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A CHANGE IN THE CHEMICAL POTENTIAL IN LIQUIDS UNDER THE ACTION OF RADIATION AND AN EXTERNAL FIELD

The influence of the spatial confinement and radiation on the thermodynamic behavior of the equilibrium properties of liquid systems has been studied. The theory of spatially confined inhomogeneous liquids has been generalized in order to take the correlation effects in such systems into account. The obtained results allow the spatial distribution of the density in binary liquid systems subjected to the action of radiation and external fields to be calculated in a wide range of thermodynamic parameters.

Keywords: phase transition, critical phenomena, chemical potential, spatially confined system, equilibrium thermodynamics.

1. Introduction

An important result of the statistical physics development in recent years was the possibility of a quantitative description of homogeneous liquid systems [1]. However, numerous studies testify that any real liquid system is always inhomogeneous: due to both the presence of surfaces (walls) that confine the system and the action of external factors such as radiation [2] and external fields [3, 4]. When calculating the thermodynamic properties of real systems, the inhomogeneity caused by the availability of walls is considered to be completely localized in a vicinity of those walls, with the dimension order of this region being of the range of action of near-surface forces [5, 6]. This supposition serves as a basis for neglecting the boundary inhomogeneity when calculating the bulk properties of sufficiently large systems. The inhomogeneity induced by radiation or the gravitational field is, in most cases, quite small at the molecular distances, which makes it possible to consider the liquid as consisting of homogeneous subsystems with different intensive parameters. Both approximations allow the properties of thermodynamic systems to be calculated with an accuracy that, in many cases, is sufficient to describe real systems.

However, there are many research results sometimes – for example, in an external field that varies strongly in space, or in a vicinity of the critical point – demonstrating that those approximations do not bring about satisfactory descriptions of experimental results [7, 8]. Therefore, to describe the properties of a real system, it is necessary to make allowance for the heterogeneity of the latter. In the general case, one has to take into account that the free energy F of an inhomogeneous system is no more a function of the temperature T and the density n. Instead, it is a functional $F = N\,F(T(\mathbf{r}), n(\mathbf{r}))$ depending on the functions $T(\mathbf{r})$ and $n(\mathbf{r})$ of the spatial coordinate $\mathbf{r}$.

In this case, the calculation of the spatial dependences of physical quantities using the statistical operator is an extremely difficult task [9, 10]. Therefore, as a rule, the behavior of the system is considered in the framework of local approximation. In this approximation, it is adopted that the system consists of “physically small” cells, which are spatial regions that are so small that they can be considered as homogeneous, i.e., the thermodynamics of homogeneous sys-

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tems can be applied to each of them. Then, in order to calculate the behavior of the system in an external field, the density of the corresponding potential, for example, the free energy density $f(\mathbf{r})$, is introduced so that [11]

$$F = \int\limits_V d\mathbf{r} f(\mathbf{r}),$$

where the integration is performed over the system volume V. In this case, the free energy remains to be a function of T and n, but those quantities, in turn, become functions of the coordinate $\mathbf{r}$, i.e., $F = Nf(T(\mathbf{r}), n(\mathbf{r}))$. In the framework of this approximation, the relationship between the chemical potential in an inhomogeneous liquid system $\mu(\mathbf{r})$ and the external field $u(\mathbf{r})$ is described by the well-known expression

$$\mu_0 - \mu(\mathbf{r}) = u(\mathbf{r}), \tag{1}$$

where μ_0 is the chemical potential in the system in the field absence. Thus, in the case where the dynamic variables change little at distances of the order of the correlation radius of the corresponding parameters, the main term of the statistical operator applied to calculate the corresponding average values takes the form of expression (1). In other words, in the formulas for calculating the equilibrium averages, it is necessary to substitute the equilibrium parameter values by their dependences on the coordinate $\mathbf{r}$. This obtained relationship can also be proved by selecting and summing up the corresponding terms in the perturbation theory series.

However, as was marked in work [12], this approach was developed only for the ranges of thermodynamic parameter change far from the points of continuous phase transformations. Therefore, finding a relationship between the chemical potential and the external field potential in an inhomogeneous liquid that is in a state in a immediate vicinity of its critical point requires a separate consideration. In particular, that is why the further development of the theoretical approach was associated with the construction of a consistent theory of the liquid density distribution $n(\mathbf{r})$ as a functional of the $\mu(\mathbf{r})$ distribution.

In this paper, a theoretical method is proposed to study the general characteristics of the behavior of an inhomogeneous system in a vicinity of its critical point, which would make it possible to calculate the density of this system.

2. General Equation for the Chemical Potential in an Inhomogeneous System

As the radius of an inhomogeneous system with correlations increases, the classical relationship (1) does not allow one to obtain real liquid density profiles. Moreover, the introduction of corrections (see, e.g., works [13, 14]) does not propose a way how the theory could be developed further in order to improve the accuracy of calculations. Therefore, there arises a necessity to develop a consistent theory based on fundamental statistical-mechanical and thermodynamic principles, which would describe the behavior of the chemical potential in an inhomogeneous system.

For this purpose, let us expand the potential of the external field $u(\mathbf{r})$ into a functional Taylor series in the deviation $\Delta n(\mathbf{r})$ of the liquid density $n(\mathbf{r})$ from its value for a homogeneous liquid,

$$\begin{aligned} \beta u(\mathbf{r}) = {} & \int\limits_V \left.\frac{\delta \beta u(\mathbf{r})}{\delta n(\mathbf{r}_1)}\right|_{\beta u=0} \Delta n(\mathbf{r}_1)\, d\mathbf{r}_1 + \ldots + \\ & + \frac{1}{2!} \int\limits_V \int\limits_V \left.\frac{\delta^2 \beta \mathrm{u}(\mathbf{r})}{\delta n(\mathbf{r}_1)\, \delta n(\mathbf{r}_2)}\right|_{\beta u=0} \times \\ & \times \Delta n(\mathbf{r}_1)\, \Delta n(\mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 + \ldots, \end{aligned} \tag{2}$$

where $\beta = (kT)^{-1}$, and k is the Boltzmann constant. Series (2) converges due to the finiteness of the integral $\int_V (\Delta n(\mathbf{r}))\, d\mathbf{r}$. Taking into account that

$$\begin{aligned} & \left.\frac{\delta^{s-1} \beta u(\mathbf{r}_1)}{\delta n(\mathbf{r}_2) \ldots \delta n(\mathbf{r}_s)}\right|_{\beta u=0} + \\ & + (-1)^s \frac{(s-2)!}{n(\mathbf{r}_1)^{s-1}} \delta(\mathbf{r}_1, \mathbf{r}_2) \ldots \delta(\mathbf{r}_1, \mathbf{r}_s) = \\ & = c_s^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_s), \end{aligned} \tag{3}$$

where $c_s^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_s)$ is either the direct correlation function of the sth order of the confined system or the direct correlation function of the homogeneous infinite system, and $\delta(\mathbf{r}_1 - \mathbf{r}_s)$ is the three-dimensional Dirac δ-function, we obtain

$$\begin{aligned} \beta u(\mathbf{r}) = {} & \int\limits_V c_2^*(\mathbf{r}, \mathbf{r}_1)\, \Delta n(\mathbf{r}_1)\, d\mathbf{r}_1 - \frac{\Delta n(\mathbf{r})}{n} + \\ & + \frac{1}{2!} \int\limits_V \int\limits_V c_3^*(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2)\, \Delta n(\mathbf{r}_1)\, \Delta n(\mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2 + \\ & + \frac{1}{2!} \frac{(\Delta n(\mathbf{r}))^2}{n^2} + \ldots + \end{aligned}$$

$$+\frac{1}{k!}\int\limits_V\int\limits_V\ldots\int\limits_V c^*_{k+1}(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_k)\prod_{i=1}^{k}\Delta n(\mathbf{r}_i)\,d\mathbf{r}_i+$$
$$+(-1)^k\frac{(k-1)!}{k!}\left(\frac{\Delta n(\mathbf{r})}{n}\right)^k+\ldots. \tag{4}$$

If the system is confined, then its direct correlation function can be expanded into a functional Taylor series near the point of the constant liquid density n_0 for the infinite system [15]:

$$c^*_2(\mathbf{r}_1,\mathbf{r}_2)=c_2(\mathbf{r}_1,\mathbf{r}_2)+\int\limits_V\left.\frac{\delta c^*_2(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r}_3)}\right|_{n(\mathbf{r})=n}\times$$
$$\times[n(\mathbf{r}_3)-n_0]\,d\mathbf{r}_3+\frac{1}{2!}\int\limits_V\int\limits_V\left.\frac{\delta^2 c^*_2(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r}_3)\,\delta n(\mathbf{r}_4)}\right|_{n(\mathbf{r})=n}\times$$
$$\times[n(\mathbf{r}_3)-n_0]\,[n(\mathbf{r}_4)-n_0]\,d\mathbf{r}_3 d\mathbf{r}_4+\ldots+$$
$$+\frac{1}{k!}\int\limits_V\int\limits_V\ldots\int\limits_V\left.\frac{\delta^k c^*_2(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r}_3)\ldots\delta n(\mathbf{r}_{k+2})}\right|_{n(\mathbf{r})=n}\times$$
$$\times\prod_{i=3}^{k+2}[n(\mathbf{r}_i)-n_0]\,d\mathbf{r}_i+\ldots, \tag{5}$$

where $c_2(\mathbf{r}_1,\mathbf{r}_2)$ is the direct pair correlation function for a homogeneous unconfined system. Thus, in the zero approximation, it can be assumed that the direct correlation functions of the confined system coincide with the direct correlation functions of the infinite homogeneous system. By writing down the following formal expression for the density deviations:

$$\Delta n(\mathbf{r}_1)=\Delta n(\mathbf{r})+[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})],$$

we obtain

$$\beta u(\mathbf{r})=\Delta n(\mathbf{r})\int\limits_V c_2(\mathbf{r},\mathbf{r}_1)\,d\mathbf{r}_1+$$
$$+\int\limits_V c_2(\mathbf{r},\mathbf{r}_1)\,[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1-\frac{\Delta n(\mathbf{r})}{n}+$$
$$+\frac{(\Delta n(\mathbf{r}))^2}{2!}\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\,d\mathbf{r}_1 d\mathbf{r}_2+$$
$$+\Delta n(\mathbf{r})\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\times$$
$$\times[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1 d\mathbf{r}_2+$$
$$+\frac{1}{2!}\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\,[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\times$$
$$\times[\Delta n(\mathbf{r}_2)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1 d\mathbf{r}_2++\frac{1}{2!}\frac{(\Delta n(\mathbf{r}))^2}{n^2}+\ldots, \tag{6}$$

where the symmetry of the direct correlation functions of the homogeneous system with respect to the permutations of their arguments was taken into account.

Performing the partial summation in series (6) and considering only the non-integral terms and the terms containing the zero moments of direct correlation functions $\int_V\int_V\ldots\int_V d\mathbf{r}_1\ldots d\mathbf{r}_s c_{s+1}(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_s)$ (the local approximation), we get

$$\beta u(\mathbf{r})=-\beta\left\{\frac{1}{n}\left(\frac{\partial p}{\partial n}\right)_T\Delta n(\mathbf{r})+\right.$$
$$\left.+\frac{1}{2!}\frac{\partial}{\partial n}\left(\frac{1}{n}\left(\frac{\partial p}{\partial n}\right)_T\right)(\Delta n(\mathbf{r}))^2+\ldots\right\}=$$
$$=-\beta\left\{\left(\frac{\partial\mu}{\partial n}\right)_T\Delta n(\mathbf{r})+\right.$$
$$\left.+\frac{1}{2!}\left(\frac{\partial^2\mu}{\partial n^2}\right)_T(\Delta n(\mathbf{r}))^2+\ldots\right\}, \tag{7}$$

where the relationship

$$\frac{\partial c(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)}{\partial n}=\int\limits_V c(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{s+1})\,d\mathbf{r}_{s+1}$$

between the derivative of the sth-order direct correlation function and the integral of the $(s+1)$th-order direct correlation function, as well as the relationship

$$\int\limits_V c(\mathbf{r},\mathbf{r}_1)\,d\mathbf{r}_1=\frac{1}{n}\left[1-\beta\left(\frac{\partial p}{\partial n}\right)_T\right],$$

was taken into account.

It is easy to see that the classical formula (1) corresponds to the local approximation when calculating the average value in the framework of the locally equilibrium ensemble approach. To obtain corrections to expression (1), the remaining terms in series (6) have to be taken into account,

$$u(\mathbf{r})=\mu_0-\mu(\mathbf{r})+\Delta\mu_{\rm cor}(\mathbf{r}), \tag{8}$$

where $\Delta\mu_{\rm corr}$ is the contribution from correlation effects to the chemical potential difference,

$$\beta\Delta\mu_{\rm cor}(\mathbf{r})=\int\limits_V c_2(\mathbf{r},\mathbf{r}_1)\,[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1+$$

$$+\Delta n(\mathbf{r})\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)\times$$
$$\times[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1 d\mathbf{r}_2+$$
$$+\frac{1}{2!}\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)[\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})]\times$$
$$\times[\Delta n(\mathbf{r}_2)-\Delta n(\mathbf{r})]\,d\mathbf{r}_1 d\mathbf{r}_2+\ldots. \quad (9)$$

In the case of a smooth spatial change in the density $\Delta n(\mathbf{r})$ at distances of the order of the radius of intermolecular force action, when the difference $\Delta n(\mathbf{r}_1)-\Delta n(\mathbf{r})$ can be expanded in a Taylor series, it is possible to obtain an approximate expression for $\Delta\mu_{\rm corr}(\mathbf{r})$ with any accuracy. Far from the critical point, the spatial derivatives of the density are small, which ensures the smallness of the $\Delta\mu_{\rm corr}(\mathbf{r})$ values.

The well-known results of Lebowitz and Percus can be easily obtained, if only the expansion terms up to the second order including are taken into account in the summand with the direct correlation function of the second order and the resulting infinite system is considered. In this case, we arrive at the relationship

$$\beta u(\mathbf{r})\approx\beta\{\mu_0-\mu(\mathbf{r})\}+$$
$$+\frac{1}{2}\boldsymbol{\nabla}^2\Delta n(\mathbf{r})\int\limits_V c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})^2\,d\mathbf{r}_1+$$
$$+\boldsymbol{\nabla}\Delta n(\mathbf{r})\int\limits_V c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})\,d\mathbf{r}_1. \quad (10)$$

Then, in the Lebowitz–Perkus approximation for $\Delta\mu_{\rm corr}(\mathbf{r})$, we obtain

$$\beta\Delta\mu_{\rm corr}=a\boldsymbol{\nabla}^2 n(\mathbf{r}), \quad (11)$$

where

$$a=\frac{1}{2}\int\limits_V d\mathbf{r}_1 c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})^2. \quad (12)$$

Thus, the Lebowitz–Percus approximation leads to the following second-order partial differential equation for the liquid density $n(\mathbf{r})$, and this equation does not contain the first derivative of the density [17]:

$$a\boldsymbol{\nabla}^2 n(\mathbf{r})=\beta u(\mathbf{r})-\beta(\mu_0-\mu(\mathbf{r})). \quad (13)$$

Furthermore, it is easy to see that the coefficient a in front of the second derivative of the density is proportional to ξ^2. Therefore, in most cases, the internal solution of the differential equation (13) is used. Such an internal solution can be considered as an approximation to the exact solution of Eq. (13) only in the case of small values of the correlation radius, i.e., far from the critical point. However, when approaching the latter, the role played by the differential term becomes decisive, and this approximation leads to a substantial error for the calculated liquid density.

The refinement of formula (11) for the infinite system follows in a natural way from the successive consideration of further terms in the expansions of all summands in series (10). In particular, by accounting for linear terms in the summand associated with the direct correlation function of the third order, we obtain the expression

$$\beta u(\mathbf{r})\approx\beta\{\mu_0-\mu(\mathbf{r})\}+$$
$$+\frac{1}{2}\boldsymbol{\nabla}^2\Delta n(\mathbf{r})\int\limits_V c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})^2\,d\mathbf{r}_1+$$
$$+\frac{1}{2}(\boldsymbol{\nabla}\Delta n(\mathbf{r}))^2\times$$
$$\times\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_2-\mathbf{r})\,d\mathbf{r}_1 d\mathbf{r}_2+$$
$$+\boldsymbol{\nabla}\Delta n(\mathbf{r})\left\{\int\limits_V c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})\,d\mathbf{r}_1+\right.$$
$$\left.+\Delta n(\mathbf{r})\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1-\mathbf{r})\,d\mathbf{r}_1 d\mathbf{r}_2\right\}. \quad (14)$$

Then the improved Lebowitz–Perkcus approximation can be written in the form [8]

$$\beta\Delta\mu_{\rm cor}=a\boldsymbol{\nabla}^2 n(\mathbf{r})+b(\boldsymbol{\nabla}n(\mathbf{r}))^2, \quad (15)$$

where

$$a=\frac{1}{2}\int\limits_V c_2(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_1-\mathbf{r})^2\,d\mathbf{r}_1, \quad (16)$$

$$b=\frac{1}{6}\int\limits_V\int\limits_V c_3(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)(\mathbf{r}_1-\mathbf{r})(\mathbf{r}_2-\mathbf{r})\,d\mathbf{r}_1 d\mathbf{r}_2. \quad (17)$$

An analysis of the obtained results testifies that the term proportional to $\boldsymbol{\nabla}n(\mathbf{r})$ differs from zero only in a confined system and equals

$$\beta\Delta\mu_{\rm cor}=a\,\boldsymbol{\nabla}^2 n(\mathbf{r})+b\,(\boldsymbol{\nabla}n(\mathbf{r}))^2+\mathbf{c}\cdot\boldsymbol{\nabla}n(\mathbf{r}), \quad (18)$$

where

$$\mathbf{c} = \int_V c_2\left(\mathbf{r}_1 - \mathbf{r}\right)\left(\mathbf{r}_1 - \mathbf{r}\right) d\mathbf{r}_1 +$$

$$+\,\Delta n(\mathbf{r}) \int\limits_V \int\limits_V c_3\left(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2\right)\left(\mathbf{r}_1 - \mathbf{r}\right) d\mathbf{r}_1 d\mathbf{r}_2. \tag{19}$$

Thus, a conclusion can be drawn that the Lebowitz–Percus approximation is valid only in the cases of infinite systems or confined systems for which the contribution by the term **c** can be neglected (this is true only for systems with confining surfaces of certain n symmetry types).

The situation occurring near the critical point in the presence of an external field (for example, a gravitational field) requires a special approach. As is known, at the critical point itself, the derivatives of $\boldsymbol{\nabla} n(\mathbf{r})$ become singular on the critical isotherm at $n(0) = n_c$, where n_c is the density at the critical point. Then, in the obtained approximation (19), the summands with gradient terms play the main role. However, if we take into account that the equation of state on the critical isotherm can be presented in the form $(\mu - \mu_c) \sim (n - n_c)^\delta$, where μ_c is the chemical potential of the system at the critical point, and δ is the critical index (in a three-dimensional system, $\delta \approx 4.6$), then the derivatives $d^k\mu/dn^k$ with $k \geq 5$ go to infinity, when approaching the critical point. This fact means that the direct correlation functions $c_k(\mathbf{r}_1, ..., \mathbf{r}_k)$ at $k \geq 6$ become long-range at the critical point, and the contribution from the terms containing those functions under the integral can become decisive when calculating the chemical potential in the presence of an external field. In addition, it is natural to conclude that if the zero moments of the direct correlation functions diverge at the critical point, then the moments of higher orders will also diverge.

The obtained results testify that Eq. (1) can be used far from the critical point. However, when approaching the critical point, the role of correlation terms $\Delta\mu_{\mathrm{corr}}(\mathbf{r})$ increases, and it is necessary to use expression (18) and take more and more correction terms into consideration. At the very critical point, the application of Eq. (1), and, even more so, Eq. (1), is doubtful [17]. In addition, when calculating the density distribution $n(\mathbf{r})$ near the critical point in a confined system, instead of the differential equation (13), we have to use the equation

$$\beta u(\mathbf{r}) = \beta(\mu_0 - \mu(\mathbf{r})) + a\boldsymbol{\nabla}^2 n(\mathbf{r}) +$$
$$+\, b(\boldsymbol{\nabla} n(\mathbf{r}))^2 + \mathbf{c} \cdot \boldsymbol{\nabla} n(\mathbf{r}), \tag{20}$$

which contains a term linear in $\boldsymbol{\nabla} n(\mathbf{r})$. This fact is important for satisfying the conditions of Tikhonov's theorem when constructing a general asymptotic expansion of the solution to the singularly perturbed equation.

3. Conclusions

A method has been proposed for calculating the chemical potential and the density in inhomogeneous liquids subjecting to the action of radiation and external fields in vicinities of their critical points by successively taking correlation terms into account. It is shown that, in a vicinity of the critical point, the account for correlation effects leads to a change in the density profile in the liquid volume that is determined by the correlation radius in the corresponding homogeneous system rather than the radius of action of the forces in the near-surface region of the wall that confines the system.

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ЗМІНА ХІМІЧНОГО ПОТЕНЦІАЛУ ФЛЮЇДУ ПІД ДІЄЮ РАДІАЦІЙНОГО ОПРОМІНЕННЯ ТА ЗОВНІШНЬОГО ПОЛЯ

Досліджено вплив просторової обмеженості та радіаційного опромінення на термодинамічну поведінку рівноважних властивостей рідинних систем. Побудовано узагальнення теорії обмежених неоднорідних рідин, яке дозволяє врахувати кореляційні властивості таких систем. Отримані результати дозволяють проводити обчислення просторового розподілу концентрації рідинної системи в широкому інтервалі зміни термодинамічних параметрів у випадку дії радіаційного опромінення та зовнішнього поля.

Ключові слова: фазовий перехід, критичні явища, хімічний потенціал, обмежена система, рівноважна термодинаміка.