

Statistical Method of Conditional Distributions

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Introduction

Many reported works are concerned with the method of BBGKY correlation functions (see, for example, original monographs [1, 2]) which consists in introduction of unconditional probabilities for arbitrary molecular groups within the whole configuration space. Two junior functions, namely, unary and binary are of greatest importance. As concerned with classical pairwise intermolecular interaction, the most important macroscopic properties of a medium may be expressed in terms of the two correlation functions. Thus, the desired relation is generally found between thermodynamic and structure properties of the material. In practice, however, search for correlation functions which are the solutions of an infinite system of coupled integro-differential equations, involves tremendous difficulties. The latter are overcome in the statistics of low density systems (rarefied gas), but the theory of condensed media fails to do this.

Within the framework of the method of unconditional distribution correlation functions the main problem seems to be unsolved: whether the Gibbsian statistical formalism contains one and the same description for solid and liquid phases, naturally including consideration of phase crystal-liquid, liquid-gas and crystal-gas transitions.

The above difficulties forced the workers to search for a new formalism in the correlation functions theory which would be most suitable for description of condensed state. The method of conditional distribution correlation functions has been developed as a supplement to the BBGKY hierarchy.

The present review is the first attempt to give a systematic description of the method of conditional distribution functions.

1. Correlation Functions of Equilibrium State

The essence of the conditional distribution method is a description of individual states of the whole system of particles rather than the states of individual molecular groups that allows a set of successive approximations for description of condensed state.

We shall first consider a homogeneous one-component molecular system with central (point) interaction. The statistical approach used implies that the whole volume V is divided into N equal cells according to the particle number in the system. For consideration of individual states of the system a set of double-index distribution functions F_{sk}^{sk} is introduced which have a meaning of conditional probability densities of certain configurations of an arbitrary molecular group in a cell considered at a certain distribution of other particles over the other cells [3].

The correlation function $F_{sk}(\mathbf{q}^1, \dots, \mathbf{q}^s)$ ($s = 0, 1, 2, \dots, k$; $k = 1, 2, \dots, n$; $n \ll N$) determines the density of probability of finding any s molecules at points $\mathbf{q}^1, \dots, \mathbf{q}^s$ within one of the cells at the condition that the other $N - s$ molecules are distributed so that more than k molecules cannot be found in any other cell.

So, for example, function $F_{11}(\mathbf{q}^1)$ refers to such states of the system when each of the cells contains a single molecule. The function $F_{22}(\mathbf{q}^1, \mathbf{q}^2)$ means the density of probability of finding any two molecules at \mathbf{q}^1 and \mathbf{q}^2 , respectively, within the molecular volume v_1 at the condition that the other $N - 2$ molecules are distributed so that more than two molecules cannot be found in any other volume v_i ($v_i = V/N$). The condition implies that cells are either empty or contain one or two molecules. Alongside with the functions F_{11} and F_{22} function $F_{12}(\mathbf{q}^1)$ is also used. These are the junior functions most important for investigation of condensed molecular systems.

Introduction of space cells in the conditional distribution method is a mathematical instrument which allows a consistent consideration of statistical properties, being by no means a physical limitation. In this respect the conditional distribution method is not a modification of the so-called cell theory although it may be associated with the latter as far as cells are concerned in both cases.

A model approach is known to neglect a priori a number of physical states although realized by a system. The conditional distribution method means nothing of the kind, since all the possibilities within the Gibbsian statistical formalism are described by the theory (see Sec. 4).

In accordance with the above definition unary function F_{11} may be expressed in terms of the configuration part of the Gibbsian distribution $D_N(\mathbf{q}_1, \dots, \mathbf{q}_N)$ for the whole system normalized to the configuration integral. In an explicit form this definition looks as follows¹⁾

$$F_{11}(\mathbf{q}^1) = N! \int_{v_1} d\mathbf{q}_2 \int_{v_2} d\mathbf{q}_3 \dots \int_{v_N} D_N d\mathbf{q}_N, \quad (1)$$

$$v_2 + v_2 + \dots + v_N = V - v_1, \quad \mathbf{q}^1 \subset v_1;$$

$$D_N = \exp \left\{ -\frac{U_N}{\Theta} \right\}, \quad U_N = \sum_{i < j}^N \Phi(|\mathbf{q}_i - \mathbf{q}_j|) \quad (2)$$

where Φ is a pairwise intermolecular potential, U_N is the potential energy of the whole system; $\Theta = kT$, where T is the absolute temperature, k is the Boltzmann constant.

The surface effects as well as presence of external field are here neglected.

¹⁾ It should be borne in mind that $\mathbf{q}^1, \mathbf{q}^2, \dots, \mathbf{q}^s$ are the coordinates of arbitrary molecules, $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$ are the coordinates of definite molecules.

We shall also give an explicit expression for the binary distribution function $F_{22}(\mathbf{q}^1, \mathbf{q}^2)$ (note that $\mathbf{q}^1, \mathbf{q}^2 \subset v_1$). According to the definition

$$\begin{aligned}
 F_{22}(\mathbf{q}^1, \mathbf{q}^2) = N(N-1) & \left\{ \int_{v_2} \int_{v_3} d\mathbf{q}_3 \int_{v_4} d\mathbf{q}_4 \cdots \int_{v_{N-1}} D_N d\mathbf{q}_N \right. \\
 & + \left. \int_{v_3} d\mathbf{q}_3 \int_{v_4} d\mathbf{q}_4 \cdots \int_{v_N} D_N d\mathbf{q}_N + \cdots \right\} + \frac{1}{2} \left[\int_{v_1} \int_{v_2} d\mathbf{q}_3 d\mathbf{q}_4 \cdots \int_{v_{N-2}} D_N d\mathbf{q}_N \right. \\
 & + \left. \int_{v_1} \int_{v_3} d\mathbf{q}_3 d\mathbf{q}_4 \cdots \int_{v_{N-1}} D_N d\mathbf{q}_N + \cdots \right] \\
 & + \frac{1}{4} \left[\int_{v_1} \int_{v_2} d\mathbf{q}_3 d\mathbf{q}_4 \int_{v_3} \int_{v_3} d\mathbf{q}_5 d\mathbf{q}_6 \cdots \int_{v_{N-3}} D_N d\mathbf{q}_N + \cdots \right] + \cdots \left. \right\}. \quad (3)
 \end{aligned}$$

Each of the above integrals in the first square brackets of the right-hand side of equation (3) accounts for such states of the system when only one of the $N-1$ cells is empty, whereas each of the others but v_1 cells contains one particle, respectively; the integrals in the second square brackets account for the states when already two cells, v_1 including, contain two particles each, etc.

Equation (3) may be abbreviated as

$$F_{22}(\mathbf{q}^1, \mathbf{q}^2) = N! \sum_{\lambda=0}^{[N-2/2]} \sum_{\substack{i, j, \dots, l \\ p, \dots, l}} \int_{v_i} \int_{v_i}^{(\lambda)} \cdots \int_{v_j} \int_{v_j} \int_{v_p} \cdots \int_{v_l}^{(N-2\lambda-2)} D_N d\mathbf{q}_3 \cdots d\mathbf{q}_N, \quad (4)$$

$$i \neq j \neq p \neq \cdots \neq l; \quad i, j, p, \dots, l = 2, 3, \dots, N.$$

The symbols (λ) and $(N-2\lambda-2)$ indicate the number of one-fold and two-fold integrations over the cells. This implies that each of $\lambda+1$ cells contains two particles while other particles are distributed one per cell.

The first sum therefore contains $C_{N-1}^{\lambda+1}$ terms; $[N-2/2]$ is the integral part. All the terms in (4) refer to different physical states of the system.

Alongside with double-index correlation functions distribution functions of the form $F_{sk}^{(p)}(\mathbf{q}^1, \dots, \mathbf{q}^{s+p})$ are also introduced. The latter determines the density of probability that an arbitrary molecular volume v_i but the considered v_1 containing p arbitrary particles at $\mathbf{q}^1, \dots, \mathbf{q}^p$, will contain s molecules at $\mathbf{q}^{p+1}, \dots, \mathbf{q}^{p+s}$, and the distribution of other particles is accounted for in the same way as by the function F_{sk} .

Functions $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2)$, $F_{12}^{(1)}(\mathbf{q}^1, \mathbf{q}^2)$, $F_{12}^{(2)}(\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^3)$ or $F_{22}^{(1)}(\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^3)$ and $F_{22}^{(2)}(\mathbf{q}^1, \dots, \mathbf{q}^4)$ are of practical significance in the theory. So, $F_{11}^{(1)}$ determines the density of probability of finding any two molecules at \mathbf{q}^1 and \mathbf{q}^2 being in two different cells v_1 and v_2 and of distributing the other molecules so that any of the other $N-2$ cells do not contain more than one molecule. Then from the definition

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2) = N! \int_{v_3} d\mathbf{q}_3 \int_{v_4} d\mathbf{q}_4 \cdots \int_{v_N} D_N d\mathbf{q}_N. \quad (5)$$

The function $F_{12}^{(2)}(\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^3)$ may be written as

$$F_{12}^{(2)} = N! \sum_{\lambda=0}^{[N-3/2]} \sum_{i, j, \dots, l} \int_{v_i} \int_{v_i}^{(\lambda)} \dots \int_{v_j} \int_{v_j}^{(\lambda)} \dots \int_{v_l}^{(N-2\lambda-3)} \int_{v_l} D_N d\mathbf{q}_4 \dots d\mathbf{q}_N, \quad (6)$$

$$i \neq j \neq p \neq \dots \neq l; \quad i, j, p, \dots, l = 2, 3, \dots, k-1, k+1, \dots, N.$$

The form (6) implies that one arbitrary molecule is in the cell v_1 at \mathbf{q}^1 and two particles are in the cell v_k at the \mathbf{q}^2 and \mathbf{q}^3 , respectively.

Functions $F_{11}^{(1)}$ and $F_{12}^{(1)}$ as well as F_{22} are of a binary type. But as distinct from $F_{22}(\mathbf{q}^1, \mathbf{q}^2)$ which determines states of two particles in one molecular cell, they describe particle distribution over two different cells. In the conditional distribution method $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2)$ is the simplest binary function.

Simultaneously with ternary function $F_{12}^{(2)}$ or $F_{22}^{(2)}$ when three particles are distributed over two cells, function $F_{11}^{(1)}$ is also used. It is now implied that the coordinates $\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^3$ for three arbitrary particles belong to three different cells, respectively. The same refers to the function $F_{12}^{(1)}$. The difference between $F_{11}^{(1)}$ and $F_{12}^{(1)}$ is that in the former case presence of only one particle in each cell is preconditioned whereas in the latter case such particle distribution over the other but the three cells is implied when among these cells there may be either empty ones or containing one or two molecules.

Besides the distribution functions which describe states of the cells containing one or more particles, functions are used which describe such states when some of the cells considered are empty. So, the functions $F_{sk}^{(0)}$ determine the density of probability that a group of s molecules will be at fixed points of an arbitrary molecular volume v_i at the condition that the first cell is empty and the other particles are distributed over the other cells in the same way as determined by the function F_{sk} . The function F_{02} which will be used further affords an example of a function which describes such states of the system when the first cell is empty and the other cells may not contain more than two particles.

In a general case multi-index correlation functions account for various approximations in the description of condensed media. Considering in the *first main approximation* (the so-called F_{11} -approximation) the distribution when *each of the cells contains one molecule*, we introduce multi-particle distribution functions of the form $F_{11}^{(n-1)}(\mathbf{q}^1, \mathbf{q}^2, \dots, \mathbf{q}^n)$. The symbol $\{n-1\}$ indicates that the group of $n-1$ molecules is fixed at the points $\mathbf{q}^1, \mathbf{q}^2, \dots, \mathbf{q}^{n-1}$ which belong to $n-1$ different cells v_1, v_2, \dots, v_{n-1} and $\mathbf{q}^n \subset v_n$. The function $F_{11}^{(1)} \equiv F_{11}^{(2)}$ is a particular case of such functions.

All the above functions of conditional distributions will also be accompanied by twice conditional functions. For example, the function $F_{11}^{(1)}(\mathbf{q}^i | \mathbf{q}^1)$ will be considered alongside with binary function $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)(\mathbf{q}^1 \subset v_1, \mathbf{q}^i \subset v_i)$. The former determines molecule distribution in the cell v_i at the condition that an arbitrary particle is fixed at the \mathbf{q}^1 in v_1 . The binary function $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)$ is related with $F_{11}(\mathbf{q}^1)$ and $F_{11}^{(1)}(\mathbf{q}^i | \mathbf{q}^1)$ by the probability relation

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) = F_{11}(\mathbf{q}^1) F_{11}^{(1)}(\mathbf{q}^i | \mathbf{q}^1) \quad (7)$$

which is actually a definition of the two-particle correlation function $F_{11}^{(1)}(\mathbf{q}^i | \mathbf{q}^1)$.

The difference between the three-particle conditional function $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i, \mathbf{q}^j)$ and the function $F_{11}^{(1)}(\mathbf{q}^j | \mathbf{q}^1, \mathbf{q}^i)$ is that in the latter case two arbitrary molecules are fixed at the coordinates \mathbf{q}^1 and \mathbf{q}^i in the cells v_1 and $v_i(\mathbf{q}^j \subset v_j)$, respectively.

The junior and major correlation functions are related by integral relationships. Contrary to the unconditional distribution method (the BBGKY-hierarchy) these relationships are more convenient, since determination of, say, the unary function requires in-

tegration of the binary function over the molecular volume rather than over the volume of the whole system

$$F_{11}(\mathbf{q}^1) = \int_{v_i} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^i. \quad (8)$$

Normalization of correlation functions of conditional distributions will be considered later on.

The following F_{12} -approximation of the theory accounts for the states of the system when an arbitrary molecular volume may contain one or two particles or the cell is empty. A set of distribution functions for this approximation is considerably wider than in the previous one. Among these are functions of unary (F_{12} , $F_{12}^{(0)}$, ...), binary (F_{22} , $F_{12}^{(1)}$, $F_{12}^{(01)}$, $F_{22}^{(0)}$, ...) etc. types.

2. Constitutive Integro-Differential Equations

The constitutive equations for correlation (partial) functions of conditional distributions may be found with the aid of an obvious differential relation for the configuration part of the Gibbsian distribution. Indeed, differentiation D_N with respect the particle coordinate over v_1 gives the equation

$$\frac{\partial D_N}{\partial \mathbf{q}_1} + \frac{1}{\Theta} \frac{\partial U_N}{\partial \mathbf{q}_1} D_N = 0. \quad (9)$$

The integro-differential equation for unary function F_{11} will be found from integration of equation (9) with respect to $\mathbf{q}_2, \dots, \mathbf{q}_N$, assuming that two or more molecules cannot be simultaneously present in every individual cell. From definition (1)

$$\int_{v_2} d\mathbf{q}_2 \int_{v_3} d\mathbf{q}_3 \cdots \int_{v_N} \frac{\partial D_N}{\partial \mathbf{q}_1} d\mathbf{q}_N = \frac{\partial}{\partial \mathbf{q}_1} \int_{v_2} d\mathbf{q}_2 \cdots \int_{v_N} D_N d\mathbf{q}_N = \frac{1}{N!} \frac{\partial F_{11}(\mathbf{q}^1)}{\partial \mathbf{q}^1}.$$

Integration of the second term in equation (9) yields

$$\int_{v_2} d\mathbf{q}_2 \cdots \int_{v_N} \frac{\partial U_N}{\partial \mathbf{q}_1} D_N d\mathbf{q}_N = \sum_{j=2}^N \int_{v_2} d\mathbf{q}_2 \cdots \int_{v_N} \frac{\partial \Phi(|\mathbf{q}_1 - \mathbf{q}_j|)}{\partial \mathbf{q}_1} D_N d\mathbf{q}_N.$$

We shall separately consider one integral of the above sum. From definition (5) we have

$$\begin{aligned} \int_{v_2} d\mathbf{q}_2 \cdots \int_{v_N} \frac{\partial \Phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} D_N d\mathbf{q}_N &= \int_{v_2} \frac{\partial \Phi(|\mathbf{q}_1 - \mathbf{q}_2|)}{\partial \mathbf{q}_1} d\mathbf{q}_2 \int_{v_3} d\mathbf{q}_3 \cdots \int_{v_N} D_N d\mathbf{q}_N \\ &= \frac{1}{N!} \int_{v_2} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^2|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2) d\mathbf{q}^2. \end{aligned}$$

The whole sum is thus equal to

$$\begin{aligned} &\frac{1}{N!} \left\{ \int_{v_2} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^2|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2) d\mathbf{q}^2 + \int_{v_3} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^3|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^3) d\mathbf{q}^3 + \dots \right\} \\ &= \frac{1}{N!} \sum_{j=1}^N \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^j|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^j) d\mathbf{q}^j. \end{aligned}$$

Integration of (9) finally results in

$$\frac{\partial F_{11}(\mathbf{q}^1)}{\partial \mathbf{q}^1} + \frac{1}{\Theta} \sum_{j \neq 1}^N \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^j|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^j) d\mathbf{q}^j = 0 \quad (10)$$

where $\mathbf{q}^1 \subset v_1$, $\mathbf{q}^j \subset V - v_1$.

The constitutive equation for the function $F_{12}(\mathbf{q}^1)$ is to be found from integration of equation (9) with respect to variables $\mathbf{q}_2, \mathbf{q}_3, \dots, \mathbf{q}_N$, however, assuming that more than two molecules cannot be contained in each of the cells v_2, v_3, \dots, v_N , with such scheme of particle combination the cells considered may either be empty or contain one or two particles. The derivation of the equation certainly becomes considerably more cumbersome. The final form of the equation

$$\begin{aligned} \frac{\partial F_{12}(\mathbf{q}^1)}{\partial \mathbf{q}^1} + \frac{1}{\Theta} \sum_{j \neq 1}^N \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^{2j}|)}{\partial \mathbf{q}^1} F_{12}^{(1)}(\mathbf{q}^1, \mathbf{q}^{2j}) d\mathbf{q}^{2j} \\ + \frac{1}{\Theta} \sum_{j \neq 1}^N \int \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^{2j}|)}{\partial \mathbf{q}^1} F_{12}^{(2)}(\mathbf{q}^1, \mathbf{q}^{2j}, \mathbf{q}^{3j}) d\mathbf{q}^{3j} = 0 \end{aligned} \quad (11)$$

where $\mathbf{q}^1 \subset v_1$; $\mathbf{q}^{2j}, \mathbf{q}^{3j} \subset V - v_1$.

We shall also present the equation for binary correlation function

$$\begin{aligned} \frac{\partial F_{22}(\mathbf{q}^1, \mathbf{q}^2)}{\partial \mathbf{q}^1} + \frac{1}{\Theta} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^2|)}{\partial \mathbf{q}^1} F_{22}(\mathbf{q}^1, \mathbf{q}^2) \\ + \frac{1}{\Theta} \sum_{j \neq 1}^N \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^{3j}|)}{\partial \mathbf{q}^1} F_{12}^{(2)}(\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^{3j}) d\mathbf{q}^{3j} \\ + \frac{1}{\Theta} \sum_{j \neq 1}^N \int \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^{3j}|)}{\partial \mathbf{q}^1} F_{22}^{(2)}(\mathbf{q}^1, \mathbf{q}^2, \mathbf{q}^{3j}, \mathbf{q}^{4j}) d\mathbf{q}^{3j} d\mathbf{q}^{4j} = 0 \end{aligned} \quad (12)$$

as well as the equation for multi-particle function

$$\frac{\partial F_{11}^{(n-1)}}{\partial \mathbf{q}^n} + \frac{1}{\Theta} \sum_{i=1}^{n-1} \frac{\partial \Phi(|\mathbf{q}^n - \mathbf{q}^i|)}{\partial \mathbf{q}^n} F_{11}^{(n-1)} + \frac{1}{\Theta} \sum_{j=n+1}^N \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^n - \mathbf{q}^j|)}{\partial \mathbf{q}^n} F_{11}^{(n)} d\mathbf{q}^j = 0. \quad (13)$$

The desired correlation functions thus satisfy an infinite system of coupled integro-differential equations, and similarly to the BBGKY-method a general problem here arises of completing this system. It will be seen from what follows that solution of this problem in the conditional distribution method is based on specific possibilities afforded by this method.

3. Method of Average Force Potentials

Practical usage of the chain of integro-differential equations requires preliminary transformation of the chain with the aid of certain approximations to a system of completed equations with respect to junior distribution functions. The BBGKY-method employs various approximations which allow equations for an unary or binary distribution functions to be completed [4-7]. The validity of each of the approximations is limited by a certain range of thermodynamic parameters of the system considered even within one phase.

The method of conditional distributions has afforded a specific solution of the completeness problem typical of this very method. Analysis of the used approximation which is called the method of average force potentials revealed that this is applicable over a wide range of thermodynamic parameters involving various states of aggregation of a molecular system.

Following works [8–10] completing procedure will be considered for a condensed system in the main F_{11} -approximation of the theory.

Equations (10) and (13) defining the unary $F_{11}(\mathbf{q}^1)$ and binary $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)$ distribution functions are to be reduced to the form containing potential of average forces. To this end the first of the above equations will be divided by $F_{11}(\mathbf{q}^1)$ and the second by $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)$ to give

$$\frac{\partial}{\partial \mathbf{q}^1} \ln F_{11}(\mathbf{q}^1) + \frac{1}{\Theta} \sum_{j \neq 1}^N \frac{\partial \varphi_{1j}(\mathbf{q}^1)}{\partial \mathbf{q}^1} = 0, \quad (14)$$

$$\begin{aligned} \frac{\partial}{\partial \mathbf{q}^1} \ln F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) + \frac{1}{\Theta} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^i|)}{\partial \mathbf{q}^1} \\ + \frac{1}{\Theta} \sum_{j \neq 1, i}^N \frac{\partial \varphi_{1j}(\mathbf{q}^1 | \mathbf{q}^i)}{\partial \mathbf{q}^1} = 0, \quad \mathbf{q}^1 \in v_1, \mathbf{q}^i \in v_i, \mathbf{q}^j \in v_j \end{aligned} \quad (15)$$

where

$$\frac{\partial \varphi_{1i}(\mathbf{q}^1)}{\partial \mathbf{q}^1} = \int_{v_i} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^i|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^i | \mathbf{q}^1) d\mathbf{q}^i, \quad (16)$$

$$\frac{\partial \varphi_{1j}(\mathbf{q}^1 | \mathbf{q}^i)}{\partial \mathbf{q}^1} = \int_{v_j} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^j|)}{\partial \mathbf{q}^1} F_{11}^{(1)}(\mathbf{q}^j | \mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^j. \quad (17)$$

In view of the definition of the twice conditional functions given in Sec. 1, $\varphi_{1j}(\mathbf{q}^1)$ may be considered as a potential of the average force exerted by a particle distributed within the cell v_j on a particle fixed at point \mathbf{q}^1 of the cell v_1 . The quantity $\varphi_{1j}(\mathbf{q}^1 | \mathbf{q}^i)$ has a similar meaning, but at an additional condition that at \mathbf{q}^i of the third cell v_i a particle is fixed. It is obvious that the introduced potentials are not uniquely defined by equations (16) and (17).

Formal solutions of equations (14) and (15) are

$$F_{11}(\mathbf{q}^1) = Q_1^{-1} \exp \left\{ -\frac{1}{\Theta} \sum_{j \neq 1}^N \varphi_{1j}(\mathbf{q}^1) \right\}, \quad (18)$$

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) = C_2(\mathbf{q}^i) \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}^1 - \mathbf{q}^i|) + \sum_{j \neq 1, i}^N \varphi_{1j}(\mathbf{q}^1 | \mathbf{q}^i) \right] \right\}. \quad (19)$$

Expressions (18) and (19) do not uniquely define potentials φ , besides they contain normalization multipliers Q_1 and $C_2(\mathbf{q}^i)$ that will further allow re-normalization potentials φ to an arbitrary summand without thinking of possible violation of distribution function normalization.

Use of relation (8) between junior and major distribution functions gives the first equation of new hierarchy that is advantageous over the initial system (10, 13). In the latter the distribution functions which sharply change at small interparticle distances are multiplied by also sharply changing derivatives of interparticle interaction potentials. This results in high sensitivity of integral terms involving such products to small vari-

ations of the distribution functions. As distinct from (10), (13) the completing factors are considered in a new hierarchy but rather represented by one integral term, namely, the average force potential.

The above mentioned property of new hierarchy allows an effective solution of the completing problem. At condensed state the average force on a molecule at $\mathbf{q}^i \subset v_i$ by a particle distributed within the cell v_j may be supposed to weakly depend on the fact whether within a certain third cell a particle is fixed or distributed over the cell volume. Therefore, the approximation seems quite reasonable

$$\varphi_{ij}(\mathbf{q}^i | \mathbf{q}^j) = \varphi_{ij}(\mathbf{q}^i) \quad (20)$$

which allows the system to be completed already by the first equation.

Making use of approximation (20) in equation (19) and of the symmetry of $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)$ with respect to particle transposition, we can write now (19) in the form

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) = Q_2^{-1} \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}^1 - \mathbf{q}^i|) + \sum_{j \neq 1, i}^N [\varphi_{1j}(\mathbf{q}^1) + \varphi_{ij}(\mathbf{q}^i)] \right] \right\}. \quad (21)$$

Use of the relation (8) between the unary and binary correlation functions, reduction of the same terms in the right-hand and lefthand sides of the equality and suitable redefinition of the potentials yield the completed integral equation

$$\exp \left\{ -\frac{1}{\Theta} \varphi_{1i}(\mathbf{q}^1) \right\} = \frac{\int_{v_i} \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}^1 - \mathbf{q}^i|) + \sum_{j \neq 1, i}^N \varphi_{ij}(\mathbf{q}^i) \right] \right\} d\mathbf{q}^i}{\int_{v_i} \exp \left\{ -\frac{1}{\Theta} \sum_{j \neq 1, i}^N \varphi_{ij}(\mathbf{q}^i) \right\} d\mathbf{q}^i}. \quad (22)$$

Equation (22) defines uniquely potentials $\varphi_{1i}(\mathbf{q}^1)^2$. The above nonuniqueness is completely transferred to the normalization constant Q_1 and Q_2 .

The above completing procedure is attractive in view of the possibility to extend it to the major equations of the hierarchy. It is convenient to use $3n$ -fold configurational space of n -particle system for this purpose.

On the base of equation (13) constitutive equation for the n -particle function in such a space can be written in the form

$$\begin{aligned} \frac{\partial \ln F_{11}^{(n-1)}}{\partial \mathbf{q}^{l_1, \dots, l_n}} + \frac{1}{\Theta} \frac{\partial}{\partial \mathbf{q}^{l_1, \dots, l_n}} \sum_{i < j}^n \Phi(|\mathbf{q}^{l_i} - \mathbf{q}^{l_j}|) \\ + \frac{1}{\Theta} \frac{\partial}{\partial \mathbf{q}^{l_1, \dots, l_n}} \sum_{l_{n+1}=1}^N \sum_{i=1}^n \varphi_{il_{n+1}}^{(n-1)} = 0, \quad l_{n+1} \neq l_1, l_2, \dots, l_n \end{aligned} \quad (23)$$

where $\varphi_{il_{n+1}}^{(n-1)} = \varphi_{il_{n+1}}^{(n-1)}(\mathbf{q}^{l_1}, \mathbf{q}^{l_2}, \dots, \mathbf{q}^{l_{i-1}}, \mathbf{q}^{l_{i+1}}, \dots, \mathbf{q}^{l_n})$ is the potential of the average force on the particle fixed at $\mathbf{q}^{l_i} \subset v_i$ by the particle distributed within the cell $v_{l_{n+1}}$ at the condition that in other $n-1$ cells particles are fixed at $\mathbf{q}^{l_1}, \mathbf{q}^{l_2}, \dots, \mathbf{q}^{l_{i-1}}, \mathbf{q}^{l_{i+1}}, \dots, \mathbf{q}^{l_n}$ and $\partial / \partial \mathbf{q}^{l_1, \dots, l_n} \equiv \sum_{j=1}^n \partial / \partial \mathbf{q}^{l_j}$.

²⁾ Expressions (22) are virtually a system of equations defining the average force potentials φ_{1i} for different relative locations of the first and the i -th cells.

The solution of equation (23) is of the form

$$F_{11}^{(n-1)} = Q_n \exp \left\{ -\frac{1}{\Theta} \left[\sum_{i < j}^n \Phi_{i j} + \sum_{l_{n+1}=1}^n \sum_{i=1}^n \varphi_{i l_{n+1}}^{(n-1)} \right] \right\}. \quad (24)$$

Use of the relation between the junior and major functions gives the chain of integral equations with respect to average force potentials

$$\exp \left\{ -\frac{1}{\Theta} \sum_{l_{n+1}=1}^n \sum_{i=1}^n \varphi_{i l_{n+1}}^{(n-1)} \right\} = \frac{Q_n}{Q_{n+1}} \int_{v_{n+1}} \exp \left\{ -\frac{1}{\Theta} \left[\sum_{i=1}^n \Phi_{i l_{n+1}} + \sum_{l_{n+2}=1}^{n+1} \sum_{i=1}^n \varphi_{i l_{n+2}}^{(n)} \right] \right\} d\mathbf{q}^{l_{n+1}}, \quad (25)$$

$$l_{n+1} \neq l_1, l_2, \dots, l_n; \quad l_{n+2} \neq l_1, l_2, \dots, l_{n+1}.$$

System (25) may be completed by any of the equations if use is made of the approximation [11]

$$\varphi_{i l_{n+2}}^{(n)}(\mathbf{q}^{l_i} | \mathbf{q}^{l_1}, \dots, \mathbf{q}^{l_{i-1}}, \mathbf{q}^{l_{i+1}}, \dots, \mathbf{q}^{l_n}) = \varphi_{i l_{n+2}}^{(n-1)}(\mathbf{q}^{l_i} | \mathbf{q}^{l_1}, \dots, \mathbf{q}^{l_{i-1}}, \mathbf{q}^{l_{i+1}}, \dots, \mathbf{q}^{l_{n-1}}). \quad (26)$$

Upon substitution of (26) into (25), re-normalization of the average force potentials and some additional manipulations the equation completed with respect to $\varphi^{(n-1)}$ may be expressed as

$$\exp \left\{ -\frac{1}{\Theta} \varphi_{i l_{n+1}}^{(n-1)} \right\} = \frac{\int_{v_{n+1}} \exp \left\{ -\frac{1}{\Theta} \left[\sum_{i=1}^n \Phi_{i l_{n+1}} + \sum_{l_{n+2}=1}^N \varphi_{i l_{n+1} l_{n+2}}^{(n-1)} \right] \right\} d\mathbf{q}^{l_{n+1}}}{\int_{v_{n+1}} \exp \left\{ -\frac{1}{\Theta} \left[\sum_{i=1}^{n-1} \Phi_{i l_{n+1}} + \sum_{l_{n+2}=1}^N \varphi_{i l_{n+1} l_{n+2}}^{(n-1)} \right] \right\} d\mathbf{q}^{l_{n+1}}}, \quad (27)$$

$$l_{n+2} \neq l_1, l_2, \dots, l_{n-1}, l_{n+1}.$$

The n -particle distribution function is expressed in terms of the average force potentials defined by equation (27) in accordance with (22).

4. Calculation of Configuration Integral and Free Energy

The configuration integral of a system is defined as

$$Q_N = \int_V d\mathbf{q}_1 \int_V d\mathbf{q}_2 \dots \int_V \exp \left\{ -\frac{U_N}{\Theta} \right\} d\mathbf{q}_N. \quad (28)$$

In view of division of volume V of the system into molecular cells in the conditional distribution method, expression (28) may be represented as

$$Q_N = \int d\mathbf{q}_1 \int d\mathbf{q}_2 \dots \int \exp \left\{ -\frac{U_N}{\Theta} \right\} d\mathbf{q}_N$$

$$\sum_{i=1}^N v_i \sum_{j=1}^N v_j \sum_{k=1}^N v_k$$

$$= \sum_{i=1}^N \sum_{j=1}^N \dots \sum_{k=1}^N \int_{v_i} d\mathbf{q}_1 \int_{v_j} d\mathbf{q}_2 \dots \int_{v_k} \exp \left\{ -\frac{U_N}{\Theta} \right\} d\mathbf{q}_N. \quad (29)$$

Among all N^N integrals of the above, both integrals which are only associated with one-fold integration over each of the cells and integrals involving two-, three- etc. up to N -fold integrations over volumes of one and more molecular cells will be encountered.

Let j be multiplicity of integration over the volume of a certain cell (this implies account for the states when the cell considered contains j particles), n_j is the number of cells of the given state containing j particles. Then the number of integrals in (29) covering the states at which there is at least one cell containing s particles and there is no cell containing more than s particles is defined by the expression

$$I_s = N! \sum_{n_j} \frac{N!}{\left(N - \sum_{j=2}^s j n_j\right)! \prod_{j=2}^s n_j! \left[\sum_{j=2}^s (j-1) n_j\right]! \prod_{j=2}^s (j!)^{n_j}} \quad (30)$$

where \sum_{n_j} indicates summation over various sets of n_j satisfying the conditions $\sum_{j=2}^s j n_j \leq N$ and $n_s \neq 0$, $\sum_{j=2}^s j n_j$ is the number of empty cells and cells containing more than one particle or the number of particles which are more than one in a cell, $\sum_{j=2}^s (j-1) n_j$ is the number of empty cells. When $s = 1$ the number of integrals representing the state when each of the cells contains one particle is $N!$. If $s = N$ is assumed, then $n_N = 1$ and $n_j = 0$ as $j \neq N$, then $I_N = N$. The latter case refers to the state when all N particles are contained by one of the cells.

Bearing in mind that function $\exp\{-U/\Theta\}$ is symmetrical with respect to particle transposition, we shall write out in an explicit form all the terms of expression (29) associated with $s = 1$ and $s = N$

$$\begin{aligned} Q_N = N! \int_{v_1} d\mathbf{q}_1 \int_{v_2} d\mathbf{q}_2 \cdots \int_{v_n} \exp\left\{-\frac{U_N}{\Theta}\right\} d\mathbf{q}_N + \cdots \\ + N \int_{v_1} d\mathbf{q}_1 \int_{v_1} d\mathbf{q}_2 \cdots \int_{v_1} \exp\left\{-\frac{U_N}{\Theta}\right\} d\mathbf{q}_N. \end{aligned} \quad (31)$$

It is the first summand here which corresponds to F_{11} -approximation of the theory. Bearing in mind definition (1) of the function $F_{11}(\mathbf{q}^1)$, we may write for this approximation [3]

$$Q_N^{(1)} = \int_{v_1} F_{11}(\mathbf{q}^1) d\mathbf{q}^1. \quad (32)$$

It should be pointed out that contrary to the BBGKY-method in which integration is extended to the whole volume of the system, in the conditional distribution method the configuration integral is calculated by integration F_{11} within one cell.

The subsequent F_{12} -approximation together with the terms associated with $s = 1$ also accounts for two-particle filling of the cells ($s = 2$). Again the configuration integral may be found from integration of the junior functions of conditional distributions over the molecular volume [3]

$$Q_N^{(2)} = F_{02} + \int_{v_1} F_{12}(\mathbf{q}^1) d\mathbf{q}^1 + \frac{1}{2} \int_{v_1} \int_{v_1} F_{22}(\mathbf{q}^1, \mathbf{q}^2) d\mathbf{q}^1 d\mathbf{q}^2. \quad (33)$$

The subsequent approximations include terms with progressively increasing values of s . However for description of systems with high densities consideration of the first F_{11} - and

F_{12} -approximations is sufficient. In this section calculation of the configuration integral and free energy in the main F_{11} -approximation will be considered.

Direct usage of expression (18) in (32) is difficult because the form of the normalization constant $Q_1(v, \theta)$ suitable for (32) cannot be in principle found from solution of a chain of equations. This difficulty may be overcome by using additional relations involving Q_N . Such possibility is afforded by the Gibbs-Helmholz equation for the potential contribution to integral energy

$$E = \theta^2 \frac{\partial(\ln Q_N)}{\partial\theta}. \tag{34}$$

Respectively, with the aid of binary function $\tilde{F}_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i)$ normalized to unity (these functions and the normalization constants associated with them are indicated by a tilde; the other functions are assumed normalized to Q_N) the potential contribution to the internal energy may be written as

$$E = \frac{N}{2} \int_{v_1} d\mathbf{q}^1 \int_{V-v_1} \Phi(|\mathbf{q}^1 - \mathbf{q}^i|) \tilde{F}_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^i. \tag{35}$$

The normalization constant for the unary distribution function follows from (18) as

$$\tilde{Q}_1 = \int_{v_1} \exp \left\{ -\frac{1}{\theta} \sum_{j=1}^N \varphi_{1j}(\mathbf{q}^1) \right\} d\mathbf{q}^1 = Q_1 Q_N^{(1)}. \tag{36}$$

A normalization factor of a binary function may be found from the iteration equation (22) multiplying the right-hand and left-hand sides by $\exp \left\{ -\frac{1}{\theta} \sum_{j=1, i}^N \varphi_{1j}(\mathbf{q}^1) \right\}$ and integrating it with respect to \mathbf{q}^1

$$\tilde{Q}_2 = \tilde{Q}_1 \tilde{Q}_{1i} = Q_2 Q_N^{(1)} \tag{37}$$

where

$$\tilde{Q}_{1i} = \int_{v_i} \exp \left\{ -\frac{1}{\theta} \sum_{j=1, i}^N \varphi_{1j}(\mathbf{q}^i) \right\} d\mathbf{q}^i. \tag{38}$$

Expression (35) may be transformed to (34) by differentiating expression (22) with (38) with respect to θ followed by multiplication of the result by $\tilde{Q}_2^{-1} \exp \left\{ -\frac{1}{\theta} \sum_{j=1, i}^N \varphi_{1j}(\mathbf{q}^1) \right\}$ and integration with respect to \mathbf{q}^1 which results in

$$\begin{aligned} \frac{\partial \ln \tilde{Q}_{1i}}{\partial\theta} - \int_{v_1} \frac{\partial[\varphi_{1i}(\mathbf{q}^1)/\theta]}{\partial\theta} \tilde{F}_{11}(\mathbf{q}^1) d\mathbf{q}^1 &= \frac{1}{\theta^2} \int_{v_1} d\mathbf{q}^1 \int_{v_i} \Phi(|\mathbf{q}^1 - \mathbf{q}^i|) \tilde{F}_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^i \\ &- \int_{v_1} \sum_{j=1, i}^N \frac{\partial[\varphi_{1j}(\mathbf{q}^1)/\theta]}{\partial\theta} \left\{ \int_{v_1} \tilde{F}_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^1 \right\} d\mathbf{q}^i. \end{aligned} \tag{39}$$

With account for the relation

$$\frac{\partial \ln \tilde{Q}_1}{\partial\theta} = - \int_{v_k} \sum_{j \neq k}^N \frac{\partial[\varphi_{kj}(\mathbf{q}^k)/\theta]}{\partial\theta} \tilde{F}_{11}(\mathbf{q}^k) d\mathbf{q}^k \tag{40}$$

equation (39) will be reduced to

$$\frac{1}{\Theta^2} U_{ii} = \frac{\partial}{\partial \Theta} \ln [\bar{Q}_{1i}/\bar{Q}_1] - 2 \int_{v_1} \frac{\partial[\varphi_{1i}(\mathbf{q}^1)/\Theta]}{\partial \Theta} \tilde{F}_{1i}(\mathbf{q}^1) d\mathbf{q}^1 \quad (41)$$

where U_{ii}/Θ^2 is determined by the first summand in the righthand side of (39). Summation of (41) over $i \neq 1$ with (35) yields the equation of the form (34)

$$E = \frac{N}{2} \sum_{i=1}^N U_{ii} = \Theta^2 \frac{\partial}{\partial \Theta} \ln \left\{ \bar{Q}_1^N \left[\prod_{i=1}^N (\bar{Q}_{1i}/\bar{Q}_1) \right]^{N/2} \right\}. \quad (42)$$

Comparison of (42) and (34) gives the configuration integral of the system to within a certain volume function

$$Q_N^{(1)} = \bar{Q}_1^N \left[\prod_{i=1}^N (\bar{Q}_{1i}/\bar{Q}_1) \right]^{N/2} f(v). \quad (43)$$

To find $f(v)$, we consider behaviour of $Q_N^{(1)}$ at high temperatures ($\Theta \gg 1$) and fixed volume. Under these conditions $\bar{Q}_1 \simeq \bar{Q}_{1i} \simeq v$ according to (36) and (38), then from (43) $Q_N^{(1)} \simeq v^N f(v)$. On the other hand, under the same conditions equation (32) implies that $Q_N^{(1)} = N! v^N$, therefore $f = N!$.

The quantity

$$F(v, \Theta) = -\Theta \ln Q \quad (44)$$

where

$$Q = \bar{Q}_1 \left[\prod_{i=1}^N (\bar{Q}_{1i}/\bar{Q}_1) \right]^{1/2} \quad (45)$$

may be conveniently used as free energy.

The pressure is then defined by

$$p = -(\partial F/\partial v)_\Theta. \quad (46)$$

The pressure calculated from (46) is consistent in the thermodynamic sense with caloric state equation (35) as far as the Gibbs-Helmholtz equation is used for determination of the normalization constant. In [12] it is demonstrated that the thermal equation of state defined in terms of the binary function

$$p = \frac{\Theta}{v} - \frac{1}{6v} \int_{v_1} d\mathbf{q}^1 \int_{v-v_1} \Phi'(|\mathbf{q}^1 - \mathbf{q}^i|) |\mathbf{q}^1 - \mathbf{q}^i| \tilde{F}_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) d\mathbf{q}^i \quad (47)$$

is equivalent to equation (46).

Thus, from approximation (20) used in the method of conditional distributions thermodynamic consistency of the thermal and caloric equations of state naturally follows. All the approximations used in the unconditional distribution method have not provided as yet this consistency [13].

5. Thermodynamics of Molecular Condensed Systems and Phase Transitions

The structure of equation (22) allows the solution to be obtained on an electronic computer using the iteration procedure. To this end, in the right-hand side of the equation a certain trial function should be substituted for potentials $\varphi_{ij}(\mathbf{q}^i)$ then upon integration

potential $\varphi_{1i}(\mathbf{q}^1)$ at the first approximation is to be obtained. Further, using the first approximation in the right-hand side of (22) gives the second approximation, and the iteration procedure is continued until two subsequent approximations appear sufficiently close to each other.

Particular calculations are made on the computer Minsk-22M for systems with the interaction governed by the Lennard-Jones potential. In [14] it was found that the maximum configuration integral at thermodynamic parameters associated with crystal state of material is realized when particles are located at points of a face-centered lattice. This determined the dominant form of the molecular crystal structure. Although the method of cell division seems to be of no essential importance, but for the sake of calculation it appeared to be convenient to have molecular cell centers at the points of a face-centered lattice also at the region of liquid and gaseous states. Within calculations use was made of some additional approximations to reduce the integral multiplicity, that is described in more details in [8, 15].

Equation (22) was solved with account for particle correlations with its twelve nearest neighbours. Convergence of the iteration procedure was determined from relative root-mean-square deviation of functions $\psi_{1i} = \exp \{-\varphi_{1i}/\Theta\}$ of two successive approximations calculated at various points of volume v_1 . The calculations were ceased when $I_n = [\sum(\psi_{1i}^{(n)} - \psi_{1i}^{(n-1)})^2 / \sum(\psi_{1i}^{(n)})^2]^{1/2}$ (the sum is taken over all the points within v_1 which were used in numerical integration; n and $n - 1$ are approximation number) reach the values of 10^{-4} . Convergence of the iteration procedure was tested for various kinds of trail functions [15]. Either the molecular potential or the average force potential at similar thermodynamic conditions was taken as trail functions.

Figures 1 and 2 furnish the Helmholtz energy isotherms calculated from (44).

Figure 1 refers to small molecular volumes and covers crystal-gas (curves 1, 2 below the triple point) and crystal-liquid (curves 3–5) phase transitions. The behaviour of the curves at the vicinity of the triple point is inherent. Whereas a liquid peak in curve 1 may be hardly seen, in curve 2 this is clearly marked. However at the temperature $\Theta = 0.78^3$ the peak is still below the common tangent to the crystalline peak and the rarefied gas curve. This indicates that $\Theta = 0.78$ is somewhat lower than the triple point temperature. But already at $\Theta = 0.80$ the rising liquid peak "divides" the tangent into two sections associated with phase transitions crystal-liquid (section $a - b$) and liquid-gas (section $c - d$; point d is outside the plot, see also Fig. 2). Here points a show the subliming points (curves 1, 2) and melting points (curves 3–5), b are crystallization points, c are evaporation points and d are sublimation (curves 1, 2) and condensation (curves 3–5) points. The sections of the Helmholtz energy isotherm to the left of a between b and c and to the right of d determine the steady state regions (of crystal, liquid and gas, respectively).

Extrapolation of crystallization lines (locus of b) and evaporation (locus of c) show that they intersect each other at $\Theta = 0.79$ which is the triple point temperature (experimental $\Theta = 0.7$). A straight-line can be drawn tangential to isotherm $\Theta = 0.79$ at three points which determine molecular volumes of the respective phases (crystal, liquid and gas). They are found to be 1.05; 1.50; 65 (experimental values are 1.035; 1.185; > 200). As was expected, the differences between measured and calculated values become appreciable for a rarefied gaseous phase. Here the F_{11} -approximation cannot pretend to the main contribution to the material description.

Figure 2 is an illustration of the behaviour of the Helmholtz energy at large volumes and temperatures below the triple point (curve 1) between triple and critical points (curve 2) and above the critical point (curve 3). In curve 1 a crystalline peak is only shown, and d lies outside the plot ($v_d > 65$). Peaks of the crystalline phase are omitted from curves 2

³⁾ Temperatures and volumes are throughout measured in units of ϵ/k and σ^3 .

and 3. In curve 2 tangent $c - d$ is drawn which indicates the liquid-gas phase transition; such a tangent cannot be drawn in curve 3, therefore the appropriate isotherms ($\Theta = 1.5$) lie above the critical point. A more detailed investigation has revealed that the critical point temperature is approximately 1.25, and molecular volume is about 4.0 (for argon the experimental values are 1.26 and 3.16, respectively).

Phase diagrams of a simple system in terms of variables (Θ, v) and (p, Θ) plotted in accordance with the developed statistical theory are presented in Figure 3. Figure 4 demonstrates agreements between calculated and experimental melting lines for argon. Information on the behaviour of a unary distribution function within the molecular volume seems useful for identification of phase transitions (Fig. 5). At the thermodynamic conditions corresponding to Helmholtz energy values to the left of a the unary function has a marked maximum at the cell centre (curves 1, 2). Already at a distance of about 0.3 of the linear cell dimension from the centre the value of the function is by five orders smaller than its maximum value, that allows us to identify the material state as a crystal. Convergence of iteration procedure in this case is fair and the solution is obtained after 6 to 10 cycles.

Upon an inconsiderable change of the volume to the right of a the behaviour of the unary function changes sharply. The probability density of finding a particle at the cell bound-

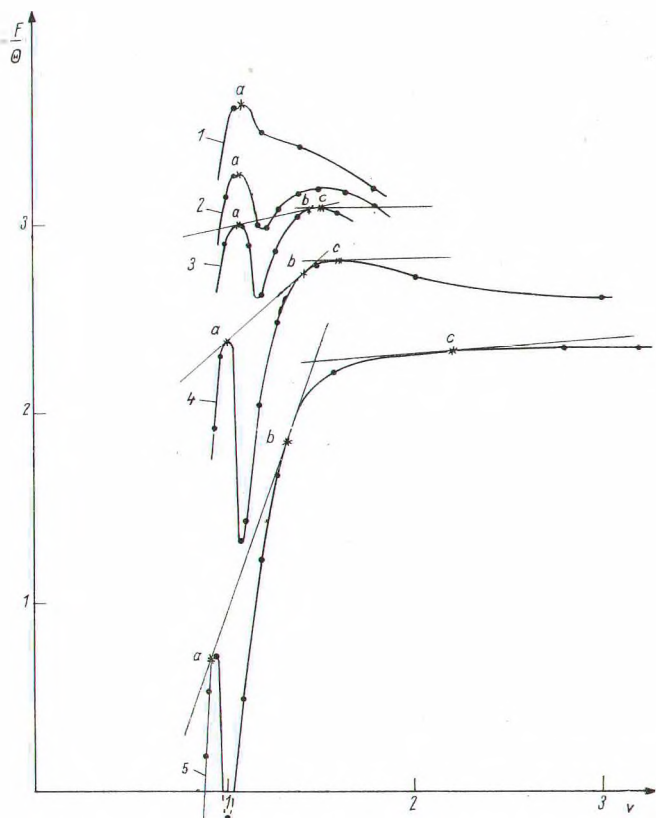


Fig. 1. Helmholtz energy isotherms at small values of molecular volume.
1, $\Theta = 0.75$; 2, $\Theta = 0.78$; 3, $\Theta = 0.80$; 4, $\Theta = 0.85$; 5, $\Theta = 1.0$
●, points calculated on a computer.

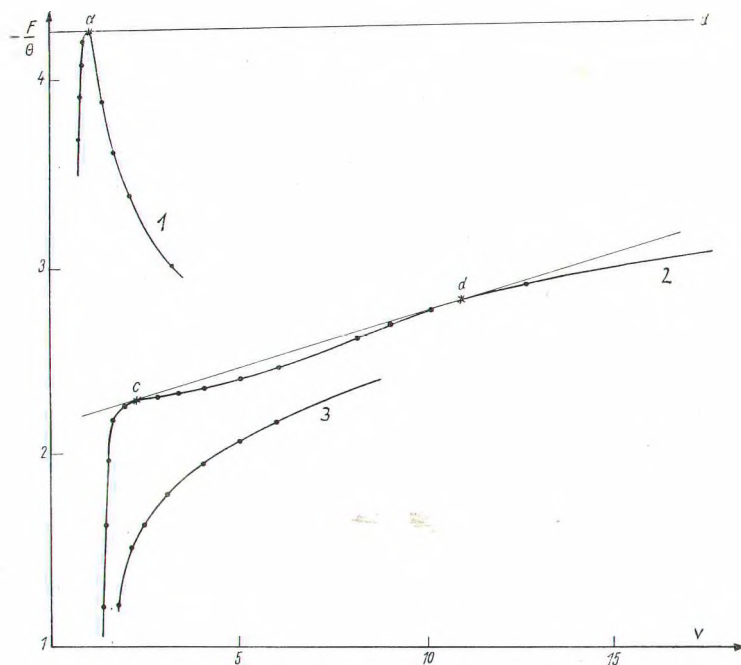


Fig. 2. Helmholtz energy isotherms at mean values of molecular volume.
 1, $\theta = 0.7$; 2, $\theta = 1.0$; 3, $\theta = 1.5$.

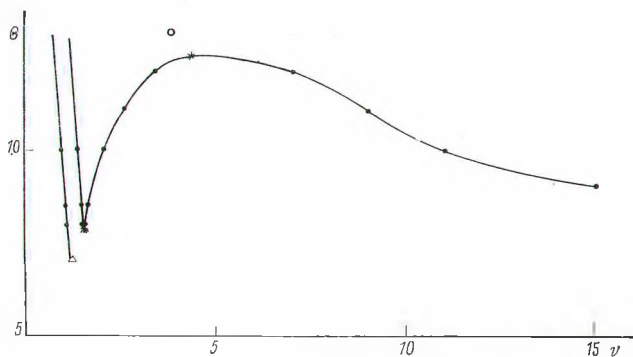


Fig. 3. Phase diagrams of a simple molecular system in F_{II} -approximation.
 (a) in $\theta - v$ variables; (b) in $p - \theta$ variables. Δ , \circ experimental triple and critical points, respectively

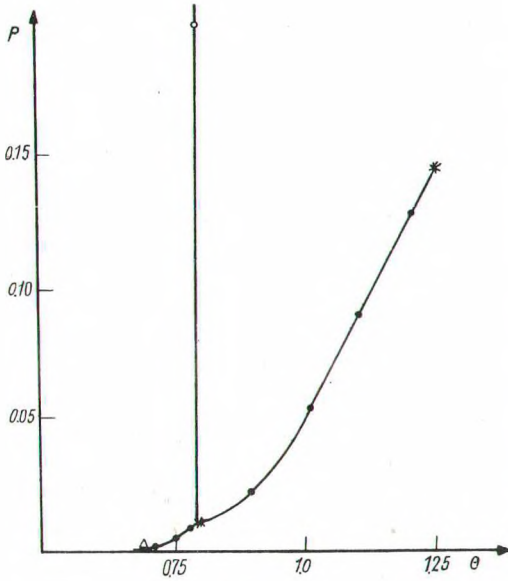


Fig. 3b

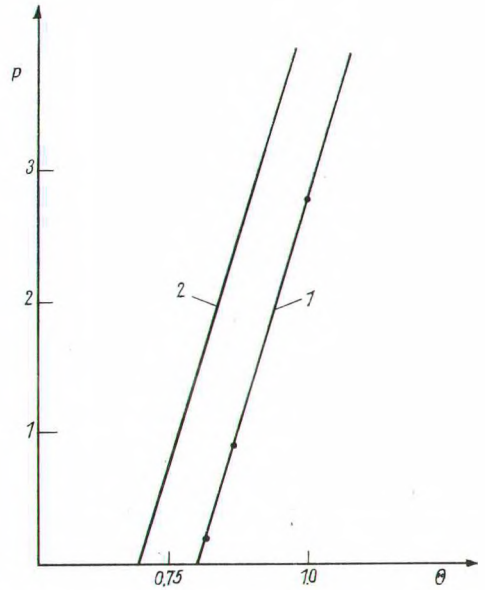


Fig. 4. Melting lines. 1, theoretical in F_{11} -approximation; 2, experimental (for argon)

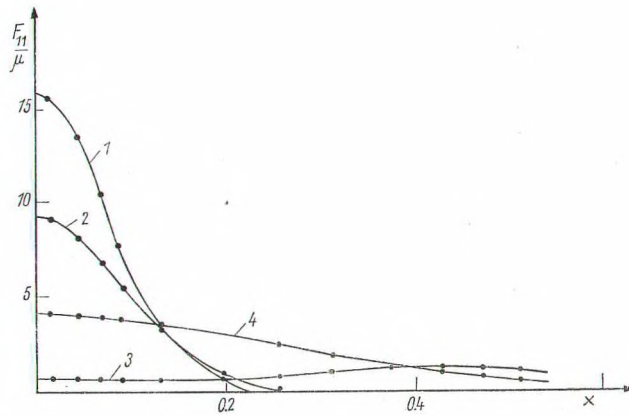


Fig. 5. Unary distribution function $F_{11}(x, 0, 0)$. Axis x is chosen in the direction of one of the nearest neighbours. $\theta = 0.85$. 1, $v = 0.96$, $\mu = 10$; 2, $v = 1.02$, $\mu = 10$; 3, $v = 1.10$, $\mu = 1$; 4, $v = 1.60$, $\mu = 1$.

ary appears to be higher than at the centre (curve 3) that indicates a sharp increase of fluctuations which causes heterogeneous state of the system. Sharp deterioration of iteration convergence is some kind of "a response" to transition of the system into the heterogeneous state. The iteration equation is only solved upon 30 or 40 cycles.

At the liquid state convergence of the iteration procedure is improved and the unary function has maximum at the cell centre, but its values at the boundary of the molecular volume are also of importance (curve 4). As the volume further increases, particle distribution tends to equiprobable one over the cells.

Existence of a crystalline phase may be inferred not only from the analysis of the unary function behaviour within the molecular volume chosen. The conditional distribution method allows demonstration in an explicit form of existence of a long-range order in crystals. Indeed, one-particle distribution function for the whole volume of the system follows in a straightforward manner from the obtained unary conditional function determined in every molecular cell. In a crystalline phase the unary function has sharp maxima at the lattice points. It may be clearly seen that the particles are localized at the lattice points. This also may be inferred from a binary function determined in any of the radial directions.

The situation is different upon transition into liquid or gaseous state. In this case unary and binary functions only reveal existence of a short-range order.

In [16] radial function $g(r)$ is calculated by integration of expression (21) from orientation of vector $\mathbf{q}^i - \mathbf{q}^1$ at the condition that one particle is fixed at the centre of the first cell ($\mathbf{q}^1 = \mathbf{q}_0^1$). It may be supposed that averaging with respect to particle locations in the first cell in the liquid region may not essentially change the result. The calculations compared with different methods are presented in Fig. 6.

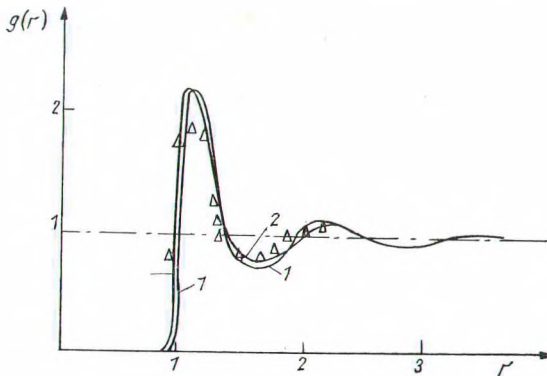


Fig. 6. Radial distribution function at $\Theta = 1.057$ and $\nu = 1.528$. 1, theoretical at F_{11} -approximation; 2, calculated by the Monte Carlo method [34]; Δ , experimental [35].

On the basis of approximation (20) the binary function may be written in terms of unary functions as

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^i) = CF_{11}(\mathbf{q}^1) F_{11}(\mathbf{q}^i) \exp \left\{ -\frac{1}{\Theta} [\Phi(|\mathbf{q}^1 - \mathbf{q}^i|) - \varphi_{1i}(\mathbf{q}^i) - \varphi_{i1}(\mathbf{q}^1)] \right\}. \quad (48)$$

Two integral terms in (48) make an essential difference between the binary conditional function approximation and the approximation of a binary function in terms of unary ones widely used in the unconditional distribution method.

6. Method of Average Force Potentials at the Second Approximation of the Theory

The main F_{11} -approximation fairly describes molecular systems at high densities. So, a melting line of a crystal obtained at this approximation differs from experimental data only by several per cents. Simultaneously the error in the crystallization line increases. This indicates that already at the liquid state region more precise definition of the theory requires consideration of the subsequent F_{12} -approximation which accounts for stronger fluctuations of particle density (the second approximation describes the states when a molecular cell may contain also two molecules).

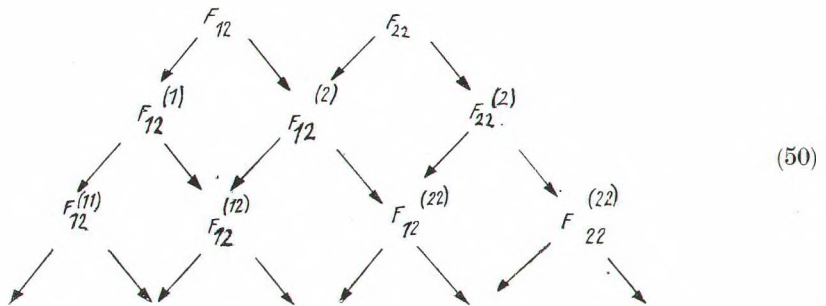
The F_{12} -approximation is of special importance in description of material, particularly, at a state approaching to a critical one when many of the delicate peculiarities of its behaviour are due to large density fluctuations which are not included by the F_{11} -approximation.

In this Section we shall briefly discuss the possibility of breaking the equation chain by the second approximation of the theory and the main difficulties involved.

As it was pointed out above, the F_{12} -approximation involves a wider set of distribution functions which account for various levels of filling molecular cells. The configuration integral in this case is defined by expression (33) or with account for certain symmetry properties by a simpler expression [17]

$$Q_N^{(2)} = \int_{v_1} F_{12}(\mathbf{q}^1) d\mathbf{q}^1 + \int_{v_1} \int_{v_1} F_{22}(\mathbf{q}^1, \mathbf{q}^2) d\mathbf{q}^1 d\mathbf{q}^2. \tag{49}$$

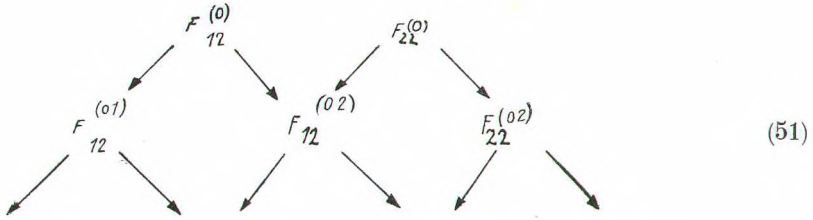
A system of constitutive integro-differential equations begins with equations (11) and (12) for unary $F_{12}(\mathbf{q}^1)$ and binary $F_{22}(\mathbf{q}^1, \mathbf{q}^2)$ distribution functions determined in one cell. Three new functions (binary $F_{12}^{(2)}$, ternary $F_{12}^{(2)} = F_{22}^{(1)}$ and four-particle $F_{22}^{(2)}$) determined already in two cells enter into the two equations. Here the functions are coupled not only according to the number of particles, but also according to the number of cells in which the functions are determined, therefore the system of equations becomes a branched one. Schematically it may be presented as



Each function of the n -th row of the scheme determined in n molecular cells is coupled via integral terms with two functions of the subsequent row determined in $n + 1$ cells. The scheme accounts for symmetricity of the functions with respect to transposition of indices (e.g. $F_{12}^{(12)} = F_{12}^{(21)} = F_{22}^{(11)}$).

A scheme analogous to (50) may also be composed for the functions of which indices involve zeroes indicating that one or several of the cells considered is empty. Functions with different number of zeroes among indices are not coupled, and for functions with the

same number of zeroes a coupling scheme is similar to (50), e.g.



Of this system we need the equation which determines function $F_{12}^{(0)}$

$$\frac{\partial F_{12}^{(0)}(1, 0i)}{\partial q^1} + \frac{1}{\Theta} \sum_{j=1, i}^N \int_{v_j} \int_{v_j} \frac{\partial \Phi(1, 2j)}{\partial q^1} [v^{-1} F_{12}^{(01)}(1, 0i, 2j) + F_{12}^{(02)}(1, 0i, 2j, 3j)] dq^{2j} dq^{3j} = 0. \tag{52}$$

Here $\Phi(1, 2j) = \Phi(|\mathbf{q}^1 - \mathbf{q}^{2j}|)$, and $F_{12}^{(02)}(1, 0i, 2j, 3j)$ determines the probability density of finding one of the molecules of the system in the first cell at \mathbf{q}^1 , that the i -th cell is empty and the two other molecules are in the j -th cell at points \mathbf{q}^{2j} and \mathbf{q}^{3j} . In this Section a figure throughout indicates a particle number, a letter shows a number of the cell containing the particle. For particles within v_1 the number of the volume is not indicated.

To break the system equations (50) transition to the average force potentials is necessary. To this end in accordance with the probability multiplication theorem we introduce twice conditional functions [17]

$$\begin{aligned} F_{12}^{(0)}(1, 0i) &= F_{02}(0i) F_{12}^{(0)}(1 | 0i), \\ F_{12}^{(1)}(1, 2i) &= F_{12}(1) F_{12}^{(1)}(2i | 1), \\ &\dots \end{aligned} \tag{53}$$

$$F_{12}^{(22)}(1, 2i, 3i, 4j, 5j) = F_{12}^{(2)}(1, 2i, 3i) F_{12}^{(22)}(4j, 5j | 1, 2i, 3i).$$

A potential of the average force is further introduced on a particle at $\mathbf{q}^1 \subset v_1$ from one or two particles in the cell v_i

$$\frac{\partial \varphi_{1i}(\mathbf{q}^1)}{\partial q^1} = \int_{v_i} \int_{v_i} \frac{\partial \Phi(1, 2i)}{\partial q^1} [v^{-1} F_{12}^{(1)}(2i | 1)] + F_{22}^{(1)}(2i | 1, 3i)] dq^{2i} dq^{3i}. \tag{54}$$

Besides, potentials of the average forces are also introduced on a particle at $\mathbf{q}^1 \subset v_1$ from the particles in v_i at additional conditions that in a third cell one or two particle is fixed, or the third cell is quite empty. To complete the system of equations, similarly to the F_{11} -approximation, the above potentials of average forces are assumed equal

$$\varphi_{1i}(1) = \varphi_{1i}(1 | 2j) = \varphi_{1i}(1 | 2j, 3j) = \varphi_{1i}(1 | 0j). \tag{55}$$

However the equations together with the mentioned potentials which are main terms also involve potential $\varphi_{11}(1)$ of the average force on a particle at point $\mathbf{q}^1 \subset v_1$, by

another particle distributed over the same cell and potential $\varphi_{1i}(1 | 2i)$ of the average force on the particle at $\mathbf{q}^1 \subset v_1$ from the particle distributed within cell v_1 and at the condition that one particle is fixed at the same cell.

The completed system of equations includes two arbitrary constants. In this case one Gibbs-Helmholtz equation is insufficient for complete determination of the constants. The condition of free energy minimum is additionally used.

7. Multicomponent Systems

The statistical method of conditional distributions described above may also be extended to multicomponent mixtures [3, 13–20]. If we bear in mind the completing procedure for initial equations with the aid of average force potentials and calculation of configuration integral, this extension is far from being trivial and involves additional principle difficulties, that will be demonstrated on an example of a binary mixture.

Let the number of particles be $n = n_a + n_b$ where n_a and n_b are the numbers of particles of the a and b species, respectively. The whole volume V is divided into n equal cells. A set of distribution functions F_{sk} is introduced for description of individual states of the system written almost in the same way as for a single-component system (the molecular species will be indicated by appropriate index at the coordinate). For example, binary function $F_{22}(\mathbf{q}_a^1, \mathbf{q}_b^2)$ means probability density of finding two arbitrary molecules of a and b species within the cell v_1 at \mathbf{q}^1 and \mathbf{q}^2 , respectively, and of finding not more than two molecules of any species in other cells. Binary function $F_{11}^{(1)}(\mathbf{q}_a^1, \mathbf{q}_b^i)$ implies that two arbitrary molecules are in different cells v_1 and v_i , and each of the other cells may not contain more than one particle. In the same F_{11} -approximation ternary correlation functions are used $F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^i, \mathbf{q}_\eta^j)$ ($\mathbf{q}_\mu^1 \subset v_1, \mathbf{q}_\nu^i \subset v_i, \mathbf{q}_\eta^j \subset v_j; \mu, \nu, \eta = a, b$). Integro-differential equations for the introduced correlation (particle) functions are obtained by a more complicated procedure, but, in principle, in the same way as for a single-component case, proceeding from the configuration part of the Gibbsian distribution for the whole system.

For unary and binary functions F_{11} and $F_{11}^{(1)}$ the equations are of the form

$$\frac{\partial F_{11}(\mathbf{q}_\mu^1)}{\partial \mathbf{q}_\mu^1} + \frac{1}{\Theta} \sum_{\nu=a,b} N_\nu \int_{V-v_1} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\nu^2|)}{\partial \mathbf{q}_\mu^1} F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^2) d\mathbf{q}_\nu^2 = 0, \quad (56)$$

N_ν is the mole fraction, of the ν component ($N_\nu = n_\nu/n$)

$$\begin{aligned} \frac{\partial F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^2)}{\partial \mathbf{q}_\mu^1} + \frac{1}{\Theta} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\nu^2|)}{\partial \mathbf{q}_\mu^1} F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^2) \\ + \frac{1}{\Theta} \sum_{\eta=a,b} N_\eta \sum_{j \neq 1, i}^n \int_{v_j} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\eta^j|)}{\partial \mathbf{q}_\mu^1} F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^i, \mathbf{q}_\eta^j) d\mathbf{q}_\eta^j = 0. \end{aligned} \quad (57)$$

The constitutive equations for functions F_{12} and F_{22} will now be presented

$$\begin{aligned} \frac{\partial F_{12}(\mathbf{q}_\mu^1)}{\partial \mathbf{q}_\mu^1} + \frac{1}{\Theta} \sum_{\nu=a,b} N_\nu \sum_{j \neq 1}^n \int_{v_j} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\nu^{2j}|)}{\partial \mathbf{q}_\mu^1} F_{12}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^{2j}) d\mathbf{q}_\nu^{2j} \\ + \frac{1}{\Theta} \sum_{\nu, \eta=a,b} N_\nu N_\eta \sum_{j \neq 1}^n \int_{v_j} \int_{v_j} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\nu^{2j}|)}{\partial \mathbf{q}_\mu^1} F_{22}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^{2j}, \mathbf{q}_\eta^{3j}) d\mathbf{q}_\nu^{2j} d\mathbf{q}_\eta^{3j} = 0, \end{aligned} \quad (58)$$

$$\begin{aligned} \frac{\partial F_{22}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^2)}{d\mathbf{q}_\mu^1} + \frac{1}{\Theta} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\nu^2|)}{d\mathbf{q}_\mu^1} F_{22} + \frac{1}{\Theta} \sum_{\eta=a,b} N_\eta \sum_{j \neq 1}^n \int_{v_j} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\eta^{3j}|)}{\partial \mathbf{q}_\mu^1} F_{22}^{(1)} d\mathbf{q}_\eta^{3j} \\ + \frac{1}{\Theta} \sum_{\eta, \zeta=a,b} N_\eta N_\zeta \sum_{j \neq 1}^n \int_{v_j} \int_{v_j} \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_\eta^{3j}|)}{\partial \mathbf{q}_\mu^1} F_{22}^{(2)} d\mathbf{q}_\eta^{3j} d\mathbf{q}_\zeta^{4j} = 0. \end{aligned} \quad (59)$$

For derivation of the constitutive equations it is convenient to introduce first the correlation functions for certain (fixed) particles and then to find the governing equations for them. The initial equation for the unary function will be

$$\frac{\partial F_{11}(\mathbf{q}_1^\mu)}{\partial \mathbf{q}_1^\mu} + \frac{1}{\Theta} \sum_{j \neq 1}^n \int_{v_j} \sum_{v=a,b} (n_v - \delta_{\mu v}) \frac{\partial \Phi(|\mathbf{q}_1^\mu - \mathbf{q}_i^v|)}{\partial \mathbf{q}_1^\mu} F_{11}^{(1)}(\mathbf{q}_1^\mu, \mathbf{q}_i^v) d\mathbf{q}_i^v = 0. \quad (60)$$

The unary and binary functions are related by the integral relation which follows from the definition

$$F_{11}(\mathbf{q}_1^\mu) = \int_{v_1} \sum_{v=a,b} (n_v - \delta_{\mu v}) F_{11}^{(1)}(\mathbf{q}_1^\mu, \mathbf{q}_i^v) d\mathbf{q}_i^v. \quad (61)$$

Practical use of equations (60) is difficult because they contain particle numbers n_a and n_b as factors. It is therefore more convenient to pass over to correlation functions dependent on the coordinates of arbitrary particles

$$F_{11}(\mathbf{q}_\mu^1) = n_\mu F_{11}(\mathbf{q}_1^\mu), \quad (62)$$

$$F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^1) = n_\mu (n_\nu - \delta_{\mu\nu}) F_{11}^{(1)}(\mathbf{q}_1^\mu, \mathbf{q}_i^v).$$

If the latter equalities are divided by $n_\mu(n-1)!$ and $n_\mu(n_\nu - \delta_{\mu\nu})(n-2)!$, respectively, and the thermodynamic limit is passed over to when $n_a, n_b \rightarrow \infty$, $V \rightarrow \infty$ but $v = V/N$ and $N_\mu = n_\mu/n$ remain constant, then after the substitution into equation (60) we get equation (56) with isolated partially concentration dependence.

Extension of the completing procedure for an infinite chain of equations with the aid of average force potentials to a binary mixture requires transition to twice conditional correlation functions

$$F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^i) = F_{11}(\mathbf{q}_\mu^1) F_{11}^{(1)}(\mathbf{q}_\nu^i | \mathbf{q}_\mu^1), \quad (63)$$

$$F_{11}^{(11)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^i, \mathbf{q}_\eta^j) = F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_\nu^i) F_{11}^{(11)}(\mathbf{q}_\eta^j | \mathbf{q}_\mu^1, \mathbf{q}_\nu^i). \quad (64)$$

These are the functions in terms of which the average force potentials are determined

$$\frac{\partial \varphi_{1i}(\mathbf{q}_\mu^1)}{\partial \mathbf{q}_\mu^1} = \int_{v_1} \sum_{v=a,b} N_v \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_i^v|)}{\partial \mathbf{q}_\mu^1} F_{11}^{(1)}(\mathbf{q}_\nu^i | \mathbf{q}_\mu^1) d\mathbf{q}_\nu^i, \quad (65)$$

$$\frac{\partial \varphi_{1i}(\mathbf{q}_\mu^1 | \mathbf{q}_\eta^j)}{\partial \mathbf{q}_\mu^1} = \int_{v_1} \sum_{v=a,b} N_v \frac{\partial \Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_i^v|)}{\partial \mathbf{q}_\mu^1} F_{11}^{(11)}(\mathbf{q}_\nu^i | \mathbf{q}_\mu^1, \mathbf{q}_\eta^j) d\mathbf{q}_\nu^i. \quad (66)$$

Here $\varphi_{1i}(\mathbf{q}_\mu^1)$ is the average force potential on a molecule of the μ species located at \mathbf{q}^1 of cell v_1 from a molecule of any species in cell v_i . Potential $\varphi_{1i}(\mathbf{q}_\mu^1 | \mathbf{q}_\eta^j)$ has the same meaning but at the additional condition of finding a particle of the η species at $\mathbf{q}^j \subset v_j$.

Using notations (65) and (66) we write down formal solutions of equations (56), (57)

$$F_{11}(\mathbf{q}_\mu^1) = \bar{C}_\mu \exp \left\{ -\frac{1}{\Theta} \sum_{j \neq 1}^n \varphi_{1j}(\mathbf{q}_\mu^1) \right\}, \quad (67)$$

$$F_{11}^{(1)}(\mathbf{q}_v^i | \mathbf{q}_\mu^1) = C_v^i(\mathbf{q}_\mu^1) \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_v^i|) + \sum_{j \neq 1, i}^n \varphi_{ij}(\mathbf{q}_v^i | \mathbf{q}_\mu^1) \right] \right\}. \quad (68)$$

Integration constants will be designated by symbol with a bar when they depend on thermodynamic variables alone.

As in the case of a condensed one-component system, it is assumed that fixed particle in the first cell v_1 slightly changes the averaged effect of the particle in the j -th cell on the particle at \mathbf{q}^i in cell v_i . Moreover, this effect is assumed to be independent of the particle species fixed in the first cell. In view of the above, approximation of the average force potentials becomes

$$\varphi_{ij}(\mathbf{q}_v^i | \mathbf{q}_\mu^1) = \varphi_{ij}(\mathbf{q}_v^i). \quad (69)$$

The relation between C_v^i and the coordinate is found from the symmetry property of the binary function

$$F_{11}(\mathbf{q}_\mu^1) F_{11}^{(1)}(\mathbf{q}_v^i | \mathbf{q}_\mu^1) = F_{11}(\mathbf{q}_v^i) F_{11}^{(1)}(\mathbf{q}_\mu^1 | \mathbf{q}_v^i). \quad (70)$$

Substitution of (67), (68) and (69) into (70) followed by separation of variables gives

$$C_v^i(\mathbf{q}_\mu^1) = \bar{\lambda}_{\mu\nu}^{1i} \exp \left\{ \frac{\varphi_{1i}(\mathbf{q}_\mu^1)}{\Theta} \right\} \quad (71)$$

where $\bar{\lambda}_{\mu\nu}^{1i}$ is the separation of variables constant depending both on mutual location of the first and the i -th cells and on molecular species contained by the cells.

Relations (67)–(69) and (71) allow the form

$$F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_v^i) = \bar{C}_{\mu\nu}^{1i} \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_v^i|) + \sum_{j \neq 1, i}^n (\varphi_{1j}(\mathbf{q}_\mu^1) + \varphi_{ij}(\mathbf{q}_v^i)) \right] \right\}, \quad (72)$$

$$\bar{C}_{\mu\nu}^{1i} = \bar{C}_\mu \bar{\lambda}_{\mu\nu}^{1i}.$$

Then use will be made of the relation for passing from major functions over to junior ones

$$F_{11}(\mathbf{q}_\mu^1) = \sum_{\nu=a,b} N_\nu \int_{v_i} F_{11}^{(1)}(\mathbf{q}_\mu^1, \mathbf{q}_v^i) d\mathbf{q}_v^i. \quad (73)$$

Substitution of (67) and (72) into (73) results in a completed system of integral equations with respect to average force potentials

$$\exp \left\{ -\frac{1}{\Theta} \varphi_{1i}(\mathbf{q}_\mu^1) \right\} = \int_{v_i} \sum_{\nu=a,b} N_\nu \frac{\bar{C}_{\mu\nu}^{1i}}{\bar{C}_\mu} \exp \left\{ -\frac{1}{\Theta} \left[\Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_v^i|) + \sum_{j \neq 1, i}^n \varphi_{ij}(\mathbf{q}_v^i) \right] \right\} d\mathbf{q}_v^i. \quad (74)$$

Equations (74) include greater number of coefficients \bar{C} compared to appropriate equations for a one-component medium. Their calculation involves considerable difficulties peculiar of multicomponent mixtures. From the condition of correlation weakening coefficients $\bar{C}_{\mu\nu}^{1i}$ may be expressed as [20]

$$\bar{C}_{\mu\nu}^{1i} = a_{1i}/Q_\mu Q_\nu \quad (75)$$

where

$$Q_\mu = \int_{v_1} \exp \left\{ -\frac{1}{\theta} \sum_{j=1}^n \varphi_{1j}(\mathbf{q}_\mu^1) \right\} d\mathbf{q}_\mu^1. \quad (76)$$

The expression for Q_ν is similar; a_{1i} is a factor dependent on locations of cells v_1 and v_i alone. Since the configuration integral of the system Q_n at the F_{11} -approximation will be

$$Q_n^{(1)} = \int_{v_1} F_{11}(\mathbf{q}_\mu^1) d\mathbf{q}_\mu^1 \quad (77)$$

then it follows from (67) and (77) that

$$\bar{C}_\mu = Q_n^{(1)}/Q_\mu, \quad \bar{C}_\nu Q_\mu = \bar{C}_\nu Q_\nu. \quad (78)$$

With account for (75) and (78) system (74) becomes

$$\exp \left\{ -\frac{1}{\theta} \varphi_{1i}(\mathbf{q}_\mu^1) \right\} = \frac{a_{1i}}{Q_n^{(1)}} \int_{v_i} \sum_{v=a,b} \frac{N_v}{Q_v} \exp \left\{ -\frac{1}{\theta} \left[\Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_v^i|) + \sum_{j=1,1}^n \varphi_{ij}(\mathbf{q}_v^i) \right] \right\} d\mathbf{q}_v^i. \quad (79)$$

The right-hand sides of each of the above equations include one and the same quantity $a_{1i}/Q_n^{(1)}$. The average force potentials may therefore be renormalized so that (79) would not contain unknown coefficients. Passing over to potentials $\varphi_{1i} + \alpha_{1i} \rightarrow \varphi_{1i}$, we get the set of equations

$$\exp \left\{ -\frac{1}{\theta} \varphi_{1i}(\mathbf{q}_\mu^1) \right\} = \frac{\int_{v_i} \sum_{v=a,b} \frac{N_v}{Q_v} \exp \left\{ -\frac{1}{\theta} \left[\Phi(|\mathbf{q}_\mu^1 - \mathbf{q}_v^i|) + \sum_{j=1,1}^n \varphi_{ij}(\mathbf{q}_v^i) \right] \right\} d\mathbf{q}_v^i}{\int_{v_i} \sum_{v=a,b} \frac{N_v}{Q_v} \exp \left\{ -\frac{1}{\theta} \sum_{j=1,1}^n \varphi_{ij}(\mathbf{q}_v^i) \right\} d\mathbf{q}_v^i}. \quad (80)$$

Uncertainty of constant α_{1i} related with a_{1i} by

$$\exp \left\{ -\frac{\alpha_{1i}}{\theta} \right\} = \frac{a_{1i}}{Q_n^{(1)}} \sum_{v=a,b} N_v Q_{1i}^v \quad (81)$$

where

$$Q_{1i}^v = \int_{v_i} \exp \left\{ -\frac{1}{\theta} \sum_{j=1,1}^n \varphi_{ij}(\mathbf{q}_v^i) \right\} d\mathbf{q}_v^i$$

is transferred to the constant in expression (67) for the unary function which is determined from the normalization condition.

System (80) may be solved on a computer using the iteration procedure. The values of the average force potentials allow the configuration integral and free energy of the mixture to be found.

8. Correlation Functions of Mixed Type

There is a wide class of physical systems whose statistical description may be effective if correlation distribution functions of mixed type are used. A binary mixture with constituent molecules with sharply different masses and interaction (e.g. helium solutions)

affords an example of such systems. The lighter component forms a "rarefied" subsystem, the heavier component should be considered as a condensed molecular medium (interstitial solutions). For such systems it is convenient to describe particle configurations of the "rarefied" subsystem using unconditional probabilities but the condensed system may be conveniently described with the aid of conditional distribution functions. The whole system is actually described by correlation functions of a mixed type [21]. Coordinates of the light particles will be designated through $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$; $\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N$ are used to denote coordinates of the heavy particles. The Gibbsian distribution function D_{N+n} then depends on $n + N$ variables and equations for $D_{N+n}(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{q}_1, \dots, \mathbf{q}_N)$ become

$$\begin{aligned} \frac{\partial D_{N+n}}{\partial \mathbf{q}_1} + \frac{1}{\Theta} \left\{ \frac{\partial}{\partial \mathbf{q}_1} \left[\sum_{j=2}^N \Phi(\mathbf{q}_1, \mathbf{q}_j) + \sum_{j=1}^n \Phi(\mathbf{q}_1, \mathbf{r}_j) \right] \right\} D_{N+n} &= 0, \\ \frac{\partial D_{N+n}}{\partial \mathbf{r}_1} + \frac{1}{\Theta} \left\{ \frac{\partial}{\partial \mathbf{r}_1} \left[\sum_{j=2}^n \Phi(\mathbf{r}_1, \mathbf{r}_j) + \sum_{j=1}^N \Phi(\mathbf{r}_1, \mathbf{q}_j) \right] \right\} D_{N+n} &= 0 \end{aligned} \quad (82)$$

where Φ are pairwise interaction potentials of respective particle species, $n \ll N$. The whole volume V of the system will again be divided into N equal cells of volume $v = V/N$ and distribution functions $F_{m(k)}^{(s)}(\mathbf{r}^1, \dots, \mathbf{r}^m, \mathbf{q}^1, \dots, \mathbf{q}^s)$ will be introduced which determine the probability density of finding m arbitrary light particles at $\mathbf{r}^1, \mathbf{r}^2, \dots, \mathbf{r}^m \subset V$ and of finding s arbitrary heavy particles in a selected molecular cell v_1 at $\mathbf{q}^1, \mathbf{q}^2, \dots, \mathbf{q}^s \subset v_1$ at the condition that each of the other molecular cells $v_i (i \neq 1)$ may not contain more than k heavy particles and $n - m$ light particles are distributed in an arbitrary way over volume V .

For example, according to this definition

$$F_{m(1)}^{(1)} = \frac{n! N!}{(n-m)!} \int_V d\mathbf{r}_{m+1} \dots \int_V d\mathbf{r}_n \int_{v_1} d\mathbf{q}_2 \dots \int_{v_N} d\mathbf{q}_N D_{N+n} \quad (83)$$

Integration of (82) gives constitutive integro-differential equations for correlation functions of a mixed type. These are for the two junior functions $F_{(1)}^{(1)}$ and $F_{1(1)}$

$$\frac{\partial F_{(1)}^{(1)}(\mathbf{q}^1)}{\partial \mathbf{q}^1} + \frac{1}{\Theta} \int_V \frac{\partial \Phi(\mathbf{q}^1, \mathbf{r}^1)}{\partial \mathbf{q}^1} F_{1(1)}^{(1)}(\mathbf{q}^1, \mathbf{r}^1) d\mathbf{r}^1 + \frac{1}{\Theta} \int_{V-v_1} \frac{\partial \Phi(\mathbf{q}^1, \mathbf{q}^2)}{\partial \mathbf{q}^1} F_{(1)}^{(11)}(\mathbf{q}^1, \mathbf{q}^2) d\mathbf{q}^2 = 0, \quad (84)$$

$$\frac{\partial F_{1(1)}^{(1)}(\mathbf{r}^1)}{\partial \mathbf{r}^1} + \frac{1}{\Theta} \int_V \frac{\partial \Phi(\mathbf{r}^1, \mathbf{r}^2)}{\partial \mathbf{r}^1} F_{2(1)}^{(1)}(\mathbf{r}^1, \mathbf{r}^2) d\mathbf{r}^2 + \frac{1}{\Theta} \int_V \frac{\partial \Phi(\mathbf{r}^1, \mathbf{q}^1)}{\partial \mathbf{r}^1} F_{1(1)}^{(11)}(\mathbf{r}^1, \mathbf{q}^1) d\mathbf{q}^1 = 0.$$

The superscripts at $F_{(1)}^{(11)}$ indicate that two heavy particles are in different cells ($\mathbf{q}^1 \subset v_1, \mathbf{q}^2 \subset v_2$).

The presented completing procedure for an infinite system of equations for correlation functions of conditional distributions may also be extended to equations (84). In this case it may be reasonably assumed that light particles have a slight effect on the distribution of heavy particles and, vice versa, distribution of the light particles is primarily determined by their correlation with solvent molecules rather than by their mutual correlation. Therefore the relation may be used

$$\begin{aligned} F_{2(1)}^{(1)}(\mathbf{r}^1, \mathbf{r}^2, \mathbf{q}^1) &= F_{1(1)}^{(1)}(\mathbf{r}^1, \mathbf{q}^1) F_{1(1)}^{(1)}(\mathbf{r}^2, \mathbf{q}^1), \\ F_{1(1)}^{(11)}(\mathbf{r}^1, \mathbf{q}^1, \mathbf{q}^2) &= F_{1(1)}^{(1)}(\mathbf{r}^1) F_{(1)}^{(11)}(\mathbf{q}^1, \mathbf{q}^2), \\ \mathbf{q}^1 &\subset v_1, \quad \mathbf{q}^2 \subset v_2. \end{aligned} \quad (85)$$

With $F_{3(1)} \ll F_{2(1)}$, a completed system of equations for unary and binary functions $F_{(1)}^{(1)}(\mathbf{q}^1)$, $F_{1(1)}(\mathbf{r}^1)$, $F_{2(1)}(\mathbf{r}^1, \mathbf{r}^2)$, $F_{(1)}^{(1)}(\mathbf{q}^1, \mathbf{q}^2)$, $F_{1(1)}^{(1)}(\mathbf{r}^1, \mathbf{q}^1)$ will be obtained.

9. Kinetic Functions. Constitutive Equations

In [22, 23] the conditional distribution method was developed for nonequilibrium processes in systems with central and noncentral intermolecular interactions. Kinetic functions of conditional distributions will be considered in this succession.

Let a one-component homogeneous system consist of N particles. As in the equilibrium case the whole volume V is divided into N cells. Kinetic function $F_{sk}(\mathbf{q}^1, \mathbf{p}^1, \dots, \mathbf{q}^s, \mathbf{p}^s, t)$ then determines the probability density that at moment t dynamic states of an arbitrary group of s molecules are associated with the values $\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, \dots, \mathbf{q}^s, \mathbf{p}^s$ coordinates and momenta in infinitesimal phase volumes $d\mathbf{q}^1 d\mathbf{p}^1, \dots, d\mathbf{q}^s d\mathbf{p}^s$, the points of the configuration space being in one of the cells v , the other $N - s$ molecules being distributed so that any other cell may not contain more than k particles.

The constitutive equations for kinetic particle functions are found from the Liouville equation with respect to the distribution function of dynamic states of the whole system $D(t, \mathbf{q}_1, \mathbf{p}_1, \dots, \mathbf{q}_N, \mathbf{p}_N)$. We shall present here equations for junior functions.

According to the definition the unary kinetic function is

$$F_{11}(\mathbf{q}^1, \mathbf{p}^1, t) = N! \int_{v_2} d\mathbf{q}_2 \int_{v_3} d\mathbf{q}_3 \dots \int_{v_N} d\mathbf{q}_N \int_{\Omega_p} D d\mathbf{p}_2 \dots d\mathbf{p}_N \quad (86)$$

where Ω_p is the momenta space.

A simplest binary function is determined as

$$F_{11}^{(1)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, t) = N! \int_{v_3} d\mathbf{q}_3 \int_{v_4} d\mathbf{q}_4 \dots \int_{v_N} d\mathbf{q}_N \int_{\Omega_p} D d\mathbf{p}_3 \dots d\mathbf{p}_N, \quad (87)$$

$$\mathbf{q}^1 \subset v_1, \quad \mathbf{q}^2 \subset v_2.$$

If the Liouville equation is now integrated over the variables $\mathbf{q}_2, \mathbf{p}_2, \dots, \mathbf{q}_N, \mathbf{p}_N$ so that each cell of the volume V cannot simultaneously contain two or more particles, then with the definition of the unary and binary functions we finally obtain

$$\frac{\partial F_{11}(\mathbf{q}^1, \mathbf{p}^1, t)}{\partial t} + \frac{\mathbf{p}^1}{m} \cdot \frac{\partial F_{11}}{\partial \mathbf{q}^1} = \int_{V-v_1} \int_{\Omega_p} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^2|)}{\partial \mathbf{q}^1} \cdot \frac{\partial F_{11}^{(1)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, t)}{\partial \mathbf{p}^1} d\mathbf{q}^2 d\mathbf{p}^2. \quad (88)$$

For function $F_{12}(\mathbf{q}^1, \mathbf{p}^1, t)$ the equation becomes

$$\frac{\partial F_{12}}{\partial t} + \frac{\mathbf{p}^1}{m} \cdot \frac{\partial F_{12}}{\partial \mathbf{q}^1} = \int_{V-v_1} \int_{\Omega_p} \frac{\partial \Phi(|\mathbf{q}^1 - \mathbf{q}^2|)}{\partial \mathbf{q}^1} \cdot \frac{\partial \tilde{F}_{12}^{(1)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, t)}{\partial \mathbf{p}^1} d\mathbf{q}^2 d\mathbf{p}^2. \quad (89)$$

The additional distribution function is here introduced $\tilde{F}_{12}^{(1)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, t) = F_{12}^{(1)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, t) + \int_{v_j} \int_{\Omega_p} F_{12}^{(2)}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{q}^2, \mathbf{p}^2, \mathbf{q}^3, \mathbf{p}^3, t) d\mathbf{q}^3 d\mathbf{p}^3$ which determines the probability

density of finding the molecule in the selected cell v_1 at point \mathbf{q}^1 with momentum \mathbf{p}^1 , of finding the second molecule in another cell v_j at \mathbf{q}^2 with momentum \mathbf{p}^2 at the condition that in the same j -th cell there is one molecule more, and the other $N - 3$ molecules are distributed over the other $N - 2$ cells so that each cell may not contain more than two molecules.

The method of obtaining integro-differential equations for kinetic functions has been extended to multi-component systems with point (central) interaction [23].

A system of nonspherical molecules with noncentral interaction will now be considered [24]. In view of a molecular system of rigid dipoles, translational and rotational degrees of freedom will only be considered. A state of an individual molecule is described in terms of a vector-radius of its inertia centre \mathbf{q} , the momentum \mathbf{p} conjugated with it, variables determining orientation of molecule α_β (a set of angular coordinates is for convenience denoted through α) and intrinsic angular momentum \mathbf{l} . Then unary function F_{11} will depend on the variables \mathbf{q} , \mathbf{p} , α , \mathbf{l} and t . Binary function $F_{11}^{(2)}$ depends now on the variables $\mathbf{q}^1, \mathbf{p}^1, \alpha^1, \mathbf{l}^1, \mathbf{q}^2, \mathbf{p}^2, \alpha^2, \mathbf{l}^2, t$.

The initial Liouville equation for the system considered is of the form

$$\frac{\partial D}{\partial t} + \sum_{k=1}^N \frac{\mathbf{p}_k}{m} \cdot \frac{\partial D}{\partial \mathbf{q}_k} + \sum_{k=1}^N \frac{d\alpha_k}{dt} \cdot \frac{\partial D}{\partial \alpha_k} + \sum_{k \neq j}^N \left(\mathbf{F}_{kj} \cdot \frac{\partial D}{\partial \mathbf{p}_k} + \mathbf{M}_{kj} \cdot \frac{\partial D}{\partial \mathbf{l}_k} \right) = 0 \quad (90)$$

where \mathbf{F}_{kj} and \mathbf{M}_{kj} are the force and the moment of couple of intermolecular interaction on molecule number k from the j -th molecule. If unit vector \mathbf{e} is introduced which is rigidly joined with the linear molecule and thus characterizes the molecule orientation, then the moment of couple may be expressed in terms of a pairwise potential as

$$\mathbf{M}_{kj} = \mathbf{e}_k \times \frac{\partial \Phi_{kj}}{\partial \mathbf{e}_k}.$$

For a system with noncentral interaction the relation holds

$$\mathbf{M}_{kj} + \mathbf{M}_{jk} + \mathbf{r}_{kj} \times \mathbf{F}_{kj} = 0, \quad \mathbf{F}_{kj} = \frac{\partial \Phi_{kj}}{\partial \mathbf{r}_{kj}}.$$

The Hamilton of the whole system may conveniently be written down as

$$H = \frac{1}{2} \sum_{k=1}^N \left[\frac{\mathbf{p}_k^2}{m} + \sum_{\alpha=1}^3 \frac{l_{k\alpha}^2}{I_\alpha} \right] + \frac{1}{2} \sum_{k \neq j}^N \Phi(\mathbf{r}_{kj}, \mathbf{e}_k, \mathbf{e}_j) \quad (91)$$

where I_α are principal moments of inertia of molecules.

With the definition of the unary function in mind

$$F_{11}(\mathbf{q}^1, \mathbf{p}^1, \alpha^1, \mathbf{l}^1, t) = N! \int_{v_2} d\mathbf{q}_2 \int_{v_3} d\mathbf{q}_3 \cdots \int_{v_N} d\mathbf{q}_N \int_{\Omega_{p\alpha 1}} D d\mathbf{p}_2 \cdots d\mathbf{p}_N d\alpha_2 \cdots d\alpha_N d\mathbf{l}_2 \cdots d\mathbf{l}_N \quad (92)$$

we shall integrate equation (90) with respect to variables $\mathbf{q}_2, \mathbf{p}_2, \alpha_2, \mathbf{l}_2, \dots, \mathbf{q}_N, \mathbf{p}_N, \alpha_N, \mathbf{l}_N$ so that any molecular cell may not contain simultaneously two or more molecules. Finally, the equation is obtained

$$\begin{aligned} \frac{\partial F_{11}}{\partial t} + \frac{\mathbf{p}^1}{m} \cdot \frac{\partial F_{11}}{\partial \mathbf{q}^1} + \dot{\alpha}^1 \cdot \frac{\partial F_{11}}{\partial \alpha^1} = & - \int_{V-v_1} \cdots \int_{\Omega_1} \mathbf{F} \cdot \frac{\partial F_{11}^{(1)}}{\partial \mathbf{p}^1} d\mathbf{q}^2 d\mathbf{p}^2 d\alpha^2 d\mathbf{l}^2 \\ & - \int_{V-v_1} \cdots \int_{\Omega_1} \mathbf{M} \cdot \frac{\partial F_{11}^{(1)}}{\partial \mathbf{l}^1} d\mathbf{q}^2 d\mathbf{p}^2 d\alpha^2 d\mathbf{l}^2 \end{aligned} \quad (93)$$

where $\mathbf{F}(\mathbf{r}^{12}, \alpha^1, \alpha^2)$ and $\mathbf{M}(\mathbf{r}^{12}, \alpha^1, \alpha^2)$ is the force and the moment of couple on a molecule at state $(\mathbf{q}^1, \mathbf{p}^1, \alpha^1, \mathbf{l}^1)$; $F_{11}^{(1)}(\mathbf{q}^1, \mathbf{q}^2, \dots)$ is the binary function $(\mathbf{q}^1 \subset v_1, \mathbf{q}^2 \subset v_i)$, $\mathbf{r}^{12} = \mathbf{q}^2 - \mathbf{q}^1$, $\dot{\alpha} \cdot \partial/\partial\alpha = \sum_{\beta=1}^3 \dot{\alpha}_{\beta} \partial/\partial\alpha_{\beta}$.

In [23–25] well-known phenomenological transfer equations (conservation laws) of continuum are obtained with the aid of kinetic functions of conditional distributions. The attention is immediately attracted to the fact that the methods of deriving transfer equations employing kinetic functions of conditional and unconditional distributions appear inadequate. The main difference consists in the fact that in accordance with the statistical method of conditional distributions used, transfer equations may be obtained in any desired approximation that makes them applicable to transfer processes in molecular condensed media.

The transfer equations were originally obtained in the F_{12} -approximation for systems with central (point) interaction. In this approximation a mean value of the physical quantity $\Psi(\mathbf{q}, \mathbf{p}, t)$ is defined by the equality

$$\langle \Psi \rangle = \frac{1}{nv} \int_{v_1} \int_{\Omega_p} \Psi(\mathbf{q} + \mathbf{R}, \mathbf{p}, t) F_{12}(\mathbf{q} + \mathbf{R}, \mathbf{p}, t) d\mathbf{R} d\mathbf{p} \tag{94}$$

where $n(\mathbf{q}, t) = \int_{\Omega_p} F_{12}(\mathbf{q}, \mathbf{p}, t) d\mathbf{p}$ is the particle number density. Vector-radius \mathbf{q} is chosen

within the molecular averaging volume. The averaging operation is usually implied. Multiplying equation (89) by Ψ and integration over the momentum space give the transfer equation for Ψ .

The developed derivation procedure of conservation laws was then extended to systems with noncentral interaction (systems of nonspherical molecules with rotational degrees of freedom) with the aid of equation (93). Particularly, for statistical justification of angular momentum conservation law of the system the following expression was chosen as the quantity Ψ to be averaged

$$\Psi = \mathbf{l}_{\alpha} - s_{\alpha} - e_{\alpha\beta\gamma} q_{\beta} (p_{\gamma} - m u_{\gamma}) \tag{95}$$

where $\mathbf{s} = (1/n) \int \mathbf{l} F_{12} d\mathbf{g}$ is mean intrinsic angular momentum of molecule; $e_{\alpha\beta\gamma}$ is the Levi-Cevita tensor; \mathbf{u} is the macroscopic flow velocity (mean particle velocity); m is the particle mass; $d\mathbf{g} = d\mathbf{p} d\mathbf{l}$.

10. Determination of Relaxation and Kinetic Characteristics of Molecular Systems

The conditional distribution method has been used for evaluation of some kinetic coefficients. These were expressed in terms of integrals of time correlation functions. Calculation of the integrals involves the extremely difficult problem of determining the time dependence of correlation functions. The problem may be somewhat simplified by introduction of the concept of mean relaxation time τ_A of certain dynamic quantity A by the equality

$$\int_0^{\infty} \langle A(0) A(t) \rangle dt = \langle A^2 \rangle \tau_A. \tag{96}$$

Here $\langle \dots \rangle$ denote statistical averaging over the equilibrium assembly. In cases of physical interest the averaging may be carried out with the aid of junior distribution functions.

Calculation of mean relaxation times is an important stage of the procedure. In [26, 27] equations for kinetic functions of conditional distributions were suggested for this calculation.

A molecular system of nonspherical particles will be now considered. The kinetic equation for unary function in the F_{11} -approximation is given by expression (93). The two-particle correlation function entering into the integral term is approximated by the following relation

$$F_{11}^{(1)} = \frac{1}{4\pi v} \varphi(\mathbf{q}^2 - \mathbf{q}^1, \alpha^1, \alpha^2, t) F_{11}(\mathbf{q}^1, \mathbf{p}^1, \alpha^1, \mathbf{l}^1, \mathbf{p}^2, \mathbf{l}^2, t). \quad (97)$$

The function φ which acts as a non-equilibrium radial function is assumed to depend only on mutual orientation of the particles and the vector-radius which connects their centers of masses. Expression (97) may be suggested valid for times in excess of those of momentum relaxation when for the latter the Maxwellian distribution may be adopted. It is evident that in this case

$$\int_{\Omega_p} \int_{\Omega_l} F_{11}(\mathbf{q}^1, \mathbf{p}^1, \alpha^1, \mathbf{l}^1, \mathbf{p}^2, \mathbf{l}^2, t) d\mathbf{p}^2 d\mathbf{l}^2 = F_{11}(\mathbf{q}^1, \mathbf{p}^1, \mathbf{l}^1, \alpha^1, t). \quad (98)$$

We so isolate the Maxwellian part from F_{11}

$$F_{11}(\mathbf{q}, \mathbf{p}, \alpha, \mathbf{l}, t) = F'_{11}(\mathbf{q}, \mathbf{p}, \alpha, \mathbf{l}, t) \exp \left\{ -\frac{p^2}{2m\Theta} - \frac{\omega \cdot \mathbf{l}}{2\Theta} \right\}. \quad (99)$$

As $t \gg \tau_p$ (τ_p is the characteristic time for the Maxwellian momentum distribution to develop or in other words, the momenta relaxation time) F'_{11} will be slightly dependent on molecular momenta.

Substitution of (97)–(99) into (93) yields now the following equation for the unary function

$$\begin{aligned} & \frac{\partial F'_{11}}{\partial t} + \mathbf{v} \cdot \frac{\partial F'_{11}}{\partial \mathbf{q}} + \boldsymbol{\omega} \cdot \frac{\partial F'_{11}}{\partial \alpha} \\ & = \left\{ \frac{1}{4\pi v} \int_{V-v_1} \int_{\Omega_\alpha} \mathbf{F}_{12} \varphi d\mathbf{q}^2 d\alpha^2 \right\} \cdot \frac{\mathbf{v}}{\Theta} F'_{11} + \left\{ \frac{1}{4\pi v} \int_{V-v_1} \int_{\Omega_\alpha} \mathbf{M}_{12} \varphi d\mathbf{q}^2 d\alpha^2 \right\} \cdot \frac{\boldsymbol{\omega}}{\Theta} F'_{11} \end{aligned} \quad (100)$$

where $\mathbf{v} = \mathbf{p}^1/m$ is the linear velocity of the centre of mass of the particle, $\boldsymbol{\omega}$ is the particle angular velocity.

Solution of equation (100) is sought as the Fourier series with the coordinates of the inertia centre and expansion with respect to generalized spherical functions $T_{mn}^{(s)}(\alpha^1)$

$$F'_{11} = \sum_{kmns} a_{kmns}(\mathbf{p}^1, \mathbf{l}^1, t) e^{i\mathbf{k} \cdot \mathbf{q}^1} T_{mn}^{(s)}(\alpha^1). \quad (101)$$

We suppose that a time exists determining relaxation of unary function F_{11} . This is equivalent to the statement that the dominant contribution to solution (101) is due to the zeroth term of the expansion.

It may be found from the equation

$$\frac{\partial a_0}{\partial t} = \left\{ \frac{1}{4\pi v} \int_{V-v_1} \int_{\Omega_\alpha} \mathbf{F}_{12} \varphi d\mathbf{q}^2 d\alpha^2 \right\} \cdot \frac{\mathbf{v}}{\Theta} a_0 + \left\{ \frac{1}{4\pi v} \int_{V-v_1} \int_{\Omega_\alpha} \mathbf{M}_{12} \varphi d\mathbf{q}^2 d\alpha^2 \right\} \cdot \frac{\boldsymbol{\omega}}{\Theta} a_0. \quad (102)$$

Solving equation (102) and assuming a certain correlation between the average force acting on the particle and the particle velocity (e.g. in the sense of the Langevin equation), we write down

$$a_0(t) \sim \exp \{-t/\tau_q - t/\tau_\varphi\}. \quad (103)$$

The above equation includes parameters τ_q and τ_φ which may be considered as mean relaxation times of the quantities determined by the coordinates of the centre of molecule inertia and the molecule orientation, respectively,

$$\tau_q = \frac{\Theta}{\langle |\mathbf{F}| \rangle \langle |\mathbf{v}| \rangle}, \quad \tau_\varphi = \frac{\Theta}{\langle |\mathbf{M}| \rangle \langle |\omega| \rangle}. \quad (104)$$

Mean absolute values of force and moment of couple acting on the molecule are defined by the expressions

$$\begin{aligned} \langle |\mathbf{F}| \rangle &= \frac{1}{4\pi v} \int_{v-v_1} \int_{\Omega_\alpha} |\mathbf{F}| \varphi(\mathbf{r}^{12}, \alpha^1, \alpha^2) d\mathbf{r}^{12} d\alpha^2, \\ \langle |\mathbf{M}| \rangle &= \frac{1}{4\pi v} \int_{v-v_1} \int_{\Omega_\alpha} |\mathbf{M}| \varphi(\mathbf{r}^{12}, \alpha^1, \alpha^2) d\mathbf{r}^{12} d\alpha^2. \end{aligned} \quad (105)$$

Here the radial equilibrium function should be used as φ . Evaluations demonstrate that τ_q and τ_φ are of the same order. Over the liquid-vapour coexistence curve in the condensed phase they are of an order of 10^{-12} s. The relaxation times τ_q and τ_φ as well as the relaxation time $\tau_1 = \tau_q \tau_\varphi / (\tau_q + \tau_\varphi)$ have been used for estimations of viscosities of simple and asymmetric media, calculation of anisotropy relaxation time in the theory of molecular light scattering. The quantities just mentioned were determined in terms of time correlation functions of the quantities dependent on the particle positions (forces, moments of couples, etc.). In [28] the procedure for determining relaxation time τ_q is extended to binary systems that allowed a discussion of experimental peculiarities of concentration behaviour of shear viscosity of hydrogen isotope mixtures.

Use of a mean relaxation time implies the assumption of exponential decay of the time correlation function. In reality the function however has a more complicated structure of which specification requires consideration of the subsequent terms of series (101) with $\mathbf{k} \neq 0$. Vector \mathbf{k} has a physical meaning of a description microscopic space nonuniformity of the medium. A supposition is thus natural that for a liquid the term associated with $k \sim v^{-1/3}$ is the next dominating term after the zeroth one. Solution of equation (100) with series (101) at $\mathbf{k} \neq 0$ implies that function $F_{11}(t)$ becomes oscillating with the oscillation period close to the relaxation time [29].

Mean relaxation times of linear and angular momentum may be readily calculated from the Langevin equation governing the Brownian molecular motion which for a point particle in the Markovian approximation is of the form

$$\frac{d\mathbf{p}}{dt} = -\frac{\xi}{m} \mathbf{p} + \mathbf{S}(t). \quad (106)$$

Friction function ξ is determined in terms of the time integral of the correlation function of the force acting on a molecule. For calculation of the integral use will be made of the relaxation time τ_q

$$\xi = \frac{1}{3\Theta} \int_0^\infty \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle dt = \frac{\langle F^2 \rangle \tau_q}{3\Theta}. \quad (107)$$

Equation (106) contains a typical parameter which may be considered as a mean time of momentum relaxation

$$\tau_p = \frac{m}{\xi} = \frac{3m\Theta}{\langle F^2 \rangle \tau_q} \quad (108)$$

It is peculiar that τ_p and τ_q are related by an inverse relation. The values estimated from (108) demonstrate that over the liquid-vapour coexistence curve in a condensed phase $\tau_p \sim 10^{-13} - 10^{-14}$ s.

Liquid shear viscosities may be calculated in terms of the relaxation times τ_q and τ_p . A strict expression of the shear viscosity on the basis of the Kubo formalism is [30]

$$\eta = \frac{1}{\Theta V} \int_0^\infty \langle \Pi_{12}(0) \Pi_{12}(t) \rangle dt \quad (109)$$

where $\Pi_{\alpha\beta}$ is the microscopic stress tensor

$$\Pi_{\alpha\beta} = - \sum_{i=1}^N \frac{p_\alpha^i p_\beta^i}{m} + \frac{1}{2} \sum_{i \neq j}^N \frac{\Phi'(|\mathbf{q}^j - \mathbf{q}^i|)}{|\mathbf{q}^j - \mathbf{q}^i|} (q_\alpha^j - q_\alpha^i) (q_\beta^j - q_\beta^i). \quad (110)$$

Use of approximation of the type (96) gives the following form of expression (109)

$$\eta = \frac{\Theta \tau_p}{v} + \frac{2\pi\tau_q}{15v^2} \int_{\tau_0}^\infty \frac{d}{dr} \left(r^4 \frac{d\Phi}{dr} \right) \varphi(r) dr \quad \left(\frac{4}{3} \pi r_0^3 = v \right) \quad (111)$$

or

$$\eta = \frac{\Theta}{v} \tau_p + \tau_q \left(\mu_\infty - \frac{\Theta}{v} \right) \quad (112)$$

where μ_∞ is the high-frequency shear modulus.

It is widely recognized that the shear viscosity is proportional to the shear modulus ($\eta = \tau\mu$). Ya. I. Frenkel interpreted the proportionality factor τ as settled lifetime of a particle [31]. In fact, as far as the liquid in the moderate temperature range is concerned (say, at the coexistence curve), the first (kinetic) term in (112) is essentially smaller than the second one (potential) and Frenkel's assumption is statistically verified.

τ_q has the meaning of the settled lifetime of the particle. At higher temperatures or at higher pressures (at a distance from the coexistence curve) however the kinetic part becomes comparable with the potential part, then the former will become in excess of the latter. The relation between viscoelasticities is now more complicated.

Alongside with the above example, we may mention of calculation of self-diffusion coefficients. Although the assumption of the Markovian motion of a molecule used here may be adopted with certain restrictions, the orders of kinetic coefficients calculated are not only correct, but also give a correct temperature behaviour.

For determination of the relaxation time of angular momentum, besides equation (106) the theorem of angular momentum change should be written down. In a general case a set of two vectorial equations is obtained which involves tensors of friction factors at translational and orientational motions of the particle as well as tensors of cross-correlations of these motions.

The Langevin equations now become [32]

$$\begin{aligned}\frac{d\mathbf{p}_0}{dt} &= -(\zeta_{qq} \cdot \mathbf{I}_{qq}^{-1} + \zeta_{q\varphi} \cdot \mathbf{I}_{\varphi q}^{-1}) \cdot \mathbf{p}_0 - (\zeta_{qq} \cdot \mathbf{I}_{qq}^{-1} + \zeta_{q\varphi} \cdot \mathbf{I}_{\varphi\varphi}^{-1}) \cdot \mathbf{l}_0 + \mathbf{S}(t), \\ \frac{d\mathbf{l}_0}{dt} &= -(\zeta_{\varphi q} \cdot \mathbf{I}_{qq}^{-1} + \zeta_{\varphi\varphi} \cdot \mathbf{I}_{\varphi q}^{-1}) \cdot \mathbf{p}_0 - (\zeta_{\varphi q} \cdot \mathbf{I}_{qq}^{-1} + \zeta_{\varphi\varphi} \cdot \mathbf{I}_{\varphi\varphi}^{-1}) \cdot \mathbf{l}_0 + \mathbf{M}(t).\end{aligned}\quad (113)$$

The pole 0 chosen here does not necessarily coincide with the centre of inertia of the molecule; $(\mathbf{I}_{qq})_{\alpha\beta} = m\delta_{\alpha\beta}$, $\mathbf{I}_{\varphi\varphi} = \mathbf{I}^{(0)}$ is the tensor of inertia moments of the particle over the pole, $\mathbf{I}_{q\varphi} = \mathbf{I}_{\varphi q}^T$ are antisymmetric pseudotensors (the superscript T indicates a transpose operation). Tensors of friction factors are determined in terms of correlation functions of the forces and moments of forces similarly to (107).

With the assumption that quickly-oscillating random forces $\mathbf{S}(t)$ and $\mathbf{M}(t)$ satisfy the requirements of Markovian-Gaussian processes the correlation matrix may be obtained

$$\mathbf{R}(\tau) = \langle \mathbf{y}^T(t) \mathbf{y}(t + \tau) \rangle^{(1)}, \quad \mathbf{y}^T = (\mathbf{v}_0, \omega) \quad (114)$$

$\langle \dots \rangle^{(1)}$ denotes averaging over equilibrium distribution of dynamic variables of all the particles in the system but the Brownian particle considered. Expression (114) may be written as

$$\begin{aligned}\mathbf{R}(\tau) &= \Theta\{\exp(-\bar{\zeta}\tau)\} \cdot \mathbf{I}^{-1}, \\ \bar{\zeta} &= \mathbf{I}^{-1} \cdot \zeta = \begin{pmatrix} \mathbf{I}_{qq}^{-1} & \mathbf{I}_{q\varphi}^{-1} \\ \mathbf{I}_{\varphi q}^{-1} & \mathbf{I}_{\varphi\varphi}^{-1} \end{pmatrix} \cdot \begin{pmatrix} \zeta_{qq} & \zeta_{q\varphi} \\ \zeta_{\varphi q} & \zeta_{\varphi\varphi} \end{pmatrix}.\end{aligned}\quad (115)$$

The matrix $\bar{\zeta}$ does determine a set of relaxation parameters.

It follows from the analysis of the matrix that the cross-correlation of translational and rotational variables is essential for a number of processes, especially those developing over time intervals of an order of relaxation times of momentum or angular momentum. In [33] it is demonstrated that this cross-correlation is very essential for dielectric behaviour of a system of polar molecules.

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