

# PAIR CORRELATION FUNCTIONS AND CRITICAL PARAMETERS OF FINITE-SIZE MULTICOMPONENT LIQUID SYSTEM

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We consider pair correlations in a liquid multicomponent finite-size system with the geometry of a plane-parallel layer. For this system, we find the general expressions for the pair correlation functions of density fluctuations. We also investigate the influence of a space limitation on the correlative behavior of the system at the critical region. The results are compared with those that exist for binary and pure liquids, and their applicability is briefly discussed.

developed for the general case of a liquid with  $N$  components in [17] and in the pioneering work [18]. These results are in the core of the isomorphism hypothesis [6] that is, in turn, a very productive method for studying the complex liquid systems. Nevertheless, the information about the density (concentration) fluctuation correlations in multicomponent systems, mostly confined, is limited.

## 1. Introduction

This paper is devoted to the investigation of a multicomponent finite-size liquid with the geometry of a plane-parallel layer. Namely here, we find the pair correlation functions of density fluctuations, simplify these expressions in the case where the system is at the close vicinity of the critical state, and then make some predictions about the critical parameters of a finite-size multicomponent system. It is necessary to accentuate that this problem has not been investigated well enough so far, meanwhile some interesting data were received in investigating the multiphase behavior and equilibrium state [1, 2] and predicting the critical points [3].

On the other hand, the significant results were obtained [4, 5] in studying the critical phenomena and phase transitions in the recent years, especially for one-component and binary liquids [6, 7], simple ferromagnets [8] and so on. There is also a set of results allowing us to conclude that the liquid-liquid phase separation in multicomponent systems is relevant to the Ising model [6, 9]. A great progress was made in studying the critical phenomena and phase transitions in finite-size systems as well [10–15]. For these purposes, the finite-size scaling techniques were developed (see, as a review, [15]). Many interesting results were obtained for confined liquid mixtures by combining a number of methods and approaches [14–16].

The theoretical analysis of critical phenomena and statistical properties for multicomponent liquid systems is based mainly on the geometric approach that was

## 2. Correlation Functions

To find the pair correlation functions of density fluctuations, we use the Ornstein–Zernike (OZ) system of integral equations

$$G_{ij}(\vec{r}_1, \vec{r}_2) = F_{ij}(\vec{r}_1, \vec{r}_2) + \sum_{k=1}^N \langle \rho_k \rangle \int F_{ik}(\vec{r}_1, \vec{r}_3) G_{kj}(\vec{r}_3, \vec{r}_2) d\vec{r}_3. \quad (1)$$

Here,  $G_{ij}(\vec{r}_1, \vec{r}_2)$  and  $F_{ij}(\vec{r}_1, \vec{r}_2)$  are the pair and direct correlation functions of density fluctuations related to the components of numbers  $i$  and  $j$  ( $i, j = 1..N$ ). They depend on the position  $\vec{r}_1$  and  $\vec{r}_2$  of correlating points. The number of components is  $N$ , and  $\langle \rho_k \rangle$  is the average density of the component with index  $k$ . The integration has to be made over the volume of the system.

To simplify a further analysis, we assume that one particle is placed at the middle of the layer, i.e. we consider correlations in respect to the middle point of the system. In this case, correlation functions have one argument only. Moreover, we normalize the correlation functions with respect to the densities as follows:

$$G_{ij}(\vec{r}) = \frac{g_{ij}(\vec{r})}{\sqrt{\langle \rho_i \rangle \langle \rho_j \rangle}}, \quad (2)$$

$$F_{ij}(\vec{r}) = \frac{f_{ij}(\vec{r})}{\sqrt{\langle \rho_i \rangle \langle \rho_j \rangle}}. \quad (3)$$

Then Eq. (1) can be presented as a matrix integral equation [19, 20]. Namely, we have

$$\hat{g}(\vec{r}) = \hat{f}(\vec{r}) + \int \hat{f}(\vec{r}_*) \hat{g}(\vec{r} - \vec{r}_*) d\vec{r}_*. \quad (4)$$

In Eq. (4), elements of the matrices  $\hat{g}(\vec{r})$  and  $\hat{f}(\vec{r})$  (their rank is  $N$ ) are the pair  $g_{ij}(\vec{r})$  and direct  $f_{ij}(\vec{r})$  correlation functions, respectively.

We consider a system with short-range interactions. For such a kind of systems, the direct correlations are localized in small (in comparison with the correlation length and linear size of the system) regions. So, we can make integration over the localization region of direct correlation functions. This allows us, in turn, to transform the integral equation (4) to a differential equation [19, 20]. Making the Taylor expansion for the pair correlation functions, we get

$$\hat{g}(\vec{r}) = \hat{f}(\vec{r}) + \hat{A}\hat{g}(\vec{r}) + \hat{B}\nabla^2\hat{g}(\vec{r}), \quad (5)$$

where the following spatial moments of the direct correlation functions were used:

$$\hat{A} = \int \hat{f}(\vec{r}) d\vec{r}, \quad (6)$$

$$\hat{B} = \frac{1}{6} \int \hat{f}(\vec{r}) r^2 d\vec{r}. \quad (7)$$

Let  $2h$  be the layer thickness. We direct the  $z$ -axis perpendicularly to the layer in such a way that the  $z$ -coordinate changes from  $-h$  to  $h$ . We consider the zero boundary conditions to satisfy the limiting transition to the infinite system (when  $h \rightarrow \infty$ ). So we can present the correlation functions as follows:

$$\hat{g}(\rho, z) = \sum_{n=0}^{\infty} \hat{g}^{(n)}(\rho) \cos\left(\frac{\pi(2n+1)z}{2h}\right), \quad (8)$$

$$\hat{f}(\rho, z) = \sum_{n=0}^{\infty} \hat{f}^{(n)}(\rho) \cos\left(\frac{\pi(2n+1)z}{2h}\right). \quad (9)$$

This yields the next equation for the harmonics of correlation functions:

$$\hat{g}^{(n)}(\rho) = \hat{f}^{(n)}(\rho) + \left(\hat{A} - \frac{\pi^2(2n+1)^2}{4h^2}\hat{B}\right)\hat{g}^{(n)}(\rho) + \hat{B}\nabla_{\rho}^2\hat{g}^{(n)}(\rho). \quad (10)$$

Lastly, after the Fourier transformation, we have

$$\left(\hat{E}q^2 + \frac{\pi^2(2n+1)^2}{4h^2}\hat{E} + \hat{\Lambda}\right)\hat{g}^{(n)}(q) = \hat{B}^{-1}\hat{f}^{(n)}(q), \quad (11)$$

where  $\hat{E}$  is the unit matrix and  $\hat{\Lambda} = \hat{B}^{-1}(\hat{E} - \hat{A})$ . To find the asymptotic expressions for pair correlation functions, we have to know direct correlation functions. Nevertheless, we can use the same two-moment approximation that was used above while deriving the differential equation. Namely, we could assume that  $\hat{f}(q) = \hat{A} - \hat{B}q^2$  for a spatially infinite system. But it is easy to show that, in this case, the second term with  $q^2$  yields the Dirac delta-function only in the  $\vec{r}$ -space in the final expression. So we can take an expression for the matrix of direct correlation functions like  $\hat{f}(q) = \hat{A}$  that means, in turn,  $\hat{f}(\vec{r}) = \hat{A}\delta(\vec{r})$ . This approximation was used in [20] while finding the correlation functions for a binary mixture. So we have  $\hat{f}^{(n)}(\rho) = \delta(\rho)\hat{A}/h$ . Then Eq. (11) yields

$$\hat{q}^{(n)}(q) = \left(\hat{E}q^2 + \frac{\pi^2(2n+1)^2}{4h^2}\hat{E} + \hat{\Lambda}\right)^{-1} \frac{\hat{B}^{-1}\hat{A}}{h}. \quad (12)$$

If  $q_i^2$  are the eigenvalues of the matrix  $\hat{\Lambda}$  and

$$q_{i(n)}^2 = q_i^2 + \frac{\pi^2(2n+1)^2}{4h^2}, \quad (13)$$

then the matrix  $\hat{g}^{(n)}(q)$  can be presented as

$$\hat{g}^{(n)}(q) = \frac{\hat{B}^{-1}\hat{A}}{h} \sum_{m=1}^N \frac{\hat{\alpha}_m}{q^2 + q_{m(n)}^2} \quad (14)$$

and the matrices  $\hat{\alpha}_m$  are determined by the relations

$$\hat{\alpha}_m = \prod_{l=1, l \neq m}^N \frac{\hat{E}q_l^2 - \hat{\Lambda}}{q_l^2 - q_m^2} \quad (15)$$

and

$$\sum_{m=1}^N \hat{\alpha}_m = \hat{E}. \quad (16)$$

Finally, we find expressions for the pair correlation functions in the form

$$\hat{g}(\rho, z) = \frac{\hat{B}^{-1}\hat{A}}{2\pi h} \sum_{n=0}^{\infty} \sum_{m=1}^N \hat{\alpha}_m K_0(q_{m(n)}\rho) \cos\left(\frac{\pi(2n+1)z}{2h}\right), \quad (17)$$

where  $K_0(t)$  is the Macdonald function. This expression transforms naturally into the pair correlation functions of a pure finite-size fluid [16] and a binary mixture [20] if one stands  $N$  for 1 and 2, respectively.

### 3. Critical State

It is known that the light scattering intensity in liquid systems is determined mainly by the Fourier transform of pair correlation functions [21]. So, in order to analyze a near-critical state of the system, it is natural to consider the matrix of pair correlation functions that is defined by Eq. (14). We may expect that the critical state is realized when one of the eigenvalues  $q_{m(n)}^2$  approaches zero. We consider eigenvalues for the smallest harmonics, i.e.  $n = 0$ . For the sake of simplicity, we denote the eigenvalue approaching zero as  $\kappa_*^2$ . This eigenvalue is related obviously to the eigenvalue  $\kappa^2$  of the infinite system in such a way:

$$\kappa_*^2 = \kappa^2 + \frac{\pi^2}{4h^2}. \tag{18}$$

A similar equation was firstly obtained in [16] for a one-component confined system. From this equation, it is clearly seen that the critical state is "shifted" in a finite-size system as compared to the infinite one. Indeed, even when  $\kappa^2 = 0$  that means the critical state for the infinite system, a finite-size system is not at the critical state because  $\kappa_*^2 \neq 0$ . This obvious result is in good agreement with numerous data for confined systems (see, e.g., [7, 14, 15]). Here, we should mention that the parameter  $\kappa^2$  "below" the critical hyper-surface for the infinite system has to be taken with the minus sign. So the possibility for  $\kappa_*^2$  to be zero still exists.

It is understandable that, at the close region of the critical state for a confined system, we can restrict the matrix of pair correlation functions with the term that corresponds to the vanishing eigenvalue. This means that, at the critical region, the pair correlation functions are

$$G_{ij}(\rho, z) \sim K_0(\kappa_*\rho) \cos\left(\frac{\pi z}{2h}\right). \tag{19}$$

This result is quite similar for both simple and binary fluids [16].

Equation (18) can be used to estimate the dependence of effective critical parameters of the system on its linear size  $h$ . But to do that, we should know how the eigenvalue  $\kappa^2$  (and  $\kappa_*^2$  as well) depends on the thermodynamic parameters of the system. Namely, according to [17], a state of the  $N$ -component system is characterized by a point in the  $(N + 1)$ -dimensional space of thermodynamic variables. Then the critical hypersurface is of dimension  $N - 1$ . Critical divergences are characterized by scaling-like relations when approaching this hypersurface. In other words, we assume that the eigenvalue of the infinite system

$\kappa^2$  depends on the thermodynamic variable  $\eta$  as follows [9, 17]:

$$\kappa^2 = \kappa_0^2 \left(\frac{\eta - \eta_c}{\eta_c}\right)^{2\lambda}. \tag{20}$$

Here,  $\eta_c$  is the critical value of the variable  $\eta$ , and  $\kappa_0^2$  is the amplitude that does not depend on  $\eta$ . The critical index  $\lambda$  of the infinite system depends essentially on the way the hypersurface is being approached. This means that the critical exponent depends on how we have fixed the thermodynamic variables (all but  $\eta$ ) [6, 17, 18].

Then the eigenvalue of a finite-size system is as follows:

$$\kappa_*^2 = \kappa_0^2 \left(\frac{\eta - \eta_c}{\eta_c}\right)^{2\lambda} + \frac{\pi^2}{4h^2}. \tag{21}$$

Nevertheless, we can assume that the dependence of a finite-size system eigenvalue on the thermodynamic variable is of the same form as that for the infinite system, i.e.

$$\kappa^2 = \kappa_0^2 \left(\frac{\eta - \eta_c^*}{\eta_c^*}\right)^{2\lambda_*} \tag{22}$$

but with the critical parameter  $\eta_c^*$  and the effective critical index  $\lambda_*$  to be changed (for the sake of simplicity, we suppose that the amplitude  $\kappa_0^2$  is not changed). Thus, the critical parameters of a finite-size system are the functions of its linear size, i.e.  $\eta_c^* = \eta_c(h)$  and  $\lambda^* = \lambda(h)$ .

From these relations, we can estimate a shift of the critical parameter. Namely, we take into account that when  $\eta = \eta_c^*$ , then  $\kappa_*^2 = 0$ . This yields (in this case, we take  $\kappa^2$  with the minus sign):

$$\Delta_\eta \equiv \frac{\eta_c(\infty) - \eta_c(h)}{\eta_c(\infty)} = \left(\frac{\pi}{2h\kappa_0}\right)^{1/\lambda(\infty)} \sim h^{-1/\lambda(\infty)}. \tag{23}$$

We have to draw attention that this is not a precise relation but only the estimation of the shift in the critical state of a confined system. This shift depends on the linear size of the system (more precisely, on the geometric factor  $K = h\kappa_0$ ) as well as on the critical index  $\lambda$  of the infinite system. It is not surprising that the dependence of the critical parameter on  $h$  is of a scaling-law form. Fig. 1 shows this dependence.

The shift of the critical index is related to a shift of the critical parameter and can be estimated at the critical state of the infinite system as

$$\Delta_\lambda \equiv \frac{\lambda(h) - \lambda(\infty)}{\lambda(\infty)} = \frac{\ln(1 - \Delta_\eta)}{\ln(\Delta_\eta) - \ln(1 - \Delta_\eta)}, \tag{24}$$

where  $\Delta_\eta$  is the normalized shift of the critical parameter from Eq. (23). The dependence of a critical index shift

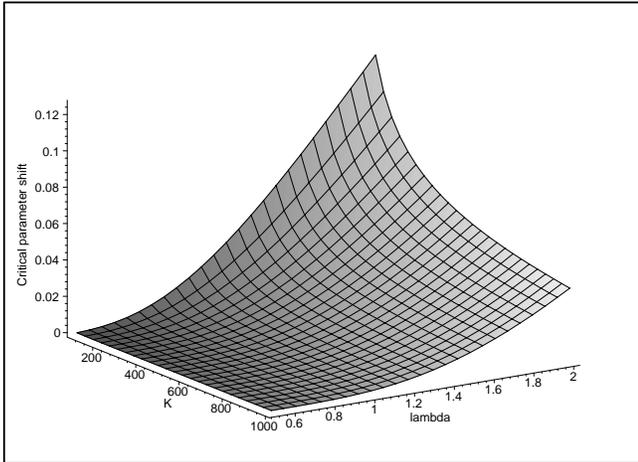


Fig. 1. Dependence of the critical parameter shift  $\Delta_\eta$  on the geometric factor  $K$  and the critical index  $\lambda(\infty)$  of the infinite system

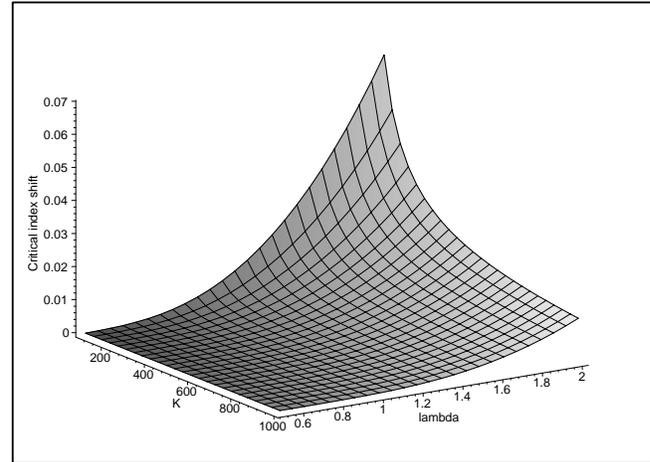


Fig. 2. Dependence of the critical index shift  $\Delta_\lambda$  on the geometric factor  $K$  and critical index  $\lambda(\infty)$  of the infinite system

on the layer thickness and on the critical index of the infinite system is shown in Fig. 2.

It can be easily seen from Figs. 1 and 2 that shifts are greater for thinner layers and bigger critical indices  $\lambda(\infty)$ . It should be mentioned, nevertheless, that Eqs. (23) and (24) are valid due to the obvious reasons only for big values of the geometric factor  $K$ .

In Fig. 3, one can see how the critical index and critical parameter shifts are related to each other depending on the layer thickness and  $\lambda(\infty)$ .

It is notable that the critical index shift is much smaller than a shift of the critical parameter for not very strong divergencies, i.e. for small  $\lambda(\infty)$ .

#### 4. Conclusions

Equation (17) for pair correlation functions that is obtained above is the general equation to determine the pair correlation functions for multicomponent systems. On the other hand, at the critical state, that term in Eq. (17) is important only, for which the eigenvalue approaches zero. In this case, the pair correlation functions of a multicomponent system formally coincide with the pair correlation function of a one-component system. This means that, at the close vicinity of the critical state, a multicomponent system should behave similarly to a one-component system when thermodynamic variables are fixed “in the right way” [6, 17, 18]. In this sense, our result does not contradict to the existing data for complex mixtures. Defining the “right way” for fixing the variables is, nevertheless, beyond the scope of this paper. But in any case, Eq. (17)

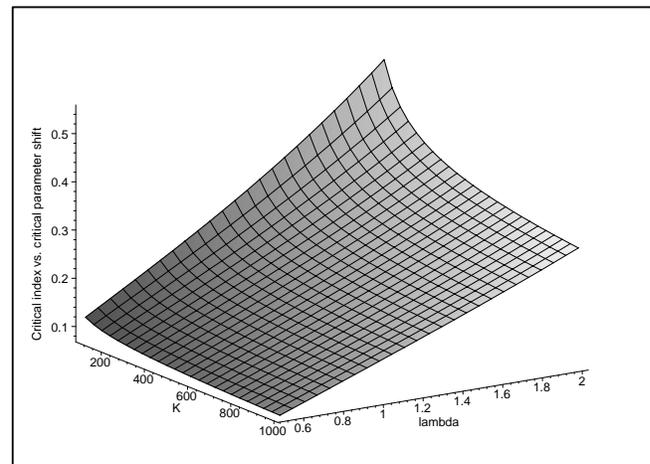


Fig. 3. Dependence of the critical index shift in respect to the critical parameter shift  $\Delta_\lambda/\Delta_\eta$  on the geometric factor  $K$  and critical index  $\lambda(\infty)$  of the infinite system

gives the total structure of the pair correlation functions in a multicomponent confined system. On the other hand, the drawback of this method is that those expressions were derived within the OZ theory and thus may be valid only in the first order of the  $\varepsilon$ -expansion [6, 7].

The estimations for shifts of the critical parameters (in spite of that they are not precise, but only are estimations) can be useful in experimental researches, especially when these shifts are not too big.

1. *Gauter K., Peters C.J.*// Fluid Phase Equilibria. **150-151** (1998) 501.

2. *Gauter K., Heidemann R.A., Peters C.J.*//Ibid. **158-160** (1999) 133.
3. *Kolar P., Kajima K.*//Ibid. **118** (1996) 175.
4. *Fisher M.E.*// Rev. Mod. Phys. **46** (1974) 597.
5. *Fisher M.E.*//Ibid.**70** (1998) 653.
6. *Anisimov M.*Critical Phenomena in Liquids and Liquid Crystals. — Moskow: Nauka, 1987(in Russian).
7. *Patashinskii A.Z., Pokrovskii V.L.* The Fluctuation Theory of Phase Transitions. — Oxford: Pergamon Press, 1979.
8. *Sengers J.V., Sengers L.*// Ann. Rev. Phys. Chem. **37** (1986) 189.
9. *Bellocq A.M., Gazeau D.*// J. Phys. Chem. **94** (1990) 8933.
10. *Fisher M.E. Critical Phenomena* // Proc. 51st Enrico Fermi Summer School, Varenna, Italy / Ed. by M.S. Green. — New York: Acad. Press, 1971.
11. *Fisher M.E., Barber M.N.*// Phys. Rev. Lett. **28** (1972) 151.
12. *Finite Size Scaling*/ J.L. Cardy (ed.). — Amsterdam: North Holland, 1988.
13. *Wilding N.B.*// J. Phys.: Condens. Matter, **9** (1997) 585.
14. *Binder K.*// Ann. Rev. Phys. Chem. **43** (1992) 33.
15. *Finite Size Scaling and Numerical Simulation of Statistical Systems*/ V. Privman (ed.). — Singapore: World Scientific, 1990.
16. *A. Chalyi*// J. Mol. Liquids, **58** (1993) 179.
17. *Griffiths R.B., Wheeler J.C.*// Phys. Rev. A, **2** (1970) 1047.
18. *Fisher M.E.*// Phys. Rev. **176** (1968), 257.
19. *Vasiliev A.*// Theor. Math. Phys. **135** (2003) 714.
20. *Chalyi A. et. al.*// Cond. Mater. Phys. **22** (2000) 335.
21. *Chalyi A.*// Sov. Sci. Rev. A: Phys. **16** (1992) 1.

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ПАРНІ КОРЕЛЯЦІЙНІ ФУНКЦІЇ ТА КРИТИЧНІ  
ПАРАМЕТРИ БАГАТОКОМПОНЕНТНОЇ  
ПРОСТОРОВО ОБМЕЖЕНОЇ  
РІДКОЇ СИСТЕМИ

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Резюме

Розглядається багатокомпонентна рідка просторово обмежена система з геометрією плоского паралельного прошарку. Для цієї системи знайдено парні кореляційні функції флуктуацій густини. Досліджено вплив просторового обмеження на критичну поведінку системи. Отримані результати порівняно з наявними даними для однокомпонентних та бінарних рідин.