
CALCULATION OF PAIR CORRELATION FUNCTIONS FOR MULTICOMPONENT LIQUIDS WITH REGARD FOR THE ANOMALOUS DIMENSION INDEX

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We have considered a multicomponent liquid system, for which the pair correlation functions of density fluctuations are calculated. These functions are calculated in the approximation of anomalous dimension, which allows us to obtain the expressions for correlation functions of the scaling type, i.e., such that correspond to the positions of the theory of scaling invariance. The expressions obtained become simpler in the case where a system is at a close vicinity of the critical state. It is shown that then all correlation functions are described by a single general expression, whose structure is similar to that of the pair correlation function of a one-component system.

the task to find a pair correlation function from this equation is not so simple. As a rule, one uses certain approximations and estimates.

2. One-component Liquids

It is known that, for a wide class of liquid systems, the correlative behavior is universal in the sense that is weakly dependent on a specific form of the intermolecular interaction potential. The main thing consists in that such an interaction should be short-range. For a direct correlation function, this gives the basis to use the so-called two-moment approximation which is reduced to the expansion of the direct correlation function in the Fourier-space in a series in the wave vector [2, 4]:

1. Introduction

The Ornstein–Zernike equation (OZ) gives the zero value for the critical index of anomalous dimension η . In many cases, such a situation is quite suitable. On the other hand, the problem of the calculation of the expressions for pair correlation functions such that they would satisfy the postulates of the theory of scaling invariance [1] is rather urgent.

The OZ integral equation for one-component systems connects the pair $g(r)$ and direct $f(r)$ correlation functions [2]:

$$g(r) = f(r) + \int f(r_1)g(|\vec{r} - \vec{r}_1|)dV. \quad (1)$$

Here, both the pair and direct correlation functions are normed to the local density [3]. However, since the exact expression for the pair correlation function is unknown,

$$f(q) = C_0 - C_2q^2. \quad (2)$$

Here, the following designations for the spatial moments of the direct correlation function are introduced:

$$C_n = \frac{1}{(n+1)!} \int f(r)r^n dV, \quad (3)$$

and the index $n = 0, 2$. Then we get the pair correlation function as

$$g(r) = \frac{C_0 \exp(-\kappa r)}{4\pi C_2 r}, \quad (4)$$

where $\kappa^2 = (1 - C_0)/C_2$. It is the asymptotic formula for the pair correlation function describing the correlations at great distances. However, the problem is related to

the fact that the second spatial moment of a direct correlation function exists not in all the cases. In addition, at the critical point where $\kappa = 0$, we have the asymptotics $g(r) \sim 1/r$ for the pair correlation function instead of the scaling expression $g(r) \sim 1/r^{1+\eta}$ (see, e.g., [1, 5, 6]). Though the critical index of anomalous dimension η for three-dimensional systems is quite insignificant (of the order of 0.034 [5, 6]), such a disagreement creates inconveniences for the interpretation of data in some cases.

To eliminate the problem, we use a more general approximation for the direct correlation function as compared with formula (2). In particular, in studies of the critical behavior of liquids, the nonanalyticity of functional dependences which describe the state or characteristics of a system is usually assumed [1, 2]. Here, we assume the nonanalyticity of the dependence of a direct correlation function on the wave vector and write an approximation for the direct correlation function in the form

$$f(q) = C_0 - Dq^{2-\eta}, \tag{5}$$

where the coefficient D can be defined as the second spatial moment of the function $\phi(r)$,

$$D = \frac{1}{6} \int \phi(r)r^2 dV, \tag{6}$$

and the Fourier transform of the function $\phi(q)$ is related to the Fourier transform of the direct correlation function $f(q)$ by the formula

$$\phi(q) = (f(q) - C_0)q^\eta. \tag{7}$$

In this case, the correlation function $G(r) = g(r) + \delta(r)$ in the Fourier-space reads

$$G(q) = \frac{1}{1 - f(q)} = \frac{1}{D(\xi^2 + q^{2-\eta})}, \tag{8}$$

where the parameter $\xi^2 = (1 - C_0)/D$ is introduced. By performing the inverse Fourier transformation for the pair correlation function, we obtain

$$G(r) = \frac{C_0}{2\pi^2 D r^{1+\eta}} \int_0^\infty \frac{z \sin(z) dz}{z^{2-\eta} + \xi^2 r^{2-\eta}}. \tag{9}$$

Let us study the function $I(\eta)$ set by the integral

$$I(\eta) = \int_0^\infty \frac{z \sin(z) dz}{z^{2-\eta} + \xi^2 r^{2-\eta}}. \tag{10}$$

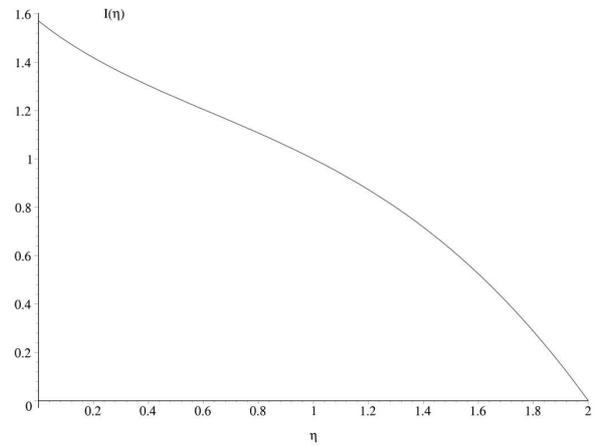


Fig. 1. Dependence of the integral $I(\eta)$ on the critical index of anomalous dimension η at $\xi = 0$

In the limiting case where $\eta = 0$, we have

$$I(\eta = 0) = \int_0^\infty \frac{z \sin(z) dz}{z^2 + \xi^2 r^2} = \frac{\pi \exp(-\xi r)}{2}. \tag{11}$$

In this case, it should be remember that the parameter ξ is also a function of the critical index η . In the first turn, we are interested in the critical state of the system which corresponds to the value $\xi = 0$. In this case, we get

$$I(\eta) = \int_0^\infty \frac{\sin(z) dz}{z^{1-\eta}} = \frac{\sqrt{\pi} \Gamma(\frac{1+\eta}{2})}{2^{1-\eta} \Gamma(1 - \frac{\eta}{2})}. \tag{12}$$

The dependence of the corresponding integral on the critical index of anomalous dimension is presented in Fig. 1.

For the zero critical index, $I(\eta = 0) \approx 1.57$, whereas $I(\eta = 0.034) \approx 1.54$. Thus, the difference is of the order of 0.03, which means the error in the limits of 1.94%. In Fig. 2, we show how the mentioned integral depends on both the closeness of the system to the critical state and the distance r (the closeness to the critical state is determined by the parameter ξ).

If we set the critical index of anomalous dimension to be equal to zero, the dependence of the integral on the parameters ξ and r is almost invariable qualitatively. The error which is introduced in this case can be estimated by Fig. 3, where it is shown how the relation $I(\eta = 0.034)/I(\eta = 0)$ depends on ξ and r .

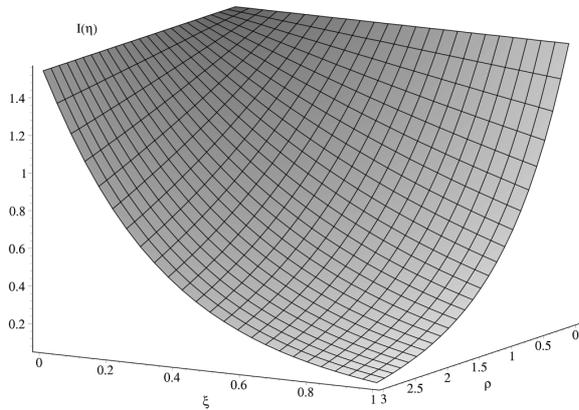


Fig. 2. Dependence of the integral $I(\eta = 0.034)$ on the parameters ξ and r

It is close to 1 in a wide range of values of the parameters ξ and r . This allows us, while calculating the integral in formula (9), to set $\eta = 0$. Then, for the pair correlation function of a one-component system, we can write

$$G(r) = \frac{C_0 \exp(-\xi r)}{4\pi D r^{1+\eta}}. \tag{13}$$

This formula gives the proper asymptotics $G(r) \sim 1/r^{1+\eta}$ for the pair correlation function at the critical point ($\xi = 0$). A consequence of such a result would be the assertion about the adequacy of the initial approximation (5) for the direct correlation function.

3. Multicomponent Liquids

In a natural way, we are faced with the question about the calculation of the pair correlation functions of a system which includes an arbitrary number of components. For the Fourier transform of the matrix $\hat{f}(q)$ of direct correlation functions $f_{ij}(q)$ ($i, j = 1, 2, \dots, N$, where N is the number of components in a mixture), it is logical, with regard for the above-presented discussion, to set

$$\hat{f}(q) = \hat{A} - \hat{D}q^{2-\eta}, \tag{14}$$

where the matrix \hat{A} of zero spatial moments of the direct correlation functions is determined by the relation

$$\hat{A} = \int \hat{f}(r) dV. \tag{15}$$

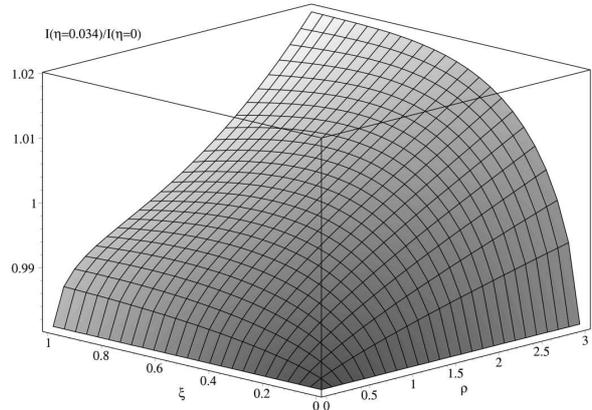


Fig. 3. Dependence of the relation $I(\eta = 0.034)/I(\eta = 0)$ on the parameters ξ and r

As for the matrix \hat{D} , we can write

$$\hat{D} = \frac{1}{6} \int \hat{\phi}(r) r^2 dV, \tag{16}$$

where we denote

$$\hat{\phi}(q) = (\hat{f}(q) - \hat{A})q^\eta. \tag{17}$$

In the limiting case where $\eta = 0$, the matrix \hat{D} coincides with the matrix of spatial second-order moments for direct correlation functions.

In the matrix form, the OZ equation for the multicomponent system has the form

$$\hat{G}(r) = \hat{E}\delta(r) + \int \hat{f}(r_1)\hat{G}(|\vec{r} - \vec{r}_1|)dV_1, \tag{18}$$

where \hat{E} is the identity matrix of rank N . Using this equation, the Fourier transform of the matrix of pair correlation functions can be expressed in terms of the Fourier transform of the matrix of direct correlation functions as follows:

$$\hat{G}(q) = (\hat{E} - \hat{f}(q))^{-1}. \tag{19}$$

By using approximation (14) and the method of spectral decomposition of the inverse matrix [3], we obtain the matrix of pair correlation functions in the following form:

$$\hat{G}(q) = \sum_{k=1}^N \frac{\hat{S}_k}{q^{2-\eta} + \xi_k^2}. \tag{20}$$

Here, the matrices of spectral decomposition \hat{S}_k are determined by the relations

$$\hat{S}_k = \hat{D}^{-1} \prod_{i=1, i \neq k}^N \frac{\hat{E}\xi_i^2 - \hat{A}}{\xi_i^2 - \xi_k^2}, \tag{21}$$

and the parameters ξ_k^2 are the eigenvalues of the matrix

$$\hat{\Lambda} = \hat{D}^{-1}(\hat{E} - \hat{A}). \tag{22}$$

Then, in the r -space, the matrix of pair correlation functions takes the following form:

$$\hat{G}(r) = \frac{1}{4\pi r^{1+\eta}} \sum_{k=1}^N \hat{S}_k \exp(-\xi_k r). \tag{23}$$

In the limiting case of the zero index of anomalous dimension $\eta = 0$, this formula coincides, incidentally, with the expression for pair correlation functions of a multicomponent system obtained in the approximation of two spatial moments [3].

4. Limiting Cases

Thus, the structure of pair correlation functions is fixed: it is a linear combination of functions of the form

$$\Phi_k(r) = \frac{\exp(-\xi_k r)}{r^{1+\eta}}. \tag{24}$$

The correlative behavior of the system is determined by the collection of eigenvalues ξ_k^2 ($k = 1, 2, \dots, N$). The behavior of the system is qualitatively changed if one of these eigenvalues tends to zero. In this case, the term corresponding to the eigenvalue ξ^2 close to zero will be dominant. Therefore, we can consider, on the one hand,

$$G_{ij} \sim \frac{\exp(-\xi r)}{r^{1+\eta}} \tag{25}$$

for all $i, j = 1, 2, \dots, N$. But, on the other hand, this corresponds to the situation where a solution for pair correlation functions should be sought in the form $\hat{G}(r) = \hat{U}h(r)$, where $h(r)$ is the unknown scalar function, and the matrix \hat{U} is the matrix of coefficients. It follows from the OZ matrix equation for the functions $\hat{G}(r)$ and $\hat{F}(r) = \hat{f}(r) - \hat{E}\delta(r)$,

$$\int \hat{F}(r_1) \hat{G}(|\vec{r} - \vec{r}_1|) dV_1 = -\hat{E}\delta(r), \tag{26}$$

that $\hat{F}(r) = \hat{U}^{-1}C(r)$. Moreover, for the scalar functions $h(r)$ and $C(r)$, we obtain an equation of the OZ type,

$$\int C(r_1) h(|\vec{r} - \vec{r}_1|) dV_1 = -\delta(r). \tag{27}$$

Whence, for the Fourier transform of the pair correlation function $h(q)$, we get

$$h(q) = \frac{1}{C(q)} = \frac{1}{\varepsilon^2 + q^{2-\eta}} \tag{28}$$

under the initial assumption for the direct correlation function:

$$C(q) \approx -(\varepsilon^2 + q^{2-\eta}). \tag{29}$$

The parameter ε^2 and the matrix \hat{U} are determined from the following relations:

$$\hat{U} = \hat{D}^{-1}, \tag{30}$$

$$\varepsilon^2 \hat{E} = \hat{D}^{-1}(\hat{E} - \hat{A}). \tag{31}$$

Moreover, if relation (30) is correct under the condition of nondegeneracy of the matrix \hat{D} , then Eq. (31) has a solution by no means in all the cases. In view of the above-obtained results, we have reasons to assume that such a solution arises while the system approaches the critical state.

5. Discussion and Conclusions

Thus, we have obtained the formulas for pair correlation functions of a multicomponent liquid which correspond to the positions of the theory of scaling invariance. Several points which are of importance from the viewpoint of the derivation of the mentioned result should be emphasized.

First, as a foundation, we took the special approximation for direct correlation functions. This approximation is a consequence of the well-known asymptotics for the pair correlation function of a one-component system. Thus, the general formula for pair correlation functions of the multicomponent system is a consequence of the relevant expression for a one-component system. This consequence is not trivial and occurs by no means for every form of a direct correlation function.

Second, in a close vicinity of the critical state, all the correlation functions of the multicomponent system are described by a single function, which agrees quite well with predictions of the hypothesis of the isomorphism of critical phenomena [5, 7, 8]. In addition, the system can be described in such a case by an equation of the OZ type, like for a one-component system.

The formulas for pair correlation functions are obtained, as was mentioned above, in the approximation of anomalous dimension. As distinct from the relevant expressions obtained in the approximation of two spatial moments of the direct correlation function [3], there

exists the possibility, in this case, to take the nonzero critical index of anomalous dimension into account. From the practical viewpoint, it is quite sufficient to use the two-moment approximation in the analysis and the processing of experimental data [9–11]. But the formulas in the approximation of anomalous dimension are more general. In the limiting case of the zero critical index, the pair correlation functions obtained by us coincide with pair correlation functions constructed in the approximation of two spatial moments [3].

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РОЗРАХУНОК ПАРНИХ КОРЕЛЯЦІЙНИХ ФУНКЦІЙ БАГАТОКОМПОНЕНТНОЇ РІДИНИ З УРАХУВАННЯМ ІНДЕКСУ АНОМАЛЬНОЇ РОЗМІРНОСТІ

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Резюме

Розглядається багатокомпонентна рідка система, для якої розраховуються парні кореляційні функції флуктуацій густини. Функції розраховуються в наближенні аномальної розмірності, що дозволяє отримати вирази для кореляційних функцій скейлінгового типу, тобто таких, що відповідають положенням теорії масштабної інваріантності. Отримані вирази спрощуються для випадку, коли система перебуває в малому околі критичного стану. Показано, що тоді всі кореляційні функції описуються єдиним загальним виразом, який подібний за своєю структурою до парної кореляційної функції однокомпонентної системи.