

NONSINGULAR EXPRESSIONS FOR PAIR CORRELATION FUNCTIONS OF A FINITE-SIZE MULTICOMPONENT LIQUID SYSTEM

A.N. VASIL'EV, A.V. CHALYI

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Taras Shevchenko Kyiv National University, Faculty of Physics
(6, Academician Glushkov Ave., Kyiv 03022, Ukraine; e-mail: vasilev@univ.kiev.ua)

The method that allows one to find nonsingular expressions for the pair correlation functions of a finite-size multicomponent liquid system has been proposed. The system with the geometry of a plane-parallel layer has been considered as an example. For this system, we find the asymptotic expressions for the pair correlation functions of density fluctuations and then we use a special iteration procedure to get the next approximation for them. These expressions do not involve singularities at the zero point, in contrast to the asymptotic ones.

1. Introduction

The study of liquid systems in the framework of statistical methods faces a number of difficulties of principal character. Nontrivial is the problem of studying even the simplest systems, to say nothing of multicomponent liquids [1–8]. Important system characteristics can be calculated knowing the pair correlation functions of density fluctuations of the liquid components [9, 10]. Unfortunately, the straightforward calculation of correlation functions is rather a difficult and laborious task. One of the consistent approaches to solve this problem comprises the use of the Ornstein–Zernike (OZ) system of integral equations [11]. The integral equations are reduced to differential ones, and the latter can be used to calculate the asymptotic expressions for the pair correlation functions [12] which describe correlations at large distances rather well (more precisely, they are valid in a linear approximation of the ε -expansion). Their essential shortcoming is their inadequacy at small distances. Moreover, the corresponding expressions have singularities at the zero point. It is its turn, this results in certain complications, especially when studying finite-size systems [13]. Therefore, challenging is the problem of calculating the expressions for the pair correlation functions which would behave more realistically at short distances as well. In this work, we seek for the expressions for the pair correlation functions of a finite-size multicomponent liquid system which would be regular at the zero point.

The relevant method is based on an iterative procedure which has been proposed first for single-component unconfined systems [11] and afterwards extended and applied to binary finite- and non-finite-size mixtures [13].

2. Formulation of the Problem

The essence of the method used in this work can be explained as follows. First, the asymptotic solutions of the OZ system of differential equations are found. Further, these solutions are used in the OZ system of integral equations to find approximate solutions for the direct correlation functions of the system. At last, on the basis of the latter, the first approximation of the pair correlation functions is determined from the OZ system of differential equations. As was already mentioned, such a procedure was applied earlier when studying simpler systems [11, 13, 14]. In this paper, we consider, as an example, a finite-size N -component liquid system with the geometry of a plane-parallel layer of thickness $2L$.

The initial system of the OZ integral equations can be written down in the matrix form as follows:

$$\hat{G}(\vec{r}) = \hat{F}(\vec{r}) + \int \hat{F}(\vec{r}_1) \hat{G}(\vec{r} - \vec{r}_1) d\vec{r}_1. \quad (1)$$

In this equation, $\hat{G}(\vec{r})$ denotes the matrix of the pair correlation functions and $\hat{F}(\vec{r})$ stands for the matrix of direct correlation functions. These functions are normalized by densities and, in the case of a finite-size system, depend, strictly speaking, on two arguments. Here, for the sake of simplicity, we consider fluctuation correlations for the configuration, where one of the particles is situated in the layer middle-point. In this case, the correlation functions would depend on a single argument – the radius-vector of the second particle with respect to the first one. It should be noted that, provided the system is finite-size, the correlation functions even in such simple configuration would depend not only on the distance between particles but also on the direction of the radius-vector.

In the routine of applying the method, various approximations for the pair correlation functions were searched on the basis of the OZ differential equation which looks like

$$\Delta \hat{G}(\vec{r}) - \hat{C}_2^{-1}(\hat{I} - \hat{C}_0)\hat{G}(\vec{r}) = -\hat{C}_2^{-1}\hat{F}(\vec{r}). \quad (2)$$

The notation \hat{I} in this equation stands for the unity matrix of rank N . The equation also includes the matrices of the pair spatial moments of the direct correlation functions

$$\hat{C}_0 = \int \hat{F}(\vec{r}) d\vec{r}, \quad (3)$$

$$\hat{C}_2 = \frac{1}{6} \int \hat{F}(\vec{r}) r^2 d\vec{r}. \quad (4)$$

The OZ differential equation itself can be deduced from the OZ integral equation by expanding the pair correlation functions in their Taylor series [11]. The necessary condition in this case is the short-range character of the direct correlation functions. Therefore, the results obtained below can be applied only to liquids, in which the long-range order is absent, i.e. the intermolecular interaction potential is short-range for all the components.

While considering a finite-size system, it is necessary that the boundary conditions be determined at the surfaces that confine it. In particular, we assume that the correlation functions at each of the two surfaces that confine the layer are equal to zero. There are two reasons for this assumption. First, such conditions provide an opportunity for the system under consideration to be continuously transformed into the one unconfined in space. Secondly, the zero-value boundary conditions are the most convenient ones from the viewpoint of carrying out the experiment, because they affect the character of critical anomalies identically for the layers with various thicknesses. In addition, they are rather easy to be realized in practice [15].

3. Realization of the Method

Taking into account both the symmetry of the problem and the fact that the correlation functions are nullified at the system boundaries, we may present these functions in the form of Fourier series, namely,

$$\hat{G}(\rho, z) = \sum_{m=0}^{\infty} \hat{G}_m(\rho) \cos\left(\frac{(2m+1)\pi z}{2L}\right), \quad (5)$$

$$\hat{F}(\rho, z) = \sum_{m=0}^{\infty} \hat{F}_m(\rho) \cos\left(\frac{(2m+1)\pi z}{2L}\right). \quad (6)$$

Here, ρ is the component of the distance (absolute value) between the correlated particles (one of them is in the middle of the layer) in the layer plane, and z is the corresponding component in the perpendicular direction, i.e. in the direction perpendicular to the layer plane. In this case, the system of integral equations (1) for separate harmonics can be written down as

$$\hat{G}_m(\rho) = \hat{F}_m(\rho) + L \int \hat{F}_m(\rho_1) \hat{G}_m(|\vec{\rho} - \vec{\rho}_1|) d\vec{\rho}_1. \quad (7)$$

The OZ differential equation for various harmonics looks like

$$\begin{aligned} \Delta \hat{G}_m(\rho) - \left(\hat{I} \frac{\pi^2(2m+1)^2}{4L^2} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0)\right) \hat{G}_m(\rho) = \\ = -\hat{C}_2^{-1} \hat{F}_m(\rho). \end{aligned} \quad (8)$$

Asymptotic expressions for the pair correlation functions can be deduced from the OZ system of differential equations if one takes the direct correlation functions, in the zero-order approximation, to be proportional to the Dirac delta-function: $\hat{F}(\vec{r}) = \hat{C}_0 \delta(\vec{r})$ [12]. However, it should be noted that this assumption is not fundamental; but this technique allows the correct result to be obtained in the simplest way.

Having expanded the delta-function into its Fourier series, we obtain the equation in the matrix form, from which the asymptotic expressions for the pair correlation functions are determined immediately:

$$\begin{aligned} \Delta \hat{G}_m(\rho) - \left(\frac{\pi^2(2m+1)^2}{4L^2} \hat{I} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0)\right) \hat{G}_m(\rho) = \\ = -\hat{C}_2^{-1} \hat{C}_0 \frac{\delta(\vec{\rho})}{L}. \end{aligned} \quad (9)$$

After its Fourier-transforming in the layer plane, the equation reads

$$\begin{aligned} \left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2}) \hat{I} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0)\right) \hat{G}_m(q) = \\ = \hat{C}_2^{-1} \hat{C}_0 \frac{1}{L}. \end{aligned} \quad (10)$$

In this case, the Fourier-images of the pair correlation functions equal

$$\hat{G}_m(q) =$$

$$\left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2})\hat{I} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0) \right)^{-1} \frac{\hat{C}_2^{-1}\hat{C}_0}{L}. \quad (11)$$

The inverse matrix in Eq. (11) can be expressed in terms of the eigenvalues of the matrix $\hat{\Xi} = \hat{C}_2^{-1}(\hat{I} - \hat{C}_0)$. Let us designate them as ξ_i^2 ($i = 1, 2, \dots, N$). For the sake of simplicity, those eigenvalues will be considered positive and different from each other (this assumption does not affect the ultimate result qualitatively but simplifies substantially the analysis). Then, using the spectral expansion, we get

$$\begin{aligned} & \left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2})\hat{I} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0) \right)^{-1} = \\ & = \sum_{i=1}^N \frac{\hat{\gamma}_i}{q^2 + \xi_i^2 + \pi^2(m+1/2)^2/L^2}. \end{aligned} \quad (12)$$

The matrices of the spectral expansion are defined as

$$\hat{\gamma}_i = \prod_{\substack{k=1, \\ k \neq i}}^N \frac{\hat{I}\xi_k^2 - \hat{\Xi}}{\xi_k^2 - \xi_i^2} \quad (13)$$

with the relation

$$\sum_{i=1}^N \hat{\gamma}_i = \hat{I} \quad (14)$$

being valid for them. Expressions (11) and (12) can be used to restore the expressions for the pair correlation functions in the \vec{r} -space. However, we shall not make it at this stage. Instead, we shall use them to find the Fourier-image of the matrix of direct correlation functions on the basis of the OZ integral equation, the matrix form of which in the Fourier-space can be written down as follows:

$$\hat{F}_m(q) = \hat{G}_m(q)(\hat{I} + L\hat{G}_m(q))^{-1}. \quad (15)$$

Expression (11) is the zero-order, or asymptotic, approximation for the pair correlation functions. Taking this circumstance into account, the first approximation for the matrix of direct correlation functions can be obtained as

$$\hat{F}_m^{(1)}(q) = \left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2})\hat{I} + \hat{C}_2^{-1} \right)^{-1} \frac{\hat{C}_2^{-1}\hat{C}_0}{L}. \quad (16)$$

Now, having executed the Fourier transformation of the differential matrix equation (9), we find the first approximation for the matrix of pair correlation functions:

$$\begin{aligned} \hat{G}_m^{(1)}(q) = & \frac{1}{L} \left[\left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2})\hat{I} + \hat{C}_2^{-1}(\hat{I} - \hat{C}_0) \right)^{-1} - \right. \\ & \left. - \left((q^2 + \frac{\pi^2(2m+1)^2}{4L^2})\hat{I} + \hat{C}_2^{-1} \right)^{-1} \right] \hat{C}_2^{-1}. \end{aligned} \quad (17)$$

On the basis of expressions (11), (12), (16), and (17), one can find the pair and direct correlation functions in the \vec{r} -space in the first approximation. It should be noted that analogous formulae for binary systems similar to Eq. (17) have already been obtained earlier [13].

4. Expressions for Correlation Functions

In order to calculate the pair and direct correlation functions in the first approximation, it is necessary to know the eigenvalues κ_i^2 ($i = 1, 2, \dots, N$) of the matrix $\hat{\Xi} + \hat{C}_2^{-1}\hat{C}_0 = \hat{C}_2^{-1}$. Having executed the spectral expansion and the inverse Fourier transformation, we obtain the following expression for the harmonics of direct correlation functions:

$$\hat{F}_m^{(1)}(\rho) = \frac{\hat{C}_2^{-1}\hat{C}_0}{2\pi L} \sum_{i=1}^N \hat{\gamma}_i K_0 \left(\rho \sqrt{\kappa_i^2 + \frac{\pi^2(2m+1)^2}{4L^2}} \right), \quad (18)$$

where $K_0(u)$ is the Macdonald function of the zero order. The matrices of the spectral expansion $\hat{\gamma}_i$ are found by the relation

$$\hat{\gamma}_i = \prod_{\substack{k=1, \\ k \neq i}}^N \frac{\hat{I}\kappa_k^2 - \hat{C}_2^{-1}}{\kappa_k^2 - \kappa_i^2}. \quad (19)$$

Similarly to the $\hat{\gamma}_i$ matrices, the equality

$$\sum_{i=1}^N \hat{\gamma}_i = \hat{I} \quad (20)$$

is valid for the matrices of the spectral expansion $\hat{\gamma}_i$. Therefore, the expressions for the harmonics of pair correlation functions in the first approximation look like

$$\hat{G}_m^{(1)}(\rho) = \frac{\hat{C}_2^{-1}}{2\pi L} \sum_{i=1}^N \left[\hat{\gamma}_i K_0 \left(\rho \sqrt{\xi_i^2 + \frac{\pi^2(2m+1)^2}{4L^2}} \right) - \right.$$

$$-\hat{\eta}_i K_0 \left(\rho \sqrt{\kappa_i^2 + \frac{\pi^2(2m+1)^2}{4L^2}} \right) \Big]. \quad (21)$$

For comparison, the harmonics of the matrix of pair correlation functions in the zero-order approximation are determined by the expression

$$\hat{G}_m(\rho) = \frac{\hat{C}_2^{-1} \hat{C}_0}{2\pi L} \sum_{i=1}^N \hat{\eta}_i K_0 \left(\rho \sqrt{\xi_i^2 + \frac{\pi^2(2m+1)^2}{4L^2}} \right). \quad (22)$$

Though those presented results for the correlation functions in various approximations are cumbersome, they do allow a certain comparative analysis to be carried out.

5. Analysis of the Results and Conclusions

It is quite evident that the expressions for the pair correlation functions in the zero-order approximation and for the direct correlation functions in the first approximation possess a singularity at the zero point. The basic difference between them is the issue: which magnitudes do the corresponding eigenvalues, which are calculated from the spectral expansion of the inverse matrices, acquire while the system is approaching its critical state? This question is rather a non-trivial one and requires a separate research which is beyond the scope of this work. Nevertheless, it is worth noting that, from physical considerations, one may expect that the direct correlation functions would remain short-range even in this case. It was this assumption that was used while deriving the expressions for the correlation functions of the system in various approximations.

The absence of a singularity in the first approximation for the pair correlation functions is not so obvious. However, if one should take into account that the Macdonald functions have a logarithmic singularity at the zero point, and the sum of the matrices of the spectral expansion is equal to the unity matrix [see relations (14) and (20)], it is easy to verify that it is true.

To summarize, we draw attention to the fact that the properties of various approximations of the pair and direct correlation functions of the multicomponent system, which were considered above, coincide completely with those of the pair and direct correlation functions of single-component systems [11].

1. *Anisimov M.A.* Critical Phenomena in Liquids and Liquid Crystals. — Moscow: Nauka, 1987 (in Russian).
2. *Patashinskii A.Z., Pokrovskii V.L.* Fluctuation Theory of Phase Transitions. — Moscow: Nauka, 1982 (in Russian).
3. *Finite Size Scaling and Numerical Simulation of Statistical Systems.* / Ed. by V. Privman. — Singapore: World Scientific, 1990.
4. *Shang-Keng Ma.* Modern Theory of Critical Phenomena. — London: Benjamin, 1976.
5. *Wilding N.B.* // J. Phys. Cond. Matter. — 1997. — **9**. — P. 585–612.
6. *Yukhnovskii I.R.* Phase Transitions of the Second Kind. The Method of Collective Variables. — Kyiv, Naukova Dumka, 1985 (in Russian).
7. *Kovalenko N.P., Fisher I.Z.* // Zh. Fiz. Khim. — 1966. — **40**, N 3. — P. 649–656.
8. *Griffiths R.B., Wheeler J.C.* // Phys. Rev. A. — 1970. — **2**. — P. 1047 — 1064.
9. *Belloq A.M., Gazeau D.* // J. Phys. Chem. — 1990. — **94**, N 26. — P. 8933–8938.
10. *Formisano F., Teixeira J.* // Eur. Phys. J. E. — 2000. — **1**. — P. 1–4.
11. *Münster A.* // Thermodynamics of Irreversible Processes. Proceedings of the International School of Physics “Enrico Fermi”, Course X / Ed. by S.R. de Groot. — Bologna: Zanichelli, 1960. — P. 23.
12. *Vasil’ev A.* // Teor. Mat. Fiz. — 2003. — **135**, N 2. — P. 315–321.
13. *Chalyi A.V. et al.* // Cond. Matter Phys. — 2000. — **3**, N 2. — P. 335–358.
14. *Chalyi A.V., Vasil’ev A.N.* // J. Mol. Phys. — 2000. — **84**. — P. 203–213.
15. *Vasyly’ev O.M.* // Zh. Fiz. Dosl. — 2003. — **7**, N 4. — P. 387–392.

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НЕСИНГУЛЯРНІ ВИРАЗИ ДЛЯ ПАРНИХ КОРЕЛЯЦІЙНИХ ФУНКЦІЙ ПРОСТОРОВО ОБМЕЖЕНОЇ БАГАТОКОМПОНЕНТНОЇ РІДКОЇ СИСТЕМИ

О.М. Васильєв, О.В. Чалий

Резюме

Запропоновано метод, що дозволяє знаходити несингулярні вирази для парних кореляційних функцій просторово обмеженої багатокомпонентної рідкої системи. Як приклад розглянуто просторово обмежену багатокомпонентну рідку систему з геометрією плоского паралельного прошарку. Для такої системи знайдено асимптотичні вирази для парних кореляційних функцій флуктуацій густини, після чого їх було уточнено за допомогою спеціальної ітераційної процедури. Ці вирази, на відміну від асимптотичних, не містять особливостей в нулі.