}] \delta\nu_{\alpha_1}(1) \ldots \delta\nu_{\alpha_n}(n)},
\]

\[
G^{(n),T}_{\alpha_1...\alpha_n} [\{\nu_\alpha\}] (1, \ldots, n) = \frac{\delta^n \log \Xi [\{\nu_\alpha\}]}{\delta\nu_{\alpha_1}(1) \ldots \delta\nu_{\alpha_n}(n)}.
\]

Our notation emphasizes the fact that the correlation functions (connected and not connected) are functionals of the local chemical potential \( \nu_\alpha (r) \) and functions of the coordinates \( (1, 2, \ldots, n) \equiv (r_1, r_2, \ldots, r_n) \). For the sake of simplicity, we omit below the notations which indicate the functional dependence of the correlation functions of \( \nu_\alpha (r) \). In standard textbooks of liquid theory \[16\] the \( n \)-particle correlation functions are more frequently defined as functional derivatives of \( \Xi \) or \( \log \Xi \) with respect to the activities \( Z_\alpha = \exp (\nu_\alpha) \) rather than with respect to the local chemical potentials

\[
\frac{\rho_{\alpha_1...\alpha_n}(1, 2, \ldots, n)}{Z^*_{\alpha_1}(1)Z^*_{\alpha_2}(2) \ldots Z^*_{\alpha_n}(n)} = \frac{1}{\Xi} \frac{\delta^n \Xi}{\delta Z^*_{\alpha_1}(1)\delta Z^*_{\alpha_2}(2) \ldots \delta Z^*_{\alpha_n}(n)},
\]

\[
\frac{\rho^T_{\alpha_1...\alpha_n}(1, 2, \ldots, n)}{Z^*_{\alpha_1}(1)Z^*_{\alpha_2}(2) \ldots Z^*_{\alpha_n}(n)} = \frac{1}{\Xi} \frac{\delta^n \ln \Xi}{\delta Z^*_{\alpha_1}(1)\delta Z^*_{\alpha_2}(2) \ldots \delta Z^*_{\alpha_n}(n)}.
\]

We also define the partial distribution function \( g_{\alpha_1...\alpha_n} (1, 2, \ldots, n) \) and the partial correlation function \( h_{\alpha_1...\alpha_n} (1, 2, \ldots, n) \) \[20\]

\[
g_{\alpha_1...\alpha_n} (1, 2, \ldots, n) = \frac{\rho_{\alpha_1...\alpha_n}(1, 2, \ldots, n)}{\rho_{\alpha_1}(1)\rho_{\alpha_2}(2) \ldots \rho_{\alpha_n}(n)},
\]

\[
h_{\alpha_1...\alpha_n} (1, 2, \ldots, n) = \frac{\rho^T_{\alpha_1...\alpha_n}(1, 2, \ldots, n)}{\rho_{\alpha_1}(1)\rho_{\alpha_2}(2) \ldots \rho_{\alpha_n}(n)}.
\]

Expressions \[25\] and \[28\]--\[29\] differ by the terms involving products of delta functions. For instance, for \( n = 2 \) and for a homogeneous system one has

\[
G^{(2)}_{\alpha_\beta} (1, 2) = \rho_\alpha \rho_\beta g_{\alpha_\beta} (1, 2) + \rho_\alpha \delta_{\alpha_\beta} \delta (1, 2),
\]

\[
G^{(2),T}_{\alpha_\beta} (1, 2) = \rho_\alpha \rho_\beta h_{\alpha_\beta} (1, 2) + \rho_\alpha \delta_{\alpha_\beta} \delta (1, 2),
\]

(30)
where \( \rho_\alpha \) is the equilibrium density of the species \( \alpha \). Besides, functions \( h_{\alpha\beta}(r) \) and \( g_{\alpha\beta}(r) \) are connected by the relation \( h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \) for a homogeneous case.

### 3.2 CV field correlations

Let us consider the correlations of fields \( \rho_\alpha \) and \( \omega_\alpha \). We start with the definitions of the correlation functions

\[
G_{\rho_{\alpha_1}...\rho_{\alpha_n}}(\{\nu_\alpha\})(1,\ldots,n) = \left\langle \prod_{i=1}^{n} \rho_{\alpha_i}(i) \right\rangle_{CV},
\]

\[
G_{\omega_{\alpha_1}...\omega_{\alpha_n}}(\{\nu_\alpha\})(1,\ldots,n) = \left\langle \prod_{i=1}^{n} \omega_{\alpha_i}(i) \right\rangle_{CV},
\]

and their truncated (connected) parts

\[
G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)}(1,\ldots,n) = G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)}(1,\ldots,n) - \sum_{m<n} \prod_{i=1}^{m} G_{\rho_{\alpha_i}...\rho_{\alpha_m}}^{(m),T}(i_1,\ldots,i_m),
\]

\[
G_{\omega_{\alpha_1}...\omega_{\alpha_n}}^{(n)}(1,\ldots,n) = G_{\omega_{\alpha_1}...\omega_{\alpha_n}}^{(n)}(1,\ldots,n) - \sum_{m<n} \prod_{i=1}^{m} G_{\omega_{\alpha_i}...\omega_{\alpha_m}}^{(m),T}(i_1,\ldots,i_m),
\]

where the sum of products is carried out over all possible partitions of the set \( (1,\ldots,n) \) into subsets of cardinality \( m < n \).

**Correlation functions \( G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)} \).** Now we introduce the modified partition function

\[
\Xi^{1}[\{\nu_\alpha, J_\alpha\}] = \int D\rho D\omega \exp (-\mathcal{H}_{CV}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\} + \langle J_\alpha | \rho_\alpha \rangle]),
\]

where \( J_\alpha \) is a real scalar field and \( \Xi^{1}[\{\nu_\alpha, J_\alpha\}] \) is the generator of field correlation functions \( G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)} \) [19]. As a result, we have

\[
G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)}[\{\nu_\alpha\}](1,\ldots,n) = \left. \frac{1}{\Xi^{1}[\{\nu_\alpha\}]} \frac{\delta^n \Xi^{1}[\{\nu_\alpha, J_\alpha\}]}{\delta J_{\alpha_1}(1) \ldots \delta J_{\alpha_n}(n)} \right|_{J_{\alpha_i}=0},
\]

\[
G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n),T}[\{\nu_\alpha\}](1,\ldots,n) = \left. \frac{\delta^n \log \Xi^{1}[\{\nu_\alpha, J_\alpha\}]}{\delta J_{\alpha_1}(1) \ldots \delta J_{\alpha_n}(n)} \right|_{J_{\alpha_i}=0}. \tag{34}
\]

The simplest way to obtain the relations between the \( G_{\rho_{\alpha_1}...\rho_{\alpha_n}}^{(n)}[\{\nu_\alpha\}](1,\ldots,n) \) and the density correlation functions is to start from the definition (25). One has

\[
G_{\alpha_1...\alpha_n}^{(n)}(1,\ldots,n) = \left. \frac{1}{\Xi[\{\nu_\alpha\}]} \frac{\delta^n \Xi[\{\nu_\alpha\}]}{\delta \nu_{\alpha_1}(1) \ldots \delta \nu_{\alpha_n}(n)} \right|_{J_{\alpha_i}=0}.
\]
In order to relate the correlation functions the transformation is of course equal to unity and one obtains the relation

\[ w_{\alpha \beta} = -\beta w_{\alpha \beta} \]

where we introduce the notation \( \omega_{\alpha \beta} \) and use the equality

\[ \frac{\delta^n \Xi_{RS}[\{\varphi_\alpha - i\omega_\alpha\}]}{\delta \varphi_{\alpha_1}(1) \ldots \delta \varphi_{\alpha_n}(n)} = (i)^n \frac{\delta^n \Xi_{RS}[\{\varphi_\alpha - i\omega_\alpha\}]}{\delta \varphi_{\alpha_1}(1) \ldots \delta \varphi_{\alpha_n}(n)}. \]  

Performing now \( n \) integral by parts yields

\[
G_{\alpha_1 \ldots \alpha_n}^{(n)}(1, \ldots, n) = \frac{(-i)^n}{\Xi[\{\varphi_\alpha\}]} \int \mathcal{D}\rho \mathcal{D}\omega \exp \left( \frac{1}{2} \langle \rho_\alpha | w^*_{\alpha \beta} | \rho_\beta \rangle + i \langle \omega_\alpha | \rho_\alpha \rangle \right) + \ln \Xi_{RS}[\{\varphi_\alpha - i\omega_\alpha\}] \frac{\delta^n \exp(i \langle \omega_\alpha | \rho_\alpha \rangle)}{\delta \varphi_{\alpha_1}(1) \ldots \delta \varphi_{\alpha_n}(n)} \\
= \left\langle \prod_{i=1}^{n} \rho_{\alpha_i}(i) \right\rangle_{CV}.
\]

We have just proved the expected result

\[ G_{\alpha_1 \ldots \alpha_n}^{(n)}[\{\varphi_\alpha\}](1, \ldots, n) = G_{\rho_1 \ldots \rho_n}^{(n)}[\{\varphi_\alpha\}](1, \ldots, n). \]  

Obviously, the following relation is also valid for the truncated (connected) correlation functions

\[ G_{\omega_1 \ldots \omega_n}^{(n)T}[\{\varphi_\alpha\}](1, \ldots, n) = G_{\rho_1 \ldots \rho_n}^{(n)T}[\{\varphi_\alpha\}](1, \ldots, n). \]  

### Correlation functions \( G_{\alpha_1 \ldots \alpha_n}^{(n)} \)

Let us define the modified partition function

\[ \Xi^2[\{\varphi_\alpha, J_\alpha\}] = \int \mathcal{D}\rho \mathcal{D}\omega \exp(-\mathcal{H}_{CV}[\{\varphi_\alpha, \rho_\alpha, \omega_\alpha\}] + \langle J_\alpha | \omega_\alpha \rangle), \]  

where \( J_\alpha \) is a real scalar field. \( \Xi^2[\{\varphi_\alpha, J_\alpha\}] \) is the generator of the functions \( G_{\omega_1 \ldots \omega_n}^{(n)} \) and we thus have

\[
G_{\omega_1 \ldots \omega_n}^{(n)}[\{\varphi_\alpha\}](1, \ldots, n) = \frac{1}{\Xi^2[\{\varphi_\alpha\}]} \left. \frac{\delta^n \Xi^2[\{\varphi_\alpha, J_\alpha\}]}{\delta J_{\alpha_1}(1) \ldots \delta J_{\alpha_n}(n)} \right|_{J_{\alpha_i} = 0}, \]

\[
G_{\omega_1 \ldots \omega_n}^{(n)T}[\{\varphi_\alpha\}](1, \ldots, n) = \left. \frac{\delta^n \log \Xi^2[\{\varphi_\alpha, J_\alpha\}]}{\delta J_{\alpha_1}(1) \ldots \delta J_{\alpha_n}(n)} \right|_{J_{\alpha_i} = 0}.
\]

In order to relate the correlation functions \( G_{\omega_1 \ldots \omega_n}^{(n)} \) and \( G_{\alpha_1 \ldots \alpha_n}^{(n)}(1, \ldots, n) \) we perform the change of variables \( \rho_\alpha \to \rho_\alpha + iJ_\alpha \) in eq. (38). The functional Jacobian of the transformation is of course equal to unity and one obtains the relation

\[ \ln \Xi^2[\{\varphi_\alpha, J_\alpha\}] = -\frac{1}{2} \langle J_\alpha | w^*_{\alpha \beta} | J_\beta \rangle + \ln \Xi^1[\{\varphi_\alpha, i w^*_{\alpha \beta} \ast J_\beta\}], \]
where the star $\ast$ means space convolution and $\Xi^1$ is defined in (33). The idea is to perform now $n$ successive functional derivatives of both sides of eq. (40) with respect to $J_\alpha$. Since it follows from the expression (34) that

$$
\delta^n \log \Xi^1[\{\nu_\alpha, i\omega^*_{\alpha\beta} \ast J_\beta\}]_{J_\alpha=0} = i^n w^*_{\alpha_1\beta_1}(1, 1') \ldots w^*_{\alpha_n\beta_n}(n, n')
$$

one obtains

$$
\langle \omega_{\alpha_1}(1) \rangle_{\text{CV}} = i w^*_{\alpha_1\beta_1}(1, 1') \langle \rho_{\beta_1}(1') \rangle_{\text{CV}},
$$

$$
G_{\omega_{\alpha_1}\omega_{\alpha_2}}^{(2),T}[[\nu_\alpha]](1, 2) = -w^*_{\alpha_1\alpha_2}(1, 2) - w^*_{\alpha_1\beta_1}(1, 1')
$$

$$
\times w^*_{\alpha_2\alpha_3}(2, 2') G_{\rho_{\beta_1}\rho_{\beta_2}}^{(2),T}[[\nu_\alpha]](1', 2'),
$$

$$
G_{\omega_{\alpha_1} \ldots \omega_{\alpha_n}}^{(n),T}[[\nu_\alpha]](1, \ldots, n) = i^n w^*_{\alpha_1\beta_1}(1, 1') \ldots w^*_{\alpha_n\beta_n}(n, n')
$$

$$
\times G_{\rho_{\beta_1} \ldots \rho_{\beta_n}}^{(n),T}[[\nu_\alpha]](1', \ldots, n'), \quad n \geq 3.
$$

### 4 The perturbation theory

#### 4.1 Mean-field theory

Let us consider the functional of the GC partition function (13) with the action given by eq. (21) for the case of an isotropic interaction potential $w_{\alpha\beta}(r)$. At the MF level one has (19)

$$
\Xi_{\text{MF}}[\{\nu_\alpha\}] = \exp(-\mathcal{H}[\{\nu_\alpha, \bar{\rho}_\alpha, \bar{\omega}_\alpha\}]),
$$

where, for $\bar{\rho}_\alpha$ and $\bar{\omega}_\alpha$, the action is stationary, i.e.

$$
\frac{\delta \mathcal{H}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}]}{\delta \rho_\alpha}|_{(\bar{\rho}_\alpha, \bar{\omega}_\alpha)} = \frac{\delta \mathcal{H}[\{\nu_\alpha, \rho_\alpha, \omega_\alpha\}]}{\delta \omega_\alpha}|_{(\bar{\rho}_\alpha, \bar{\omega}_\alpha)} = 0.
$$

Replacing the CV action by its expression (21) in eq. (43) leads to implicit equations for $\bar{\rho}_\alpha$ and $\bar{\omega}_\alpha$:

$$
\bar{\rho}_\alpha(1) = \bar{\rho}_\alpha^{MF}(1) = \rho_\alpha^{RS}[\{\bar{\nu}_\alpha - i\bar{\omega}_\alpha\}](1),
$$

$$
i \bar{\omega}_\alpha(1) = \Phi_{\alpha\beta}(1, 2) \bar{\rho}_\beta(2),
$$

where $\rho_\alpha^{RS}[\{\bar{\nu}_\alpha - i\bar{\omega}_\alpha\}](i)$ denotes the $\alpha$th species number density of the RS fluid with the chemical potentials $\{\bar{\nu}_\alpha - i\bar{\omega}_\alpha\}$. For a homogeneous system (14) can be rewritten in the form

$$
\bar{\rho}_\alpha = \bar{\rho}_\alpha^{MF} = \rho_\alpha^{RS}[\{\bar{\nu}_\alpha - i\bar{\omega}_\alpha\}],
$$

$$
i \bar{\omega}_\alpha = \bar{\rho}_\beta \Phi_{\alpha\beta}(0),
$$

(45)
It follows from the stationary condition (43) that the MF density is given by
\[
\rho_{\alpha}^{\text{MF}} \{ \nu_{\alpha} \} (1) = \frac{\delta \ln \Xi_{\text{MF}} \{ \nu_{\alpha} \}}{\delta \nu_{\alpha}(1)} = \rho_{\alpha}^{\text{RS}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} (1),
\]
and that the MF grand potential reads
\[
\ln \Xi_{\text{MF}} \{ \nu_{\alpha} \} = \ln \Xi_{\text{RS}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} + \frac{\beta}{2} \langle \rho_{\alpha}^{\text{MF}} | w_{\alpha\beta} | \rho_{\beta}^{\text{MF}} \rangle .
\]
The MF Kohn-Scham free energy of a multicomponent system defined as the Legendre transform
\[
\beta A_{\text{MF}} \{ \rho_{\alpha} \} = \sup_{\nu_{\alpha}} \{ \langle \rho_{\alpha} | \nu_{\alpha} \rangle - \ln \Xi_{\text{MF}} \{ \nu_{\alpha} \} \},
\]
has the following form in the MF approximation
\[
\beta A_{\text{MF}} \{ \rho_{\alpha} \} = \beta A_{\text{RS}} \{ \rho_{\alpha} \} + \frac{\beta}{2} \langle \rho_{\alpha} | w_{\alpha\beta} | \rho_{\beta} \rangle - \frac{\beta}{2} \int_{\Omega} d\mathbf{r} w_{\alpha\alpha}(0) \rho_{\alpha}(\mathbf{r}) .
\]
Using the formulas
\[
\begin{align*}
C_{\text{MF,} \alpha_{1}\alpha_{2}}^{(2),T} \{ \nu_{\alpha} \} (1, 2) &= \frac{\delta^{2} \ln \Xi_{\text{MF}} \{ \nu_{\alpha} \}}{\delta \nu_{\alpha_{1}}(1) \delta \nu_{\alpha_{2}}(2)}, \\
C_{\text{MF,} \alpha_{1}\alpha_{2}}^{(2)} \{ \rho_{\alpha} \} (1, 2) &= -\frac{\delta^{2} \beta A_{\text{MF}} \{ \rho_{\alpha} \}}{\delta \rho_{\alpha_{1}}(1) \delta \rho_{\alpha_{2}}(2)},
\end{align*}
\]
where \((1, 2, \ldots, n) \equiv (\mathbf{r}_{1}, \mathbf{r}_{2}, \ldots, \mathbf{r}_{n})\), one can get the well-known expressions for the partial pair correlation and vertex (or direct correlation) functions in the MF approximation. \(C_{\text{MF,} \alpha_{1}\alpha_{2}}^{(2)} \{ \rho_{\alpha} \} (1, 2)\) is obtained readily from the expression (49)
\[
C_{\text{MF,} \alpha_{\beta}}^{(2)} (1, 2) = -G_{\text{MF,} \alpha_{\beta}}^{(2),T^{-1}} (1, 2) = C_{\text{RS,} \alpha_{\beta}}^{(2)} (1, 2) - w_{\alpha\beta} (1, 2),
\]
where \(C_{\text{RS,} \alpha_{\beta}}^{(2)} (1, 2)\) means the exact two-point proper vertex of the RS fluid at the mean field density \(\rho_{\alpha}^{\text{MF}}\). The two-point vertex function \(C_{\text{MF,} \alpha_{\beta}}^{(2)}\) is connected to the usual direct correlation function of the theory of liquids \(c_{\text{MF,} \alpha_{\beta}} (1, 2)\)
\[
c_{\text{MF,} \alpha_{\beta}}^{(2)} (1, 2) = c_{\text{MF,} \alpha_{\beta}} (1, 2) - \frac{1}{\rho_{\alpha}(1)} \delta_{\alpha\beta}(1, 2).
\]
In order to calculate \(C_{\text{MF,} \alpha_{\beta}}^{(2),T} (1, 2)\) we start with equation
\[
C_{\text{MF,} \alpha_{\beta}}^{(2),T} (1, 2) = \frac{\partial \rho_{\alpha}^{\text{MF}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} (1)}{\partial \nu_{\beta}(2)} = \frac{\partial \rho_{\alpha}^{\text{RS}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} (1)}{\partial \nu_{\beta}(2)}.
\]
\(\rho_{\alpha}^{\text{RS}} \{ \nu_{\alpha} \} \) depends on \(\nu_{\alpha}\) directly but also through the mean field \(\mathbf{w}_{\alpha}\). Therefore, one has
\[
C_{\text{MF,} \alpha_{\beta}}^{(2),T} (1, 2) = \frac{\partial \rho_{\alpha}^{\text{RS}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} (1)}{\partial \nu_{\beta}(2)} \bigg|_{\mathbf{w}_{\alpha}} + \frac{\partial \rho_{\alpha}^{\text{RS}} \{ [\mathbf{v}_{\alpha} - i\mathbf{w}_{\alpha}] \} (1)}{\partial \mathbf{w}_{\alpha}(3)} \bigg|_{\nu_{\alpha}}
\]
\times \frac{\partial \mathbf{w}_{\gamma}(3)}{\partial \nu_{\beta}(2)}.
\]
Taking into account (44) and (50) we obtain finally
\[ G^{(2),T}_{\text{MF},\alpha\beta}(1, 2) = G^{(2),T}_{\text{RS},\alpha\beta}(1, 2) - \beta G^{(2),T}_{\text{MF},\alpha\gamma}(1, 3) w\gamma\delta(3, 4) G^{T}_{\text{RS},\delta\beta}(4, 2). \quad (52) \]

(52) can be rewritten in a matricial form as
\[ G^{(2),T}_{\text{MF}}(1, 2) = G^{(2),T}_{\text{RS}}(1, 2) - G^{(2),T}_{\text{MF}}(1, 3) w(3, 4) G^{(2),T}_{\text{RS}}(4, 2), \quad (53) \]
where \( G^{(2),T}_{\text{MF}}(i, j) \) denotes the matrix of elements \( G^{(2),T}_{\text{MF},\alpha\beta}(i, j) \) and \( w(i, j) \) that of elements \( \beta w_{\alpha\beta}(i, j) \). The formal solution of eq. (53) is then
\[ G^{(2),T}_{\text{MF}}(1, 2) = \left( 1 + w * G^{(2),T}_{\text{RS}} \right)^{-1} * G^{(2),T}_{\text{RS}}(1, 2), \quad (54) \]
where \( 1 = \delta_{\alpha\beta}\delta(1, 2) \) is the unit operator and the “*” denotes a convolution in space.

### 4.2 Beyond the MF approximation

In order to take into account fluctuations we present CVs \( \rho_{\alpha} \) and \( \omega_{\alpha} \) in the form:
\[ \rho_{\alpha}(1) = \overline{\rho}_{\alpha} + \delta\rho_{\alpha}(1), \quad \omega_{\alpha}(1) = \overline{\omega}_{\alpha} + \delta\omega_{\alpha}(1), \]
where the quantities with a bar are given by (44).

The function \( \ln \Xi_{\text{RS}}[\{\overline{\rho}_{\alpha}; -i\omega_{\alpha}\}] \) in (44) can be presented in the form of the cumulant expansion
\[ \ln \Xi_{\text{RS}}[\{\overline{\rho}_{\alpha} - i\omega_{\alpha}\}] = \sum_{n \geq 1} (-i)^{n} \sum_{\alpha_{1}, \ldots, \alpha_{n}} \int d1 \ldots d n \times \mathcal{M}_{\alpha_{1}, \ldots, \alpha_{n}}(1, \ldots, n) \delta\omega_{\alpha_{1}}(1) \ldots \delta\omega_{\alpha_{n}}(n), \quad (55) \]
where \( \mathcal{M}_{\alpha_{1}, \ldots, \alpha_{n}}(1, \ldots, n) \) is the \( n \)th cumulant defined by
\[ \mathcal{M}_{\alpha_{1}, \ldots, \alpha_{n}}(1, \ldots, n) = \frac{1}{(-i)^{n}} \frac{\partial^{n} \ln \Xi_{\text{RS}}[\{\overline{\rho}_{\alpha} - i\omega_{\alpha}\}]}{\partial \delta\omega_{\alpha_{1}}(1) \ldots \partial \delta\omega_{\alpha_{n}}(n)} \bigg|_{\delta\omega_{\alpha_{1}} = 0}. \quad (56) \]

As is seen from (56) and (25), the \( n \)th cumulant is equal to the \( n \)-particle partial truncated (connected) correlation function at \( \omega_{\alpha} = \overline{\omega}_{\alpha} \). The expressions for the several cumulants given in the Cartesian coordinate phase space are as follows
\[ \mathcal{M}_{\alpha_{1}}(1) = \rho_{\alpha_{1}}(1), \quad (57) \]
\[ \mathcal{M}_{\alpha_{1}\alpha_{2}}(1, 2) = \rho_{\alpha_{1}}(1) \rho_{\alpha_{2}}(2) h_{\alpha_{1}\alpha_{2}}(1, 2) + \rho_{\alpha_{1}}(1) \delta_{\alpha_{1}\alpha_{2}} \delta(1, 2), \quad (58) \]
\[ \mathcal{M}_{\alpha_{1}\alpha_{2}\alpha_{3}}(1, 2, 3) = \rho_{\alpha_{1}}(1) \rho_{\alpha_{2}}(2) \rho_{\alpha_{3}}(3) h_{\alpha_{1}\alpha_{2}\alpha_{3}}(1, 2, 3) \]
\[ + \rho_{\alpha_{1}}(1) \rho_{\alpha_{2}}(2) h_{\alpha_{1}\alpha_{2}}(1, 2) \delta_{\alpha_{1}\alpha_{2}} \delta(1, 3) \]
\[ + \rho_{\alpha_{1}}(1) \rho_{\alpha_{3}}(3) h_{\alpha_{1}\alpha_{3}}(1, 3) \delta_{\alpha_{1}\alpha_{3}} \delta(1, 2) \]
\[ + \rho_{\alpha_{2}}(2) \rho_{\alpha_{3}}(3) h_{\alpha_{2}\alpha_{3}}(2, 3) \delta_{\alpha_{2}\alpha_{3}} \delta(1, 2) \]
\[ + \rho_{\alpha_{1}}(1) \delta_{\alpha_{1}\alpha_{2}} \delta_{\alpha_{1}\alpha_{3}} \delta(1, 2) \delta(1, 3), \quad (59) \]
\[ \mathcal{M}_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(1, 2, 3, 4) = \rho_{\alpha_1}(1)\rho_{\alpha_2}(2)\rho_{\alpha_3}(3)\rho_{\alpha_4}(4) h_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(1, 2, 3, 4) + \sum_{i,j,k,l} \rho_{\alpha_i}(i)\rho_{\alpha_j}(j)\rho_{\alpha_k}(k) h_{\alpha_i \alpha_j \alpha_k}(i, j, k) \times \delta_{\alpha_i \alpha_j} \delta(i, l) + \sum_{i,j,k,l} \rho_{\alpha_i}(i)\rho_{\alpha_k}(k) h_{\alpha_i \alpha_k}(i, k) \times \delta_{\alpha_i \alpha_k} \delta(i, l) + \sum_{i,j,k,l} \rho_{\alpha_i}(i)\rho_{\alpha_l}(l) \times \delta_{\alpha_i \alpha_l} \delta(i, l) + \sum_{i,j,k,l} \rho_{\alpha_i}(i) \delta_{\alpha_i \alpha_k} \delta(i, k) + \rho_{\alpha_1}(1) \times \delta_{\alpha_1 \alpha_2} \delta_{\alpha_1 \alpha_3} \delta_{\alpha_1 \alpha_4} \delta(1, 2) \delta(1, 3) \delta(1, 4). \] (60)

In the above formulas \( \rho_{\alpha_i}(i) \) is the local density of the \( \alpha_i \)th species in the RS and \( h_{\alpha_1 \ldots \alpha_n}(1, \ldots, n) \) is the \( n \)-particle partial correlation function of a \( m \)-component RS, defined in the GC ensemble (see eqs. \[28]-\[29]\):

\[
\begin{align*}
    h_{\alpha_1 \alpha_2}(1, 2) &= g_{\alpha_1 \alpha_2}(1, 2) - g_{\alpha_1}(1) g_{\alpha_2}(2), \\
    h_{\alpha_1 \alpha_2 \alpha_3}(1, 2, 3) &= g_{\alpha_1 \alpha_2 \alpha_3}(1, 2, 3) - g_{\alpha_1 \alpha_2}(1, 2) g_{\alpha_3}(3)
    - g_{\alpha_1 \alpha_3}(1, 3) g_{\alpha_2}(2) - g_{\alpha_2 \alpha_3}(2, 3) g_{\alpha_1}(1)
    + 2 g_{\alpha_1}(1) g_{\alpha_2}(2) g_{\alpha_3}(3), \\
    h_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(1, 2, 3, 4) &= g_{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(1, 2, 3, 4) - \ldots. \quad (61)
\end{align*}
\]

In the case of a homogeneous system a Fourier image of the \( n \)th cumulant can be presented in the form

\[
\mathcal{M}_{\alpha_1 \ldots \alpha_n}(k_1, \ldots, k_n) = (\langle N_{\alpha_1} \rangle, \ldots, \langle N_{\alpha_n} \rangle)^{1/n} S_{\alpha_1 \ldots \alpha_n}(k_1, \ldots, k_n) \times \delta_{k_1 + \ldots + k_n}. \quad (62)
\]

where \( S_{\alpha_1 \ldots \alpha_n}(k_1, \ldots, k_n) \) is the \( n \)-particle partial structure factor of the RS. Substituting (55) in (13) one can obtain

\[
\Xi[\{\nu_\alpha\}] = \Xi_{\text{RS}} [\{\varpi_\alpha - i\varpi_\alpha\}] \int \mathcal{D}\delta\rho\mathcal{D}\delta\omega \exp \left\{ -\frac{\beta}{2} \langle \delta\rho_\alpha w_{\alpha\beta} | \delta\rho_\beta \rangle \right\}
+i \langle \delta\omega_\alpha | \delta\rho_\alpha \rangle + \sum_{n \geq 2} \frac{(-i)^n}{n!} \sum_{\alpha_1, \ldots, \alpha_n} \int d1 \ldots \int dn \times \mathcal{M}_{\alpha_1 \ldots \alpha_n}(1, \ldots, n) \delta\omega_\alpha(1) \ldots \delta\omega_\alpha(n) \right\}. \quad (63)
\]

Integrating in (63) over \( \delta\omega_\alpha(i) \) we have in the homogeneous case

\[
\Xi[\{\nu_\alpha\}] = \Xi_{\text{MF}} \Xi' \int (d\delta\rho) \exp \left\{ -\frac{1}{2!} \sum_{\alpha, \beta} \sum_k L_{\alpha\beta}(k) \delta\rho_{k,\alpha} \delta\rho_{-k,\beta} \right. \left. + \sum_{n \geq 3} \mathcal{H}_n(\delta\rho_\alpha) \right\}. \quad (64)
\]
Gaussian approximation. In the Gaussian approximation, which corresponds to taking into account in (64) only the terms with \( n \leq 2 \) (\( \mathcal{H}_n \equiv 0 \)), we have \( L_{\alpha\beta}(k) = C_{\alpha\beta}(k) \), where \( C_{\alpha\beta}(k) \) are the Fourier transforms of the partial direct correlation functions. After integrating in (64) we arrive at the GPF of a \( m \)-component system in the random phase approximation (RPA).

Using the Gaussian averages one can develop a loop expansion of \( \Xi[\{\nu_{\alpha}\}] \) in the CV representation as it was done recently for a one-component fluid [13].

5 Conclusion

Using the CV method we have reconsidered the basic relations of statistical field theory of a multicomponent non-homogeneous fluids that follow from this approach. In contrary to the KSSHE theory [12] the corresponding CV action depends on two sets scalar fields - field \( \rho_{\alpha} \) connected to the number density of the \( \alpha \)th species particles and field \( \omega_{\alpha} \) conjugate to \( \rho_{\alpha} \). We derive the explicit expressions for the CV field correlations and obtain their relation to the density correlation functions of a multicomponent system.

Contrary to the theories based on the Stratonovich-Hubbard transformation [2, 3], the CV representation has some important advantages which could be very useful for more complicate models of fluids. In particular, it is valid for an arbitrary pair potential (including a pair interaction \( w_{\alpha\beta}(1,2) \) which does not possess an inverse) and is easily generalized for the case of \( n \)-body interparticle interactions with \( n > 2 \).

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