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STATISTICAL THEORY OF NONUNIFORM SYSTEMS AND REDUCED DESCRIPTION IN THE DENSITY FLUCTUATION THEORY

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A statistical theory of nonuniform systems is developed, based on the conditional distribution method. Junior correlation functions of a nonuniform system have been used to obtain an explicit expression for the Helmholtz free energy and the effective Hamiltonian as functionals of the particle number density field. The structure of a transient layer at the liquid–gas interface and a surface sorption effect have been studied. A method of reduced description in the fluctuation theory, using the conditional correlation functions of the particle number density distribution, is suggested. An infinite system of integro–differential equations is obtained for the correlation functions introduced. A method for its truncation is proposed. As a result, the grand statistical integral, which takes into account the density field fluctuations of the system in equilibrium with a thermostat, is calculated.

1. Introduction

The simplest phenomenological theory of nonuniform systems suggested almost 100 years ago by van der Waals^{1}) employed the concept of a free energy dnesity (a function of position). The total free energy F, which is a functional of the density field $\rho(\boldsymbol{r})$ may then be written as

$$F = \int_V f(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}. \tag{1}$$

In more recent publications (see ref. 2) it was assumed that the density f (or a density of the thermodynamic potential Ω in the fluctuation theory^{3,4}) is a function of position and a functional of the field density $\rho(\boldsymbol{r})$.

A possibility of principle to find the expression for a free energy density is implied by statistical mechanics^{3}). Practical use of a statistical approach is however as difficult as in the case of uniform systems, the difficulties being in fact even greater (concerning the BBGKY method see, for example, original monographs^{5,6}) and also$^{7-10}$). This may primarily be attributed to a necessity to solve a basic problem of truncation of a chain of integro–differential equations for the correlation functions, which are now functionals of the particle number density field[7,11]). Because of the lack of information on the behaviour of the correlation functions in nonuniform systems, a two-particle function of a nonuniform system should often be simulated with a quite well-known radial function of a uniform system[2,12–18]).

The problem becomes even more complicated, when it is necessary to construct a statistical fluctuation theory in order to calculate a functional integral after the effective Hamiltonian has been determined. It is known, for example, that in Landau's thermodynamic theory, calculation of this integral for the effective Hamiltonian is impossible[3]).

In this work a statistical theory is developed for a nonuniform system, based on the conditional correlation functions (see also refs. 20–22). The essence of the method is to introduce such a succession of the correlation functions, which would describe not the states of particular groups but particular states of the whole particle set. As was expected[19]), this method can be used for practice because quite high densities typical for the condensed state of molecular systems make it possible to introduce successive approximations in the description of their statistical properties. If the total volume V of the system is divided into N equal cells (according to the number of particles in the uniform system), the basic states in the particle distribution are such that each of the molecular cells contains one molecule (the F_{11}-approximation). States, involving stronger fluctuations of the particle density are considered by the subsequent approximations. Within this method a truncation procedure is specific for uniform systems but may be extended to nonuniform ones.

In section 2 correlation functions of a nonuniform system have been used to find an explicit expression for the free energy as a functional of the particle number density field. Later, the general relations obtained are used for studying the structure of a transient layer at the liquid–gas interface and the surface adsorption effect (subsection 2.3).

In section 3, where an open system in equilibrium with a thermostat, is analysed, statistical expressions are obtained for the effective Hamiltonian and the distribution function of the particle number density fluctuations. The difficulty due to the necessity of calculating a functional integral in the fluctuation theory, is overcome using the idea of a reduced description. Its practical use becomes possible since the effective Hamiltonian in this approach appears to be a function of N variables which determine the particle number distribution field in the system.

With the aid of effective Hamiltonian expansion with respect to the irreducible effective potentials a concept of effective potentials of the "interaction" of the density fluctuations with one another and with the generating medium is introduced (see subsection 3.1). General expressions are written for the new conditional correlation functions of the density distribution and an infinite chain of the constitutive integro–differential equations is obtained. A method is developed for their truncation and use to calculate the grand statistical integral with account for the density field fluctuations (subsection 3.2).

It should be noted that the suggested method of description of the contributions to the statistical integral of the states with prescribed density fields with subsequent summation over the fields is an extension of the basic idea of the conditional distribution method, which, as was mentioned above, operates to describe particular states of the whole system.

2. Statistical theory of nonuniform molecular systems

Consider a molecular system with a prescribed but arbitrary density field in a three-dimensional space ($\rho = \rho(\boldsymbol{r})$). As follows from the basic idea of the conditional distribution method, the volume V is divided into equal cells so that their number N exceeds the total number of the particles in the system. Thus, it can be possible, even within the first F_{11}-approximation of the conditional distribution method^{19}), to consider such particle configurations in the phase space, which are peculiar of nonuniform systems with a prescribed density field. Now, such states will correspond to the first F_{11}-approximation when each of the cells is either empty or contains one particle^{23,24}) (a similar approach in the uniform system theory was used in ref. 25). The second approximation considers the states when the cells may contain also two particles and so on. In connection with this, the division into cells is a mathematical method and a three-dimensional system of cells is a kind of frame of reference for many particles. In order to consider only the first approximations, we will divide the whole volume V into cells of quite a small size ($\omega = V/N \approx \sigma^3$, σ is the Lennard–Jones potential parameter). Then, a probability of two particles to occur in one cell will be small and the idea of the approach suggested can be described as the F_{11}-approximation. Changes due to the use of the second approximation for pure systems or for multicomponent mixtures, will not involve additional difficulties.

The system with occupied or empty cells may formally be considered as a two-component system, which consists of N_a real molecules of species a and N_b fictitious molecules (they do not interact with each other and with the real molecules) of species b. With the presence of a fine three-dimensional system of cells in view, the macroscopic density field $\rho(\boldsymbol{r})$ may be prescribed by a set of N quantities, which give the density value of each of the cells ($\rho(\boldsymbol{r}_k) = \{\rho_k\}$, k is is the cell number, $\boldsymbol{r}_k$ is the position vector of the cell center). The average amount of the particles of different species (a local concentration) in the kth cell is found as

$$n^a_k = \rho_k \omega, \quad n^b_k = 1 - n^a_k = 1 - \rho_k \omega. \tag{2.1}$$

The configuration integral of the system containing N_a particles with a prescribed density field will be expressed in terms of a configuration integral of a "two-component" system[23]) (see also chap. IX in ref. 19) as

$$Q_{N_a}\{\rho_k\} = \omega^{-N_b} Q_N\{n^a_k\}, \quad N = N_a + N_b. \tag{2.2}$$

The factor ω^{-N_b} is a compensation for the contribution of the integration with respect to the fictitious particle coordinates.

An infinite chain of equations for the correlation functions of the conditional distribution method is obtained for a nonuniform system with a standard method from the equation for the Gibbsian distribution function

$$\frac{\partial \mathscr{D}_N}{\partial \boldsymbol{q}^{\mu}_{i}} + \frac{1}{\theta} \frac{\partial U_N}{\partial \boldsymbol{q}^{\mu}_{i}} \mathscr{D}_N = 0, \tag{2.3}$$

where U_N is the potential energy of a "two-component" system of N_a particles of species a, and N_b particles of species b distributed one in each of the cells (the F_{11}-*approximation*), $\theta = kT$ is the dimensionless temperature (k is the Boltzmann constant).

Eq. (2.3) will be integrated over that area of the phase space of all the variables except $\boldsymbol{q}^{i}_{\mu} \in \omega_i$, which satisfies the prescribed particle number density field distribution, say, particles of species a (because of cells ω_i present, integration over the phase space means integration over the coordinates within each of the cells and summation over physically different configurations of the particle location in N cells). This will result in the first equation of an infinite chain

$$\frac{\partial F_{11}(\boldsymbol{q}^{i}_{\mu})}{\partial \boldsymbol{q}^{i}_{\mu}} + \frac{1}{\theta} \sum_{\nu} n^{\nu}_{j} \sum_{j \neq i}^{N} \int_{\omega_j} \frac{\partial \phi(|\boldsymbol{q}^{i}_{\mu} - \boldsymbol{q}^{j}_{\nu}|)}{\partial \boldsymbol{q}^{i}_{\mu}} F^{(1)}_{11}(\boldsymbol{q}^{i}_{\mu}, \boldsymbol{q}^{j}_{\nu})\, \mathrm{d}\boldsymbol{q}^{j}_{\nu} = 0. \tag{2.4}$$

Here $F_{11}(\boldsymbol{q}^{i}_{\mu}, \{n_k\})$ is a one-particle function, which determines the density of the probability that an arbitrary molecule of species μ is near the coordinate $\boldsymbol{q}^{i}$ of the cell ω_i and the others are distributed in accordance with the prescribed field $n_k = n(r_k)$, each cell containing no more than one molecule. Consequently, $F_{11}(\boldsymbol{q}^{i}_{\mu})$ is a function of the particle position within the volume V (it depends on the cell position and the particle position in the cell) and a functional of the density field. Likewise $F_{11}(\boldsymbol{q}^{i}_{\mu}, \boldsymbol{q}^{j}_{\nu}, \{n_k\})$ is a two-particle correlation function, which determines the distribution of two particles in two cells ($\boldsymbol{q}^{i}_{\mu} \in \omega_i$, $\boldsymbol{q}^{i}_{\nu} \in \omega_j$).

The constitutive equations for two-particle and major correlation functions of a nonuniform system are obtained in a similar way.

2.1. *The method of conditional correlation functions in a system with nonuniform density distribution*

For the calculation of a configuration integral of a "two-component system" with junior correlation functions, it is necessary to solve the problem of truncation of the chain (2.4). The first equation of the chain will be written as

$$\frac{\partial \ln F_{11}(\mathbf{q}_\mu^i)}{\partial \mathbf{q}_\mu^i} + \frac{1}{\theta}\sum_{j\neq i}^{N}\sum_{\nu} n_j^\nu \int\limits_{\omega_j} \frac{\partial \phi(|\mathbf{q}_\mu^i - \mathbf{q}_\nu^j|)}{\partial \mathbf{q}_\mu^i} F_{11}^{(1)}(\mathbf{q}_\nu^j \mid \mathbf{q}_\mu^i)\, \mathrm{d}\mathbf{q}_\nu^j = 0. \tag{2.1.1}$$

The two-particle distribution function is related with $F_{11}(\mathbf{q}_\mu^i)$ and $F_{11}(\mathbf{q}_\nu^j/\mathbf{q}_\mu^i)$ by the probability relation

$$F_{11}^{(1)}(\mathbf{q}_\mu^i, \mathbf{q}_\nu^j, \{n_k^a\}) = F_{11}(\mathbf{q}_\mu^i, \{n_k^a\}) \cdot F_{11}^{(1)}(\mathbf{q}_\nu^j \mid \mathbf{q}_\mu^i, \{n_k^a\}), \tag{2.1.2}$$

which is virtually a definition of the correlation function $F_{11}(\mathbf{q}_\nu^j/\mathbf{q}_\mu^i)$ that determines the distribution of a particle of species ν in the cell ω_j, provided that an arbitrary particle of species μ is fixed at $\mathbf{q}_\mu^i$.

We will define the average force potentials

$$\frac{\partial \varphi_{ij}(\mathbf{q}_\mu^i)}{\partial \mathbf{q}_\mu^i} = \sum_{\nu} n_j^\nu \int\limits_{\omega_j} \frac{\partial \phi(|\mathbf{q}_\mu^i - \mathbf{q}_\nu^j|)}{\partial \mathbf{q}_\mu^i} F_{11}^{(1)}(\mathbf{q}_\nu^j \mid \mathbf{q}_\mu^i)\, \mathrm{d}\mathbf{q}_\nu^j, \tag{2.1.3}$$

exerted on a particle of species μ at $\mathbf{q}^i \in \omega_i$ by the molecule distributed within the cell ω_j in accordance with the correlation function $F_{11}(\mathbf{q}_\nu^j/\mathbf{q}_\mu^i)$. Making use of the potentials $\varphi_{ij}(\mathbf{q}_\mu^i)$, which are also functionals of the density field, we integrate (2.1.1) as

$$F_{11}(\mathbf{q}_\mu^i) = C_i^\mu \exp\left\{-\frac{1}{\theta}\sum_{j\neq i}^{N} \varphi_{ij}(\mathbf{q}_\mu^i)\right\}. \tag{2.1.4}$$

Similarly, the expression for a conditional two-particle function is obtained:

$$F_{11}^{(1)}(\mathbf{q}_\nu^j/\mathbf{q}_\mu^i) = C_{ij}^{\mu\nu}(\mathbf{q}_\mu^i) \exp\left\{-\frac{1}{\theta}\left[\phi(|\mathbf{q}_\mu^i - \mathbf{q}_\nu^j|) + \sum_{k\neq i,j}^{N} \varphi_{jk}(\mathbf{q}_\nu^j \mid \mathbf{q}_\mu^i)\right]\right\}, \quad i\neq j \tag{2.1.5}$$

Here $\varphi_{jk}(\mathbf{q}_\nu^j/\mathbf{q}_\mu^i)$ is the average force potential, similar to $\varphi_{jk}(\mathbf{q}_\nu^j)$, determined under the additional condition that a particle of species μ is fixed at $\mathbf{q}_\mu^i \in \omega_i$.

Truncation of the infinite chain of equations for correlation functions is based upon approximation of the integral terms, which are average force potentials (the method of average force potentials[19]). According to eq. (2.1.5) the correlation function $F_{11}(q_\nu^j/q_\mu^i)$ depends on the coordinates q_μ^i of a fixed particle of species μ because of two reasons. First, there is an explicit relation in terms of a pairwise intermolecular potential, and second, the particle of species μ fixed at q_μ^i has an indirect effect upon the averaged interaction of a molecule of species ν in the cell ω_j with the particles, distributed over the volume ω_k. This interaction is described in terms of the potential $\varphi_{jk}(q_\nu^j/q_\mu^i)$. Since in the condensed state the behaviour of a particle depends on all its neighbours, then if one of them is fixed at q_μ^i, it will not essentially influence the averaged interaction of the particle with the remaining neighbours. Therefore, if for truncation a direct correlation is taken into account and the indirect one is neglected for the first approximation, use can be made of the approximation

$$\varphi_{jk}(q_\nu^j \mid q_\mu^i, \{n_k^\sigma\}) \approx \varphi_{jk}(q_\nu^j, \{n_k^\sigma\}). \tag{2.1.6}$$

It should be noted that there is a possibility to include the indirect correlation also, if truncation is performed at the subsequent equation of the chain. Furthermore, symmetrizing the expression (2.1.2) for the function $F_{11}(q_\mu^i, q_\nu^j)$ with account of eqs. (2.1.4) through (2.1.6), we find the integration constant $C_{ij}^{\mu\nu}(q_\mu^i)$ as

$$C_{ij}^{\mu\nu}(q_\mu^i) = \lambda_{ij}^{\mu\nu} \exp\left\{\frac{1}{\theta}\varphi_{ij}(q_\mu^i)\right\}.$$

Here $\lambda_{ij}^{\mu\nu}$ is the constant of separation of variables q_μ^i and q_ν^j, which is therefore independent of the particle coordinates within the cells ω_i and ω_j.

A final expression for the two-particle function in the method of average force potentials is found in the form

$$F_{11}^{(1)}(q_\mu^i, q_\nu^j) = C_{ij}^{\mu\nu} \exp\left\{-\frac{1}{\theta}\left[\phi(|q_\mu^i - q_\nu^j|) + \sum_{k\neq i,j}^{N} \varphi_{ik}(q_\mu^i) + \sum_{k\neq i,j}^{N} \varphi_{jk}(q_\nu^j)\right]\right\}, \tag{2.1.7}$$

$$C_{ij}^{\mu\nu} = C_i^\mu \lambda_{ij}^{\mu\nu}. \tag{2.1.8}$$

Making use of the equation

$$F_{11}(q_\mu^i) = \sum_\nu n_j^\nu \int_{\omega_j} F_{11}^{(1)}(q_\mu^i, q_\nu^j)\, \mathrm{d}q_\nu^j, \quad \mu = a, b, \tag{2.1.9}$$

that relates the one-particle and two-particle correleation functions, we obtain a closed system of integral equations for the average force potentials

$$\exp\left\{-\frac{1}{\theta}\varphi_{ij}(q_\mu^i)\right\} = \sum_\nu n_j^\nu \frac{Q_i^\mu}{Q_{ij}^{\mu\nu}} \int_{\omega_j} \exp\left\{-\frac{1}{\theta}\left[\phi(|q_\mu^i - q_\nu^j|) + \sum_{k\neq i,j}^{N} \varphi_{jk}(q_\nu^j)\right]\right\} \mathrm{d}q_\nu^j. \tag{2.1.10}$$

Here the normalization conditions

$$\int_{\omega_i} F_{11}(\boldsymbol{q}^i_\mu)\,\mathrm{d}\boldsymbol{q}^i_\mu = 1, \tag{2.1.11}$$

$$\int_{\omega_i}\int_{\omega_j} F^{(1)}_{11}(\boldsymbol{q}^i_\mu, \boldsymbol{q}^j_\nu)\,\mathrm{d}\boldsymbol{q}^i_\mu\,\mathrm{d}\boldsymbol{q}^j_\nu \approx 1, \tag{2.1.12}$$

are used to determine the integration constants C^μ_i and $C^{\mu\nu}_{ij}$

$$1/C^\mu_i = Q^\mu_i = \int_{\omega_i} \exp\left\{-\frac{1}{\theta}\sum_{j\neq i}^{N} \varphi_{ij}(\boldsymbol{q}^i_\mu)\right\}\mathrm{d}\boldsymbol{q}^i_\mu, \tag{2.1.13}$$

$$\begin{aligned}1/C^{\mu\nu}_{ij} = Q^{\mu\nu}_{ij} = \int_{\omega_i}\int_{\omega_j} \exp\biggl\{-\frac{1}{\theta}\biggl[\phi(|\boldsymbol{q}^i_\mu - \boldsymbol{q}^j_\nu|) + \sum_{k\neq i,j}^{N} \varphi_{ik}(\boldsymbol{q}^i_\mu)\\ + \sum_{k\neq i,j}^{N} \varphi_{jk}(\boldsymbol{q}^j_\nu)\biggr]\biggr\}\,\mathrm{d}\boldsymbol{q}^i_\mu\,\mathrm{d}\boldsymbol{q}^j_\nu.\end{aligned} \tag{2.1.14}$$

It should be noted that the condition (2.1.12) is an approximate one. However, this is not essential for the presentation of the basic idea of the present approach to nonuniform systems since it will not influence the general composition of the statistical fluctuation theory devoped in section 3 using a reduced description. More accurate definitions, which are possible, may only affect a particular form of the closed system (2.1.10) (which, because of the closure, is always approximate) and the expression for the functional $G_i\{n_k\}$ obtained in the following section, which gives the configuration integral of the nonuniform system by eq. (2.2.14).

2.2. *Calculation of the configuration integral and the free energy of a system with a prescribed density field*

Because of the existence of a closed system of integral equations (2.1.10), it is possible (just in the case of a uniform density distribution) to determine the junior correlation functions and to use them for calculation of the average potential energy of the system with a prescribed density field $n_i = n(r_i)$[19,23,24])

$$U\{n_k\} = \frac{1}{2}\sum_{i\neq j}^{N} U_{ij}\{n_k\}, \quad n_k \equiv n^\alpha_k, \tag{2.2.1}$$

$$U_{ij}\{n_k\} = \sum_\mu \sum_\nu n^\mu_i n^\nu_j \int_{\omega_i}\int_{\omega_j} \phi(|\boldsymbol{q}^i_\mu - \boldsymbol{q}^j_\nu|)\hat{F}^{(1)}_{11}(\boldsymbol{q}^i_\mu, \boldsymbol{q}^j_\nu)\,\mathrm{d}\boldsymbol{q}^i_\mu\,\mathrm{d}\boldsymbol{q}^j_\nu. \tag{2.2.2}$$

Here $\hat{F}^{(1)}_{11}$ is the distribution function normalized to unity.

We will differentiate eq. (2.1.10) with respect to the temperature θ, then multiply the result by $n_i^\mu \exp\{-(1/\theta)\sum_{k\neq i,j}^N \varphi_{ik}(\boldsymbol{q}_\mu^i)\}$, integrate with respect to $\boldsymbol{q}_\mu^i$ and sum over μ. Then after simple transformations we get

$$\begin{aligned} U_{ij}\{n_k\}/\theta^2 = {} & n_i^\mu n_j^\nu \frac{\partial}{\partial\theta} \ln \prod_{\mu,\nu} (Q_{ij}^{\mu\nu}/Q_i^\mu Q_j^\nu) \\ & + \sum_\mu n_i^\mu \int_{\omega_i} \frac{\partial}{\partial\theta}\left[-\frac{1}{\theta}\varphi_{ij}(\boldsymbol{q}_\mu^i)\right]\hat{F}_{11}(\boldsymbol{q}_\mu^i)\,\mathrm{d}\boldsymbol{q}_\mu^i \\ & + \sum_\nu n_j^\nu \int_{\omega_j} \frac{\partial}{\partial\theta}\left[-\frac{1}{\theta}\varphi_{ji}(\boldsymbol{q}_\nu^j)\right]\hat{F}_{11}(\boldsymbol{q}_\nu^j)\,\mathrm{d}\boldsymbol{q}_\nu^j. \end{aligned} \tag{2.2.3}$$

A final expression for the internal energy of the system with a prescribed density field will be obtained after the summation over i and j in eq. (2.2.1) with (2.2.3):

$$U\{n_k\} = \frac{1}{2}\theta^2 \frac{\partial}{\partial\theta} \ln \prod_{i=1}^N Q_i\{n_k\}, \tag{2.2.4}$$

where

$$Q_i\{n_k\} = \prod_\mu (Q_i^\mu)^{2n_i^\mu} \prod_{j\neq i}^N \prod_{\mu,\nu} (Q_{ij}^{\mu\nu}/Q_i^\mu Q_j^\nu)^{n_i^\mu n_j^\nu}. \tag{2.2.5}$$

Using the analogue of the Gibbs–Helmholz equation for a nonuniform system as

$$U\{n_k\} = \theta^2 \frac{\partial}{\partial\theta} \ln Q_N\{n_k\}, \tag{2.2.6}$$

we find the configuration integral of the system for the given density field as

$$Q_N\{n_k\} = P\{n_k\} \prod_{i=1}^N Q_i^{1/2}\{n_k\}, \tag{2.2.7}$$

where $P\{n_k\}$ is a combinatorial factor, which is given by the number of physically different distributions of N_a particles of species a over N cells so that a density field determined by a prescribed set of n_k would be obtained. The total number of physically different configurations is obtained after the summation of $P\{n_k\}$ over all the possible density fields within the volume or after integrating it with respect to all n_k for continuous distribution over the fields. Then $P\{n_k\}$ will determine the distribution density of the number of physically different particle configurations in the system over the space of variables n_k satisfying the condition of conservation of the total number of particles in the volume

$$\sum_{k=1}^{N} n_k^a = N_a.$$

Since the total number of physically different configurations in the F_{11}-approximation is $N!/N_a!N_b!$, the normalization condition for $P\{n_k\}$ is

$$\sum_{\{n_k\}} P\{n_k\} = N!/N_a!N_b!, \quad \sum_{k=1}^{N} n_k^\mu = N_\mu. \tag{2.2.8}$$

The form of the function $P\{n_k\}$ can be found as follows. The phase space Λ of the variables n_k will be divided into a finite number of non-overlapping subspaces Λ_α that are formed by the values of the variables n_k satisfying the condition ($\Lambda = \bigcup_\alpha \Lambda_\alpha$, $\alpha = 1, 2, \ldots, M$, $\Delta n = 1/M$)$n_k \in \Lambda_\alpha$, if

$$n_\alpha^\mu \leqslant n_k^\mu < n_\alpha^\mu + \Delta n. \tag{2.2.9}$$

We will find the number of particles of species a and b, which belong to each of the subspaces for the prescribed density field

$$N_\alpha^\mu = \sum_{k \in \Lambda_\alpha} n_k^\mu.$$

Now it is possible to determine $P\{n_k\}$ as the number of physically different distributions of N_μ particles of species μ over M "boxes", which in the present case are the introduced subspaces Λ_α:

$$P\{n_k\} = \prod_{\alpha=1}^{M} N_\alpha!/N_\alpha^a!N_\alpha^b! \simeq \prod_{\alpha=1}^{M} [(n_\alpha^a)^{-n_\alpha^a}(n_\alpha^b)^{-n_\alpha^b}]^{N_\alpha} \tag{2.2.10}$$

Here the Stirling formula is used and a mean particle concentration of species μ in the subspace Λ_α is introduced:

$$n_\alpha^\mu = N_\alpha^\mu/N_\alpha, \quad N_\alpha = N_\alpha^a + N_\alpha^b.$$

Since all $n_k \in \Lambda_\alpha$ satisfy eq. (2.2.9), the expression for $P(n_k\}$ becomes then

$$P\{n_k\} = \prod_{k=1}^{N} \prod_{\mu} (n_k^\mu)^{-n_k^\mu}. \tag{2.2.11}$$

It should be noted that the function $P\{n_k\}$ is approximate because of the use of the Stirling formula, which is quite reasonable because of the necessity to perform the limit transition $V \to \infty$ ($N = V/\omega \to \infty$) with a fixed mean density ($\bar{\rho} = \bar{n}/\omega$, $\bar{n} = \bar{N}_a/N$).

A final expression for the configuration integral of a non-uniform single-component system with the derived expressions for $P\{n_k\}$, $Q_N\{n_k\}$ and eq.

(2.2) included is

$$Q_{N_a}\{n_k\} = \prod_{i=1}^{N} G_i\{n_k\}, \tag{2.2.12}$$

$$G_i\{n_k\} = \omega^{-(1-n_i)} P_i(n_i) \cdot Q_i^{1/2}\{n_k\}, \quad P_i = \prod_{\nu} (n_i^{\nu})^{-n_i^{\nu}}. \tag{2.2.13}$$

The free energy of a nonuniform system, corresponding to the configuration integral expressed by eq. (2.2.12)

$$F\{n_k\} = -\theta \ln Q_{N_a}\{n_k\} = -\theta \sum_{i=1}^{N} \ln G_i\{n_k\},$$

gives the free energy density

$$f(r_i, \{n_k\}) = \frac{\theta}{\omega} \ln G_i\{n_k\},$$

which, as is postulated at present by the generalized van der Waals theory (see a review in ref. 2), is a position function and a functional of the density field.

If the summation is performed over all the possible sets of n_k, the particle number conservation within the volume and the normalization condition (2.2.8) for $P\{n_k\}$ being taken into account, the configuration integral of the system with all nonuniformities due to the density field fluctuations included is then obtained as

$$Q_N(\bar{n}, \theta, V) = \sum_{\{n_k\}} \prod_{i=1}^{N} G_i\{n_k^a\}, \quad \sum_{k=1}^{N} n_k^a = N_a. \tag{2.2.14}$$

Before proceeding to practical application of the results, it is necessary to carry out the so-called renormalization of the average force potentials satisfying eqs. (2.1.10), that determine them up to a certain constant $\lambda_{ij}(\lambda_{ij} = f(\theta, v, \{n_k\}),\ v = V/N_a)$. This ambiguity is caused by the fact that a change of the average force potential by λ_{ij} does not change the normalized correlation functions (their normalization is only changed) and consequently, neither the configuration integral, which has been calculated with them. This degeneration may be eliminated just as in the uniform system theory[19-22]). Eqs. (2.1.10) will be rearranged to equations of the iteration type[26,27]), whose peculiar feature is that when its solution is changed by λ_{ij}, it stops being a solution.

It must be emphasized that in the theory of nonuniform systems, just as in the case of uniform ones[19-22,25-30]), different modifications of a closed system of the integral equations are possible because of renormalization of the average force potentials.

In order to solve the above problem, eq. (2.1.10) will be multiplied by

$Q_{ij}^{\mu\mu}/Q_{j(i)}^{\mu}$ and the potentials will be shifted according to the expression

$$\varphi_{ij}(\boldsymbol{q}_{\mu}^{i}) = \varphi_{ij}^{*}(\boldsymbol{q}_{\mu}^{i}) + \lambda_{ij}^{\mu}. \tag{2.2.15}$$

The substitution of eq. (2.2.15) into eq. (2.2.10) with

$$\lambda_{ij}^{\mu} = \theta \ln(Q_{ij}^{\mu\mu}/Q_{i}^{\mu}Q_{j(i)}^{\mu}) \tag{2.2.16}$$

gives a closed system for the potentials φ_{ij}^{*} (because of the above considerations the subscript * is omitted in the following)

$$\exp\left\{-\frac{1}{\theta}\varphi_{ij}(\boldsymbol{q}_{\mu}^{i})\right\} = \sum_{\nu} n_{j}^{\nu}\frac{Q_{i}^{\mu(\mu)}}{Q_{i}^{\mu(\nu)}Q_{j(i)}^{\nu}}\int_{\omega_j} \exp\left\{-\frac{1}{\theta}\left[\phi(|\boldsymbol{q}_{\mu}^{i}-\boldsymbol{q}_{\nu}^{j}|)\right.\right.$$
$$\left.\left.+\sum_{k\neq i,j}^{N}\varphi_{jk}(\boldsymbol{q}_{\nu}^{j})\right]\right\}\mathrm{d}\boldsymbol{q}_{\nu}^{j}. \tag{2.2.17}$$

Here

$$Q_{i}^{\mu(\nu)} = Q_{ij}^{\mu\nu}/Q_{j(i)}^{\nu}, \quad Q_{j(i)}^{\nu} = \int_{\omega_j} \exp\left\{-\frac{1}{\theta}\sum_{k\neq i,j}^{N}\varphi_{jk}(\boldsymbol{q}_{\nu}^{j})\right\}\mathrm{d}\boldsymbol{q}_{\nu}^{j}. \tag{2.2.18}$$

The further analysis is based on using expression (2.2.14) (written in terms of the potentials φ_{ij}^{*}) for the description of heterogeneous systems, sorption and the density fluctuation theory.

2.3. *Application of the nonuniform system theory to the description of a transient layer at the liquid–gas interface and sorption*

As an application of the theory, we will consider a heterogeneous system with a plane interface. In this case the density depends on one coordinate ($\rho = \rho(z)$). The density distribution will be characterized by a set of concentrations of particles of species μ in every layer with the number l, formed by one row of the cells, whose centers lie on a plane perpendicular to the z-axis. In the coordinate space these layers correspond to the introduced subspace Λ_α of the cells, that belong to the lth layer, for which

$$n_i = n_l, \quad G_i\{n_k\} = G_l\{n_m\}, \quad P_i(n_i) = P_l(n_l), \quad Q_i\{n_k\} = Q_l\{n_m\},$$

with $i \in l$ (since for an infinite system they are independent of the cell position with the individual lth layer, L is the number of cells in a molecular layer, Δz is the layer thickness).

The equation for the density profile of a heterogeneous system results from variation of the free energy[23,31]) (corresponding to the configuration integral (2.2.14) over the density field $\rho = \rho(z)$ (note that $\rho_i = n_i/\omega$). Its approximate analytical solution (in the vicinity of the liquid–gas critical point)

$$\rho(z) = (\rho_l + \rho_g)/2 + (\rho_l - \rho_g)/2 \,\mathrm{th}\, cl, \qquad z = l\Delta z, \tag{2.3.1}$$

actually coincides with the two-parametric trial function suggested by Toxvaerds[12]). The parameter c, which is a function of the thermodynamic variables, vanishes, when one approaches the critical point. The transient layer thickness (the number of molecular layers l_{12} in it) will be defined as region, where a relative deviation of $\tau = \rho(z) - (\rho_l + \rho_g)/2$ from its value in the bulk phases is less than ϵ_0. Then $l_{12} = (1/c)\ln(2 - \epsilon_0)/\epsilon_0$.

The surface tension, calculated with the solution of eq. (2.3.1) (in the same approximation) is defined by the expression

$$\gamma = A(\theta)(\rho_l - \rho_g)^3. \tag{2.3.2}$$

The results of calculations are presented graphically in figs. 1 and 2. All the numerical calculations are performed for the case when $\omega = 1$ and $\theta = 1$ (the unities of the cell volume and the temperature are σ^3 and ϵ/k, respectively, where ϵ and σ are parameters of the Lennard–Jones potential).

Another application of the theory developed here is a description of sorption[33]). If for simplicity, we will consider only a two-component system, the particle distribution over the volume will be determined by variation of the free energy of the heterogeneous system over the two concentration fields for species of the particles. In particular, results of the numerical solution of the equations obtained in such a way for sorption on a nonvolatile adsorbent surface are given in figs. 3 to 5. The equation governing the particle number density distribution as a function of the layer number l contains two parameters (A and B). The parameter

$$B = (\ln f_{ab} - \ln f_{aa})/\ln f_{aa} \tag{2.3.3}$$

determines the degree of the difference between the average force potentials of the adsorbate–adsorbate ($f_{aa} = \langle \exp\{-(1/\theta)\phi_{aa}\}\rangle$) and the adsorbent–ad-

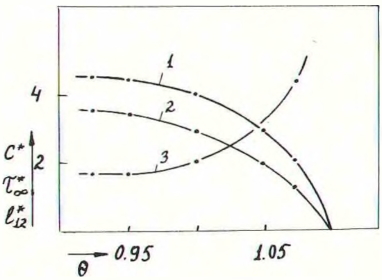

Fig. 1. Plot of c, τ_∞, l_{12} (at $\epsilon_0 = 0.001$) versus temperature: 1, $c = 0.1c^*$; 2, $\tau_\infty = 0.1\tau^*_\infty$; 3, $l_{12} = 10l^*_{12}$.

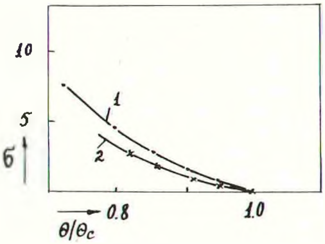

Fig. 2. Comparison of the temperature dependence of the surface tension calculated formula (2.3.2) (curve 1) with the experimental data[32]) (curve 2) correlated by the equation $\gamma = \gamma_0(1 - \theta/\theta_c)^p$, $p = 1.277$, $\gamma_0 = 37.38$ erg/cm^2.

sorbate ($f_{ab} = \langle \exp\{-(1/\theta)\phi_{ab}\}\rangle$) interactions. Angular brackets are used to denote averaging with the aid of the appropriate correlation function.

In fig. 3 curve 1 ($B = 0.4$) is the case when the interaction of molecules a and b is on the average stronger than the interaction of molecules a ($f_{ab} > f_{aa}$) and adsorption is therefore positive. When $B = -1$, adsorption is negative (curve 3), since the interaction of the adsorbate molecules is stronger than that of the adsorbate and adsorbent molecules ($f_{ab} < f_{aa}$). Curve 2 shows the density distribution for $B = -0.4$ when $f_{ab} < f_{aa}$. However, in this case also adsorption is slightly positive because the adsorbent molecule density (in the solid phase $\bar{n} = 1$) exceeds the adsorbate density in the bulk gas phase ($\bar{n} = 0.15$). As a result, the force field of the adsorbent appears to be able to make the gas phase somewhat denser though $f_{ab} < f_{aa}$.

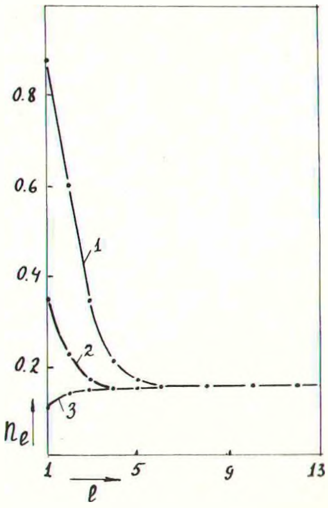

Fig. 3. Plot of density n_l versus the layer number l at three values of B: 1, $B = 0.4$; 2, $B = -0.4$; 3, $B = -1$.

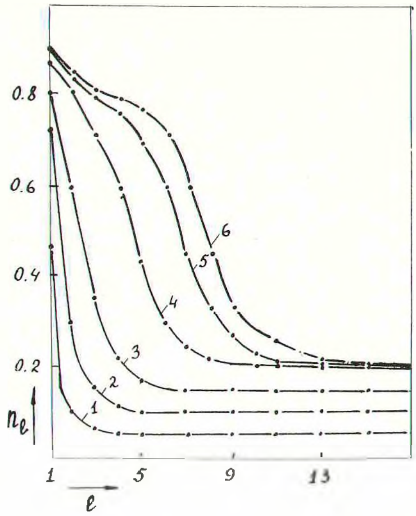

Fig. 4. Density profiles of the adsorption layer of elementary substances on the nonvolatile adsorbent surface ($B = 0.4$) at different densities in a gas phase. 1, $\bar{n} = 0.05$; 2, $\bar{n} = 0.10$; 3, $\bar{n} = 0.15$; 4, $\bar{n} = 0.19$; 5, $\bar{n} = 0.195$; 6, $\bar{n} = 0.1955$ (the gas phase at the coexistence curve at $\theta = 1$ is 0.2).

In fig. 4 a family of curves is presented, which describes the dependence of the adsorption layer microstructure on the prescribed adsorbent surface upon the gas density ($B = 0.4$). If curves 1 to 3 are certain approximation of the so-called monomolecular adsorption, then as far as the gas phase density increases and approaches the value in the coexistence curve ($\bar{n} = 0.2$ at $\theta = 1$), the layer structure drastically changes (curves 4 to 6). In curves 5, 6 an inflection point appears at a density $\bar{n} \approx 0.8$ (the liquid adsorbate density in the coexistence curve at the same temperature). The layer thickness increases

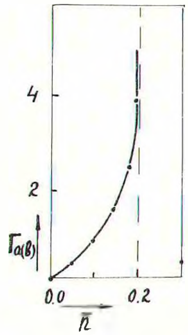

Fig. 5. Adsorption isotherm of elementary substances ($B = 0.4$, $\theta = 1$).

considerably and reaches that of 7 or 8 layers in curve 6. These data clearly indicate polycondensation of the adsorbate at a certain gas phase density. This is also confirmed by the shape of the adsorption isotherm (fig. 5)

$$\Gamma_{a(b)} = \frac{L}{S} \sum_{l=1}^{\infty} (n_l^a - \bar{n}_a), \tag{2.3.4}$$

where S is the interface area.

Thus, the developed statistical theory of nonuniform systems provides a common approach to the transient layer at the liquid–gas interface and to the adsorption layer microstructure on a nonvolatile adsorbent surface. It relates positive and negative adsorptions to the adsorbent and adsorbate intermolecular interaction parameters and makes it possible to calculate adsorption isotherms without any models.

3. Statistical fluctuation theory

As is known[3,4]), a consistent statistical theory, which takes account of the thermodynamic fluctuations of the order parameter field may be developed by determining the effective Hamiltonian for the prescribed order parameter field η and by summation over all the possible field configurations. According to expression (2.2.14) obtained for Q_{N_a}, the order parameter in the theory under development is a density field in the configuration space. Since the summation in eq. (2.2.14) is performed with an additional condition of the total particle number conservation, this restriction may be conveniently eliminated if fluctuations in an open system in equilibrium with a thermostat are considered. This will result in the effective Hamiltonian in the sense of ref. 3 as a density field functional (μ is the chemical potential)

$$\Omega\{n_k\} = -\sum_{i=1}^{N} (\mu n_i + \theta \ln G_i\{n_k\}) \tag{3.1}$$

and in the density distribution function

$$Z\{n_k\} = \exp\left\{-\frac{\Omega\{n_k\}}{\theta}\right\}, \tag{3.2}$$

as a function of N independent variables. In this approach, calculation of the functional integral is therefore equivalent to integration of the function of N variables

$$Z(\theta, \mu, V) = \int_{n_1} \cdots \int_{n_N} \exp\left\{-\frac{1}{\theta}\Omega\{n_k\}\right\} \prod_{k=1}^{N} \mathrm{d}n_k. \tag{3.3}$$

Calculation of Z from eq. (3.3) is as difficult as a calculation of Q_N by direct integration of the Gibbsian function. This is the reason why introduction of a hierarchy of the density distribution correlation functions and obtaining a chain of the equations which relate them, seems very attractive.

3.1. *Reduced description in the fluctuation theory on the basis of conditional space density distribution correlation function*

Practical application of the idea of a reduced description in the fluctuation theory is only possible with an explicit expression for the effective Hamiltonian $\Omega\{n_k\}$, which is determined from the solution of a closed system of integral equations (2.2.17) for the average force potentials. It is clear that it is difficult to find them directly from the solution of eq. (2.2.17) since it is necessary to solve equations, which are valid for the whole nonuniform part of the volume, which in a general case occupies the whole volume V. Indeed, as concerns labour consumption, this problem is to some extent similar to that of finding the Hamiltonian H for a system of N interacting particles. Therefore, just as the Hamiltonian H is simulated by two-particle or multiparticle (in a general case) potentials

$$H = \sum_{i<j}^{N} \phi_{ij} + \sum_{i<j<k}^{N} \phi_{ijk} + \cdots, \tag{3.1.1}$$

the effective Hamiltonian Ω will be expanded with respect to irreducible "interaction" potentials of the density fluctuations. To this end, the contribution to Ω of the density distribution field at certain n_k in each of the cells, say, at that set, which determines the largest contribution to Z, will be considered first.

In particular, for the case of no external fields, for a homogeneous system the equation may be written as

$$\Omega\{n_k\} = \bar{\Omega}(\bar{n}) + \bar{\Omega}\{x_k\}, \quad \bar{n} = \bar{n}_k, \tag{3.1.2}$$

where $x_k = n_k - \bar{n}$ is the density fluctuation at $r_k \in \omega_k$. The fluctuation Hamiltonian $\Omega\{x_k\}$ will be expressed in terms of the irreducible potentials

$$\bar{\Omega}\{x_k\} = \sum_{i=1}^{N} \Psi(x_i) + \sum_{i<j}^{N} \Psi(x_i, x_j) + \sum_{i<j<k}^{N} \Psi(x_i, x_j, x_k) + \cdots . \tag{3.1.3}$$

In order to determine the above potentials Ψ, it is necessary to find the configuration integral of the system with one, two and three density fluctuations within the volume from solution of the closed system of integral equations (2.2.17) for the average force potentials. As a result, expressions for the potentials, which define the effective Hamiltonian of one ($\bar{\Omega}(x_i)$), two

($\bar{\Omega}(x_i, x_j)$) and three ($\tilde{\Omega}(x_i; x_j x_k)$) fluctuations from the uniform density distribution, will be obtained. The expressions

$$
\begin{aligned}
&\Psi(x_i) = \bar{\Omega}(x_i),\\
&\Psi(x_i, x_j) = \bar{\Omega}(x_i, x_j) - \bar{\Omega}(x_i) - \bar{\Omega}(x_j),\\
&\Psi(x_i, x_j, x_k) = \bar{\Omega}(x_i, x_j, x_k) - \bar{\Omega}(x_i, x_j) - \bar{\Omega}(x_i, x_k) - \tilde{\Omega}(x_j, x_k) + \tilde{\Omega}(x_i)\\
&\qquad + \bar{\Omega}(x_j) + \bar{\Omega}(x_k)
\end{aligned}
\tag{3.1.4}
$$

will hold evidently, according to which, as usual, pairwise and triple interaction potentials vanish as their mutual distances increase infinitely. Solution of the above mentioned closed systems of equations for the average force potentials, determining $\bar{\Omega}_i$, $\bar{\Omega}_{ij}$ and $\bar{\Omega}_{ijk}$, is a still complicated but solvable problem, which will be considered separately.

Further, we will obtain the constitutive integro–differential equations for conditional space correlation functions of density[34]). We define the conditional one-particle and two-particle correlation functions, integrating the fluctuation distribution function (3.2) over all the variables but x_i and x_i, x_j, respectively:

$$
W_1(x_i) = \bar{Z}^{-1} \int\limits_{x_1} \mathrm{d}x_1 \cdots \int\limits_{x_{i-1}} \mathrm{d}x_{i-1} \int\limits_{x_{i+1}} \mathrm{d}x_{i+1} \cdots \int\limits_{x_N} \exp\left\{-\frac{1}{\theta}\bar{\Omega}\{x_k\}\right\} \mathrm{d}x_N, \tag{3.1.5}
$$

$$
\begin{aligned}
W_2(x_i, x_j) = \bar{Z}^{-1} &\int\limits_{x_1} \mathrm{d}x_1 \cdots \int\limits_{x_{i-1}} \mathrm{d}x_{i-1} \int\limits_{x_{i+1}} \mathrm{d}x_{i+1} \cdots \int\limits_{x_{j-1}} \mathrm{d}x_{j-1}\\
&\times \int\limits_{x_{j+1}} \mathrm{d}x_{j+1} \cdots \int\limits_{x_N} \exp\left\{-\frac{\bar{\Omega}\{x_k\}}{\theta}\right\} \mathrm{d}x_N.
\end{aligned}
\tag{3.1.6}
$$

A natural condition for the conditional correlation functions of density introduced follows from using the method of conditional correlation functions for the calculation of the effective Hamiltonian $\bar{\Omega}\{x_k\}$ and consists in that the particle number density n_k does not exceed unity ($\rho_k \leqslant \omega^{-1}$ when the F_{11}-approximation is used in a system containing empty cells and cells enclosing no more than one particle ($0 \leqslant \rho_k\omega \leqslant 2$) for the second approximation and so on.).

The constitutive equations are obtained by a standard method of differentiating the distribution (3.2) with respect to the appropriate variables and subsequent integration with respect to all the other variables. In the simplest case of pairwise fluctuation interactions we get

$$
\frac{\partial W_1}{\partial x_i} + \frac{1}{\theta}\frac{\partial \Psi(x_i)}{\partial x_i} W_1 + \frac{1}{\theta}\sum_{j \neq i}^{N} \int\limits_{x_j} \frac{\partial \Psi(x_i, x_j)}{\partial x_i} W_2(x_i, x_j)\, \mathrm{d}x_j = 0, \tag{3.1.7}
$$

$$\frac{\partial W_2}{\partial x_j}+\frac{1}{\theta}\frac{\partial \Psi(x_j)}{\partial x_j}W_2+\frac{1}{\theta}\frac{\partial \Psi(x_i, x_j)}{\partial x_j}W_2$$

$$+\frac{1}{\theta}\sum_{k\neq i,j}^{N}\int\limits_{x_k}\frac{\partial \Psi(x_j, x_k)}{\partial x_j}W_3(x_i, x_j, x_k)\,\mathrm{d}x_k=0. \tag{3.1.8}$$

The subsequent equations of an infinite chain of the integro-differential equations for the correlation density functions can be obtained in a similar way. Analogy between the structures of the above chain of equations and the corresponding equations for the correlation functions of the conditional distribution method in the F_{11}-approximation in the coordinate space, is striking. A certain difference may be ascribed to the second terms in the left-hand sides of eqs. (3.1.7) and (3.1.8), responsible for the interaction of single fluctuations with the external field (via the chemical potential μ) and with the medium with a uniform density distribution.

The analogy found allows the problem of truncation of the chain (3.1.7), (3.1.8) to be solved quite automatically with the aid of the method of average potentials developed earlier.

Eqs. (3.1.7) and (3.1.8) will now be written as

$$\frac{\partial \ln W_1(x_i)}{\partial x_i}=-\frac{1}{\theta}\frac{\partial \Psi(x_i)}{\partial x_i}-\frac{1}{\theta}\sum_{j\neq i}^{N}\int\limits_{x_j}\frac{\partial \Omega(x_i, x_j)}{\partial x_i}W_2(x_j/x_i)\,\mathrm{d}x_j, \tag{3.1.9}$$

$$\frac{\partial \ln W_2(x_j/x_i)}{\partial x_j}=-\frac{1}{\theta}\left[\frac{\partial \Psi(x_j)}{\partial x_j}+\frac{\partial \Psi(x_i, x_j)}{\partial x_j}\right]$$

$$-\frac{1}{\theta}\sum_{k\neq i,j}^{N}\int\limits_{x_k}\frac{\partial \Psi(x_j, x_k)}{\partial x_j}W_3(x_k/x_i, x_j)\,\mathrm{d}x_k, \tag{3.1.10}$$

$$W_2(x_j/x_i)=W_2(x_i, x_j)/W_1(x_i),\quad W_3(x_k/x_i, x_j)=W_3(x_i, x_j, x_k)/W_2(x_i, x_j). \tag{3.1.11}$$

Then it will be possible to introduce "effective average force potentials" of the fluctuation interaction. According to the definition

$$\frac{\partial \gamma_{ij}(x_i)}{\partial x_i}=\int\limits_{x_j}\frac{\partial \Psi(x_i, x_j)}{\partial x_i}W_2(x_j/x_i)\,\mathrm{d}x_j, \tag{3.1.12}$$

$$\frac{\partial \gamma_{jk}(x_j/x_i)}{\partial x_j}=\int\limits_{x_k}\frac{\partial \Psi(x_j, x_k)}{\partial x_j}W_3(x_k/x_i, x_j)\,\mathrm{d}x_k. \tag{3.1.13}$$

As a result, the solutions for $W_1(x_i)$ and $W_2(x_j/x_i)$ may be written in terms of the introduced potentials as

$$W_1(x_i) = C_i \exp\left\{-\frac{1}{\theta}\left[\Psi(x_i) + \sum_{j\neq i}^{N} \gamma_{ij}(x_i)\right]\right\}, \tag{3.1.14}$$

$$W_2(x_j/x_i) = C_{ij}(x_i) \exp\left\{-\frac{1}{\theta}\left[\Psi(x_j) + \Psi(x_i, x_j) + \sum_{k\neq i,j}^{N} \gamma_{jk}(x_j/x_i)\right]\right\}. \tag{3.1.15}$$

Now the approximation for the effective average force potentials of the fluctuation interaction defined by eqs. (3.1.12) and (3.1.13) may be expressed in the form

$$\gamma_{jk}(x_j/x_i) \simeq \gamma_{jk}(x_j). \tag{3.1.16}$$

Further symmetrization of the expression for the function $W_2(x_i, x_j)$ with account for eqs. (3.1.11), (3.1.14) through (3.1.16) gives the integration constant $C_{ij}(x_i)$. This will result in the approximate expression for a two-particle function for the density fluctuation

$$W_2(x_i, x_j) = \lambda_{ij} \exp\left\{-\frac{1}{\theta}\left[\Psi(x_i) + \Psi(x_j) + \Psi(x_i, x_j) + \sum_{k\neq i,j}^{N} (\gamma_{ik}(x_i) + \gamma_{jk}(x_j))\right]\right\}. \tag{3.1.17}$$

A closed system of the equations for the effective average force potentials follows then from the equations

$$W_1(x_i) = \int_{x_j} W_2(x_i, x_j)\, \mathrm{d}x_j \tag{3.1.18}$$

and a subsequent renormalization of the potentials γ_{ik} (it is allowable because of eq. (3.1.18) since the one-particle function has been determined within the normalization constant C_i)

$$\exp\left\{-\frac{1}{\theta}\gamma_{ij}(x_i)\right\} = \frac{\displaystyle\int_{x_j} \exp\left\{-\frac{1}{\theta}\left[\Psi(x_j) + \Psi(x_i, x_j) + \sum_{k\neq i,j}^{N} \gamma_{jk}(x_j)\right]\right\} \mathrm{d}x_j}{\displaystyle\int_{x_j} \exp\left\{-\frac{1}{\theta}\left[\Psi(x_j) + \sum_{k\neq i,j}^{N} \gamma_{jk}(x_j)\right]\right\} \mathrm{d}x_j}. \tag{3.1.19}$$

The above equations may be solved on a computer with the successive approximation method or analytically after certain simplifications, which are possible, say, in dense media or because of the Gaussian type of the first approximation.

3.2. *Calculation of the grand statistical integral with account of the density field fluctuations*

For calculation of a grand statistical integral in the fluctuation theory use will be made of the above analogy between the reduced description of the fluctuations in terms of the correlation density distribution function W and the first F_{11}-approximation of the conditional distribution method for a system with a uniform density distribution. However, attention should be paid to one difference between the reduced description in the fluctuation theory and the method of correlation functions determined in the coordinate space. In fact, the effective potentials Ψ describe "interaction" of fluctuations as that of quasiparticles which arise against the background of a uniform density distribution (e.g. average $\bar{n} = \langle n_k \rangle$). Therefore, in contrast to the potential of intermolecular interaction of particles that compose the system considered, they are dependent on the temperature, chemical potential and state of the medium, which gives rise to the density fluctuations. This peculiar feature had no effect on truncation of the chain (3.1.7), (3.1.8). It however requires that the procedure, which was developed in the case of a configuration integral of uniform^{19,20}) and nonuniform^{23,24}) systems (see also subsection 2.2 of the present work) would be changed for determination of the grand statistical integral on the basis of the correlation density functions (3.1.14), (3.1.17) and a closed system of the integral equations (3.1.19).

The expression for the grand statistical integral (3.3) with eqs. (3.1.2), (3.1.3) taken into account will be written as

$$Z(\theta, \mu, V) = \exp\left\{-\frac{\bar{\Omega}(\bar{n})}{\theta}\right\}\bar{Z}(\bar{n}). \tag{3.2.1}$$

The contribution of the density field fluctuations $\bar{Z}(\bar{n})$ to the grand statistical integral in the model of pairwise fluctuation interactions is of the following form:

$$\bar{Z}(\bar{n}) = \int_0^1 \cdots \int_0^1 \exp\left\{-\frac{1}{\theta}\left[\sum_{i=1}^{N} \Psi(x_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \Psi(x_i, x_j)\right]\right\} \prod_{k=1}^{N} \mathrm{d}n_k, \tag{3.2.2}$$

We will calculate the derivative of $\ln \bar{Z}$ with respect to the temperature θ. After the subsequent integration of each of the terms in the resulting eqs. (3.1.5) and (3.1.6) the derivative $\partial \ln \bar{Z}/\partial\theta$ may be expressed in terms of the junior conditional correlation functions of the density distribution, normalized to unity ($W_1(x_i)$ and $W_2(x_i, x_j)$) as

$$\partial \ln \bar{Z}(\bar{n})/\partial\theta = \theta^{-2}\Bigg(\sum_{i=1}^{N} \int_0^1 \Psi(x_i) W_1(x_i)\, \mathrm{d}n_i$$
$$+\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \int_0^1\int_0^1 \Psi(x_i, x_j) W_2(x_i, x_j)\, \mathrm{d}n_i\, \mathrm{d}n_j\Bigg)$$

$$-\frac{1}{\theta}\left[\sum_{i=1}^{N}\int\limits_0^1 \frac{\partial\Psi(x_i)}{\partial\theta}W_1(x_i)\,\mathrm{d}n_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int\limits_0^1\int\limits_0^1 \frac{\partial\Psi(x_i,x_j)}{\partial\theta}W_2(x_i,x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j\right]. \tag{3.2.3}$$

Expression (3.2.3), alongside with the terms, which determine a mean value of the effective Hamiltonian (a mean "effective potential energy" of fluctuations), contains also a mean value of the derivative of the effective Hamiltonian (the expression in square brackets) with respect to the temperature. Further, eq. (3.2.3) will be used for convenience in the form

$$\frac{\partial \ln \bar{Z}(\bar{n})}{\partial\theta} = -\sum_{i=1}^{N}\int\limits_0^1 \frac{\partial}{\partial\theta}\left(\frac{\Psi(x_i)}{\theta}\right)W_1(x_i)\,\mathrm{d}n_i - \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int\limits_0^1\int\limits_0^1 \frac{\partial}{\partial\theta}\left(\frac{\Psi(x_i,x_j)}{\theta}\right)W_2(x_i,x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j. \tag{3.2.4}$$

Following the basic idea of the average force potential method, we will perform a series of successive transformations of the closed system of integral equations for the average effective potentials γ_{ij} in order to calculate $\partial \ln \bar{Z}(\bar{n})/\partial\theta$ according to eq. (3.2.4). Eqs. (3.1.19) will be written in a form consistent with that of expressions (3.2.2) through (3.2.4):

$$\exp\left\{-\frac{1}{\theta}\gamma_{ij}(x_i)\right\} = \bar{Q}_{j(i)}^{-1}\int\limits_0^1 \exp\left\{-\frac{1}{\theta}\left[\Psi(x_j)+\Psi(x_i,x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\mathrm{d}n_j, \tag{3.2.5}$$

$$\bar{Q}_{j(i)} = \int\limits_0^1 \exp\left\{-\frac{1}{\theta}\left[\Psi(x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\mathrm{d}n_j. \tag{3.2.6}$$

Then we will define the normalization constant of the correlation functions $W_1(x_i)$ and $W_2(x_i, x_j)$ in eqs. (3.1.14), (3.1.17) expressed in terms of the potentials Ψ and γ as

$$\bar{C}_i^{-1} = \bar{Q}_i = \int\limits_0^1 \exp\left\{-\frac{1}{\theta}\left[\Psi(x_i)+\sum_{j\neq i}^{N}\gamma_{ij}(x_i)\right]\right\}\mathrm{d}n_i, \tag{3.2.7}$$

$$\lambda_{ij}^{-1} = \bar{Q}_{ij} = \int\limits_0^1\int\limits_0^1 \exp\left\{-\frac{1}{\theta}\left[\Psi(x_i)+\Psi(x_j)+\Psi(x_i,x_j)+\sum_{k\neq i,j}^{N}\gamma_{ik}(x_i) + \sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\mathrm{d}n_i\,\mathrm{d}n_j. \tag{3.2.8}$$

Multiplying eq. (3.2.5) by $\exp\{-(1/\theta)[\Psi(x_i)+\Sigma_{k\neq i,j}^{N}\gamma_{ik}(x_i)]\}$ and integrating with respect to n_i give

$$\bar{Q}_{ij}=\bar{Q}_i\cdot\bar{Q}_{j(i)}. \tag{3.2.9}$$

Then, differentiation of eq. (3.2.5) with respect to the temperature θ

$$\begin{aligned}&-\frac{\partial}{\partial\theta}\left(\frac{\gamma_{ij}(x_i)}{\theta}\right)\exp\left\{-\frac{1}{\theta}\gamma_{ij}(x_i)\right\}\\&\quad=-\bar{Q}_{j(i)}^{-1}\partial\ln\bar{Q}_{j(i)}/\partial\theta\int_0^1\exp\left\{-\frac{1}{\theta}\left[\Psi(x_j)+\Psi(x_i,x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\mathrm{d}n_j\\&\qquad-\bar{Q}_{j(i)}^{-1}\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{1}{\theta}\left[\Psi(x_j)+\Psi(x_i,x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\\&\qquad\times\exp\left\{-\frac{1}{\theta}\left[\Psi(x_j)+\Psi(x_i,x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}\mathrm{d}n_j\end{aligned} \tag{3.2.10}$$

multiplication of the result by

$$\tilde{Q}_i^{-1}\exp\left\{-\frac{1}{\theta}\left[\Psi(x_i)+\sum_{k\neq i,j}^{N}\gamma_{ik}(x_i)\right]\right\}$$

and integration with respect to n_i, with eqs. (3.1.14) and (3.1.17) for W_1 and W_2 and eqs. (3.2.7) through (3.2.9) taken into account, give

$$\begin{aligned}&-\int_0^1\frac{\partial}{\partial\theta}\left(\frac{\gamma_{ij}(x_i)}{\theta}\right)W_1(x_i)\,\mathrm{d}n_i=-\frac{\partial\ln\bar{Q}_{j(i)}}{\partial\theta}\\&\quad-\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{1}{\theta}[\Psi(x_j)+\Psi(x_i,x_j)]\right\}W_1(x_j)\,\mathrm{d}n_j\\&\quad+\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{\gamma_{ji}(x_j)}{\theta}\right\}W_1(x_j)\,\mathrm{d}n_j-\int_0^1\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i,x_j)}{\theta}\right\}W_2(x_i,x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j.\end{aligned} \tag{3.2.11}$$

Making use of the expression (3.2.7) for the jth cell, we may write

$$\frac{\partial\ln\tilde{Q}_j}{\partial\theta}=-\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{1}{\theta}\left[\Psi(x_j)+\sum_{k\neq i,j}^{N}\gamma_{jk}(x_j)\right]\right\}W_1(x_j)\,\mathrm{d}n_j. \tag{3.2.12}$$

With the aid of the relation (valid because the density fluctuations are considered here only against the background of a uniform distribution: $x_k=n_k-n$)

$$\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{\gamma_{ij}(x_i)}{\theta}\right\}W_1(x_i)\,\mathrm{d}n_i=\int_0^1\frac{\partial}{\partial\theta}\left\{\frac{\gamma_{ji}(x_j)}{\theta}\right\}W_1(x_j)\,\mathrm{d}n_j \tag{3.2.13}$$

and the expression (3.2.12), we may write eq. (3.2.11) as

$$-2\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\gamma_{ij}(x_i)}{\theta}\right\}W_1(x_i)\,\mathrm{d}x_i = \frac{\partial}{\partial\theta}\ln\frac{\tilde{Q}_j}{\tilde{Q}_{j(i)}} - \int_0^1\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i, x_j)}{\theta}\right\}W_2(x_i, x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j. \tag{3.2.14}$$

The above equation will be summed over $j \neq i$

$$-\int_0^1 \frac{\partial}{\partial\theta}\left\{\sum_{j\neq i}^{N}\frac{\gamma_{ij}(x_i)}{\theta}\right\}W_1(x_i)\,\mathrm{d}n_i = \frac{1}{2}\frac{\partial}{\partial\theta}\ln\prod_{j\neq i}^{N}\frac{\tilde{Q}_j}{\tilde{Q}_{j(i)}}$$
$$-\frac{1}{2}\sum_{j\neq i}^{N}\int_0^1\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i, x_j)}{\theta}\right\}W_2(x_i, x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j. \tag{3.2.15}$$

The right-hand side of eq. (3.2.15) can be transformed with the expression for the temperature derivative of $\ln \bar{Q}_i$ (similar to eq. (3.2.12)) taken into account:

$$\partial \ln \bar{Q}_i/\partial\theta + \int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i)}{\theta}\right\}W_1(x_i)\,\mathrm{d}n_i$$
$$= \frac{1}{2}\frac{\partial}{\partial\theta}\ln\prod_{j\neq i}^{N}\frac{\tilde{Q}_j}{\tilde{Q}_{j(i)}} - \frac{1}{2}\sum_{j\neq i}^{N}\int_0^1\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i, x_j)}{\theta}\right\}W_2(x_i, x_j)\,\mathrm{d}n_i\,\mathrm{d}n_j. \tag{3.2.16}$$

After the summation over all i eq. (3.2.16) may be reduced to

$$\sum_{i=1}^{N}\left(\frac{\partial \ln \bar{Q}_i}{\partial\theta} - \frac{1}{2}\frac{\partial}{\partial\theta}\ln\prod_{j\neq i}^{N}\frac{\bar{Q}_j}{\bar{Q}_{j(i)}}\right) = \sum_{i=1}^{N}\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i)}{\theta}\right\}W_1(x_i)\,\mathrm{d}n_i$$
$$-\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int_0^1\int_0^1 \frac{\partial}{\partial\theta}\left\{\frac{\Psi(x_i, x_j)}{\theta}\right\}W_2(x_i, x_j)\,\mathrm{d}n_i, \mathrm{d}n_j. \tag{3.2.17}$$

Comparing the right- and the left-hand sides of eqs. (3.2.4), (3.2.17) and bearing in mind that Q_i is independent of the subscript i ($\bar{Q}_i = \bar{Q}_1$, $\bar{Q}_{j(i)} = \bar{Q}_{j(1)}$ depends on the difference of j and 1), we find

$$\frac{\partial \ln \bar{Z}(\bar{n})}{\partial\theta} = \frac{\partial}{\partial\theta}\left\{\bar{Q}_1^N\left(\prod_{j\neq 1}^{N}\frac{\bar{Q}_{j(1)}}{\bar{Q}_j}\right)^{N/2}\right\}. \tag{3.2.18}$$

Upon integration of the above we may write ($C_1(\mu, v)$ is the integration constant)

$$\bar{Z}(\bar{n}) = \tilde{Q}_1^N\left(\prod_{j\neq 1}^{N}\bar{Q}_{j(1)}/\bar{Q}_j\right)^{N/2}C_1(\mu, v). \tag{3.2.19}$$

If differentiation with respect to the temperature is substituted by differentiation with respect to the chemical potential μ and all the calculations are repeated (beginning with eq. (3.2.4)), the following expression (instead of eq. (3.2.19)) is obtained:

$$\tilde{Z}(\bar{n}) = \tilde{Q}_1^N \left(\prod_{j \neq i}^{N} \tilde{Q}_{j(1)} / \tilde{Q}_j \right)^{N/2} C_2(\theta, v). \tag{3.2.20}$$

From comparison of eqs. (3.2.19) and (3.2.20) it follows that

$$C_1(\mu, V) = C_2(\theta, V) = C(V). \tag{3.2.21}$$

The integration constant is found after the limit transition $\theta \to \infty$. In that case Z moves to the value, which determines the statistical integral of ideal gas. In the F_{11}-approximation for a system with empty and occupied cells used here, the grand statistical integral of ideal gas is of the form

$$Z(\theta \to \infty, \mu, v) = \sum_{N_a=0}^{N} \exp\left\{ -\frac{\mu N_a}{\theta} \right\} \frac{N!}{N_a! N_b!} \omega^{N_a}. \tag{3.2.22}$$

We will perform the limit transition $\theta \to \infty$ in the expression (3.2.1) for Z, taking account of the expression (3.2.20) obtained for the fluctuation part of $\tilde{Z}$ and the thermodynamic potential $\bar{\Omega}(\bar{n})$ of the uniform system (3.1). While comparing the result with eq. (3.2.22), the fact should be borne in mind that in the approach under development the summation over the particle number in an open system has been initially replaced by the summation over all the possible density fields, later by integration with respect to n_k. The comparison gives

$$C(V) = 1. \tag{3.2.23}$$

Finally, the thermodynamic potential $\Omega = -\theta \ln Z(\mu, \theta, V)$ is expressed by the two terms

$$\Omega = \bar{\Omega}(\mu, \theta, V, \bar{n}) + \tilde{\Omega}(\mu, \theta, V, \bar{n}). \tag{3.2.24}$$

Here

$$\bar{\Omega}(\mu, \theta, V, \bar{n}) = -\bar{N}_a \left(\mu + \frac{\theta}{\bar{n}_a} \ln G(\bar{n}) \right), \tag{3.2.25}$$

$$\tilde{\Omega}(\mu, \theta, V, \bar{n}) = -\theta \ln \tilde{Z}(\mu, \theta, V, \bar{n}). \tag{3.2.26}$$

The expression for $G(\bar{n})$ which follows from eqs. (2.2.13), (2.2.5), (2.1.13) and (2.1.14) for $n_k = \bar{n}$ is related in an integral way with the potentials φ_{ij} of a uniform system and the fluctuation part of the statistical integral is expressed similarly but in terms of the average force potentials of the density fluctuation "interaction" (eqs. (3.2.20), (3.2.7) through (3.2.9)).

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