A New Approach to the Theory of Classical Fluids. II
——Multicomponent Systems——

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The results that have been derived in paper I of this series are generalized to the case of multicomponent systems. The argument is made in an almost parallel way with the one in I, though the derivation of the integral equation for the pair distribution function is given in a more intuitive way than in I. The present theory is also a generalization of Morita's theory in which the multicomponent systems were treated in the hyper-netted chain approximation.

§ 1. Introduction

In the previous paper,[1] which will be referred to as I, one-component fluid systems have been investigated by starting from the customary density expansion for the pair distribution function. An exact integral equation has been found for the pair distribution function. The integral equation is of different nature from those which are usually known in the theory of classical fluids, in the point that it involves an infinite series in itself. The Helmholtz free energy also has been expressed in a form of expansion which may be expected to converge considerably more rapidly than its customary density expansion. In the present paper the results that have been obtained in I will be generalized to the case of multicomponent systems.

In the case of multicomponent systems as well as one-component systems, a theory can be constructed by means of the integral equation method which is usually based on the Kirkwood superposition approximation.[2],[3],[4]* However, the inconsistencies which are implied in this approximation reveal themselves more drastically for the multicomponent systems than for the one-component systems. In the case of binary mixtures, for example, *four* integral equations are derived to determine *three* kinds of the pair distribution functions. It is known[4],[5] that these integral equations are mutually inconsistent and also that further approximation must be introduced to convert them into consistent equations. It may be said that such a difficulty is one of the serious defects of the integral equation method.

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* In fact it is in the theory of multicomponent systems that Kirkwood used the superposition approximation for the first time.[2]

The partial sum method for the multicomponent systems was adopted for the first time by Mayer in his theory of ionic solutions.[6] Mayer was able to obtain the Debye-Hückel limiting law by considering the terms corresponding to ring diagrams alone. After that, several authors have adopted this method mainly to investigate the ionic solutions.[4],[7] Recently Morita[8] has proposed the hyper-netted chain approximation to deal with the multicomponent systems in general. Morita's theory contains the previous works as its special case. Just as the hyper-netted chain approximation for the one-component systems appeared as the zeroth approximation to the theory presented in I, it will be shown that the above Morita's theory is contained in the present theory as a special case. In such a sense the present theory may be said to be a generalization of Morita's theory.

The content of the present paper is as follows. In § 2 the definition of the functions to be used in the following sections are given. This section corresponds to § 2 of I. In § 3 an exact integral equation for the pair distribution function is derived by starting from the density expansions of the functions which are defined in § 2. Though this section corresponds to § 3 of I, the derivation of the integral equation is given in a more intuitive way than in § 3 of I. In § 4 the expression for the Helmholtz free energy is derived and it is shown that the integral equation derived in § 3 can also be obtained from this expression for the free energy by means of a variational principle. The argument in § 4 is made in quite a parallel way with the one in § 4 and § 5 of I. In § 5 a summary of the results that are obtained in § 3 and § 4 is given and some remarks are also given.

§ 2. Notation and definition

We consider a σ-component fluid in a volume Ω and at temperature T, composed of N_1 particles of species 1, N_2 of species 2, $\cdots$, and N_σ of species σ. The interaction potential of our system is assumed to be the sum of pair interaction potentials:

$$\frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{N} \sum_{j=1}^{N} \phi_{\nu_i \nu_j}(r_{ij}), \tag{2·1}$$

where N denotes the total number of the particles and $\nu_i (i=1, 2, \cdots, N)$ denotes the species of the particle at r_i. The quantity $b_{\nu_i \nu_j}(r_{ij})$ is defined in terms of the pair interaction potential by

$$b_{\nu_i \nu_j}(r_{ij}) = e^{-\phi_{\nu_i \nu_j}(r_{ij})/kT} - 1. \tag{2·2}$$

The number density of species ν is denoted by $\rho_\nu (=N_\nu/\Omega)$.

The pair distribution function, $g_{\alpha\beta}(r_{12})$, of two particles of species α and β is given by the equation[9]

$$g_{\alpha\beta}(r_{12}) = \exp\left[-\frac{\phi_{\alpha\beta}(r_{12})}{kT} + w_{\alpha\beta}(r_{12}) \right], \tag{2·3}$$

where

$$w_{\alpha\beta}(r_{12}) = \sum_{m_1}\sum_{m_2}\cdots\sum_{m_\sigma} \frac{\rho_1^{m_1}\rho_2^{m_2}\cdots\rho_\sigma^{m_\sigma}}{m_1!\,m_2!\cdots m_\sigma!} \iint\cdots\int d\{m_1\}\,d\{m_2\}\cdots d\{m_\sigma\}$$

$$\times \sum_{m_1+m_2+\cdots+m_\sigma+2\geq i>j\geq 1}^{(W)} \prod b_{\nu_i\nu_j}(r_{ij})$$

$$\equiv \sum_m \frac{\rho^m}{m!} \int d\{m\} \sum_{m+2\geq i>j\geq 1}^{(W)} \prod b_{\nu_i\nu_j}(r_{ij}). \tag{2·4}$$

In the first line of (2·4) the volume element of m_ν particles of species ν is denoted by $d\{m_\nu\}$ ($\nu=1,2,\cdots,\sigma$). In the second line Mayer's notation for the multicomponent systems is adopted. While no explanation is given here on this notation, one will understand it if one compares the second line of (2·4) with the first line. As in I, the meaning of $\Sigma^{(W)}$ will be explained by means of the graphical representation of the product $\prod b_{\nu_i\nu_j}(r_{ij})$ in the following.

Particles 1 and 2 are represented by a white circle respectively. The set of **m** particles, over which the integration is to be performed, is represented by the set of numbered points (or numbered black circles). A factor $b_{\nu_i\nu_j}(r_{ij})$ is represented by a line (*b*-bond) which is drawn between two points i and j. Then a product $\prod_{m+2\geq i>j\geq 1} b_{\nu_i\nu_j}(r_{ij})$ is represented by a bond diagram. Two particles i and j are said to be *directly* connected if $b_{\nu_i\nu_j}(r_{ij})$ appears in the product. An *s*-point is defined in the same way as in I. It is a point through which all possible paths going from particle 1 to particle 2 must pass. In other words, it is a point by which the bond diagram can be separated into two independent parts containing particles 1 and 2 respectively.

We shall introduce the following four kinds of restrictions which are to be imposed on the summation of diagrams:

(I) *Each particle of the set* **m** *is independently connected to particles 1 and 2.*

(II) *The particles of the set* **m** *are connected among themselves independently of particles 1 and 2.*

(III) *Particles 1 and 2 are not directly connected.*

(IV) *The diagram has no s-point.*

$$(2·5)$$

Then $\Sigma^{(W)}$ in (2·4) denotes the summation over all diagrams being possible under restrictions (I), (II) and (III) (see Fig. 1 in I).[9]

Following the lines of I, we define the functions $x_{\alpha\beta}(r_{12})$, $z_{\alpha\beta}(r_{12})$ and $v_{\alpha\beta}(r_{12})$ as follows.*

$$x_{\alpha\beta}(r_{12}) = \sum_m \frac{\rho^m}{m!} \int d\{m\} \sum_{m+2\geq i>j\geq 1}^{(X)} \prod b_{\nu_i\nu_j}(r_{ij}), \tag{2·6}$$

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* The function $z_{S,\alpha\beta}(r_{12})$, corresponding to $z_S(r_{12})$ in I, may be defined in a similar way, though we shall have no need to use it in the following deduction.

where $\Sigma'^{(X)}$ denotes the summation over all diagrams being possible under restrictions (I), (II), (III) and (IV).

$$z_{\alpha\beta}(r_{12}) = \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \int d\{\mathbf{m}\} \sum^{(Z)} \prod_{\mathbf{m}+2\geq i>j\geq 1} b_{\nu_i\nu_j}(r_{ij}), \tag{2.7}$$

where $\Sigma'^{(Z)}$ denotes the summation over all diagrams being possible under restrictions (I) and (IV).

$$v_{\alpha\beta}(r_{12}) = \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \int d\{\mathbf{m}\} \sum^{(V)} \prod_{\mathbf{m}+2\geq i>j\geq 1} b_{\nu_i\nu_j}(r_{ij}), \tag{2.8}$$

where $\Sigma'^{(V)}$ denotes the summation over all diagrams being possible under restriction (I) alone.

Some diagrams appearing in $\Sigma'^{(X)}$ and $\Sigma'^{(Z)}$ are shown for a one-component system in Figs. 2 and 4 of I.

The functions defined above are not independent of each other. The next section will be devoted to the study of the relations among them.

In concluding the present section, we introduce the Fourier transforms of $w_{\alpha\beta}(r)$, $x_{\alpha\beta}(r)$, $z_{\alpha\beta}(r)$ and $v_{\alpha\beta}(r)$ which will be denoted as $W_{\alpha\beta}(k)$, $X_{\alpha\beta}(k)$, $Z_{\alpha\beta}(k)$ and $V_{\alpha\beta}(k)$, respectively. For example, we have the relations

and

$$\left.\begin{aligned} z_{\alpha\beta}(r) &= \frac{1}{\Omega} \sum_{k} Z_{\alpha\beta}(k) e^{ikr} \\ Z_{\alpha\beta}(k) &= \int dr\, z_{\alpha\beta}(r) e^{-ikr}. \end{aligned}\right\} \tag{2.9}$$

§ 3. Integral equation for the pair distribution function

We shall derive several relations among the functions which have been defined in the preceding section. Though the derivations may be made in quite a similar way as in the case of one-component systems of I, we shall here give more intuitive derivations. The relations will be seen to give an integral equation for the pair distribution function.

The diagrams appearing in $\Sigma'^{(V)}$ can be divided into two groups. One group consists of the diagrams having no s-point, which are just those appearing in $\Sigma'^{(Z)}$ (see below (2.7)). The other group consists of the diagrams which have at least one s-point. Let us consider a diagram belonging to the latter group. Let particle 3 of species ν be at the s-point nearest to particle 1. Then the diagrams which are to appear between particles 1 and 3 are restricted by restrictions (I) and (IV) of (2.5) where particles 1 and 2 must be replaced by particles 1 and 3. The diagrams which are to appear between particles 3 and 2 are restricted by restriction (I) where particles 1 and 2 must be replaced by particles 3 and 2. Therefore the total of the diagrams appearing in $v_{\alpha\beta}(r_{12})$ can be written in a symbolical way as

$$
\underset{1}{\overset{v_{\alpha\beta}}{\bigcirc\!\!-\!\!-\!\!-\!\!\bigcirc}}\;=\;\underset{1}{\overset{z_{\alpha\beta}}{\bigcirc\!\!-\!\!-\!\!-\!\!\bigcirc}}\;+\;\sum_{\nu=1}^{\sigma}\;{}'\;\underset{1}{\overset{z_{\alpha\nu}}{\bigcirc\!\!-\!\!-\!\!-\!\!\bullet}}\underset{3}{\overset{v_{\nu\beta}}{\!\!-\!\!-\!\!-\!\!\bigcirc}}\;. \tag{3.1f}
$$

This symbolical expression means (see below (3·4f) in I)

$$
v_{\alpha\beta}(r_{12}) = z_{\alpha\beta}(r_{12}) + \sum_{\nu=1}^{\sigma}{}' \rho_\nu \int d\boldsymbol{r}_3 \, z_{\alpha\nu}(r_{13}) \, v_{\nu\beta}(r_{32}), \tag{3.1}
$$

which is rewritten, with the aid of Fourier transforms, as

$$
V_{\alpha\beta}(k) = Z_{\alpha\beta}(k) + \sum_{\nu=1}^{\sigma}{}' \rho_\nu Z_{\alpha\nu}(k) \, V_{\nu\beta}(k). \tag{3.1'}
$$

If, in (3·1'), β is fixed and α is varied from 1 to σ, one obtains a set of linear equations which determines $V_{1\beta}$, $V_{2\beta}$, $\cdots$, and $V_{\sigma\beta}$ in terms of $Z_{\alpha\nu}$'s $(\alpha, \nu = 1, 2 \cdots, \sigma)$. This set of linear equations can be solved in an elementary way by the use of a determinant. The result is as follows.

$$
\rho_\alpha \rho_\beta V_{\alpha\beta}(k) = -\frac{1+\delta_{\alpha\beta}}{2} \frac{\partial \log D(k)}{\partial Z_{\alpha\beta}} - \rho_\alpha \delta_{\alpha\beta}, \tag{3.2}
$$

where

$$
D(k) = \begin{vmatrix} 1-\rho_1 Z_{11}(k) & -\rho_1 Z_{12}(k) & \cdots\cdots\cdots & -\rho_1 Z_{1\sigma}(k) \\ -\rho_2 Z_{21}(k) & 1-\rho_2 Z_{22}(k) & \cdots\cdots\cdots & -\rho_2 Z_{2\sigma}(k) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -\rho_\sigma Z_{\sigma 1}(k) & -\rho_\sigma Z_{\sigma 2}(k) & \cdots\cdots\cdots & 1-\rho_\sigma Z_{\sigma\sigma}(k) \end{vmatrix}, \tag{3.3}
$$

which may be rewritten in a symmetrical form

$$
D(k) = \begin{vmatrix} 1-\rho_1 Z_{11}(k) & -\sqrt{\rho_1\rho_2}\,Z_{12}(k) & \cdots\cdots\cdots & -\sqrt{\rho_1\rho_\sigma}\,Z_{1\sigma}(k) \\ -\sqrt{\rho_2\rho_1}\,Z_{21}(k) & 1-\rho_2 Z_{22}(k) & \cdots\cdots\cdots & -\sqrt{\rho_2\rho_\sigma}\,Z_{2\sigma}(k) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -\sqrt{\rho_\sigma\rho_1}\,Z_{\sigma 1}(k) & -\sqrt{\rho_\sigma\rho_2}\,Z_{\sigma 2}(k) & \cdots\cdots\cdots & 1-\rho_\sigma Z_{\sigma\sigma}(k) \end{vmatrix}. \tag{3.3'}
$$

In the right-hand side of (3·2), $\delta_{\alpha\beta} = 1$ for $\alpha = \beta$ and $\delta_{\alpha\beta} = 0$ for $\alpha \neq \beta$. The differentiation with respect to $Z_{\alpha\beta}(k)$ is to be made by taking account of the fact that $Z_{\alpha\beta}(k) = Z_{\beta\alpha}(k)$.

If, in (3·1'), α is fixed and β is varied from 1 to σ, one obtains a set of linear equations which determines $Z_{\alpha 1}, Z_{\alpha 2}, \cdots$, and $Z_{\alpha\sigma}$ in terms of $V_{\nu\beta}$'s $(\nu, \beta = 1, 2, \cdots, \sigma)$. This set of equations can also be solved to give the following result.

$$
\rho_\alpha \rho_\beta Z_{\alpha\beta}(k) = -\frac{1+\delta_{\alpha\beta}}{2} \frac{\partial \log \overline{D}(k)}{\partial V_{\alpha\beta}} + \rho_\alpha \delta_{\alpha\beta}, \tag{3.4}
$$

where

$$
\overline{D}(k) = \begin{vmatrix} 1+\rho_1 V_{11}(k) & \rho_1 V_{12}(k) & \cdots\cdots\cdots & \rho_1 V_{1\sigma}(k) \\ \rho_2 V_{21}(k) & 1+\rho_2 V_{22}(k) & \cdots\cdots\cdots & \rho_2 V_{2\sigma}(k) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \rho_\sigma V_{\sigma 1}(k) & \rho_\sigma V_{\sigma 2}(k) & \cdots\cdots\cdots & 1+\rho_\sigma V_{\sigma\sigma}(k) \end{vmatrix}. \tag{3.5}
$$

The argument leading to (3·1) or (3·1′) is valid also in the case of the diagrams appearing in $w_{\alpha\beta}(r_{12})$. We get, corresponding to (3·1′),

$$W_{\alpha\beta}(k) = X_{\alpha\beta}(k) + \sum_{\nu=1}^{\sigma} \rho_\nu Z_{\alpha\nu}(k) V_{\nu\beta}(k). \tag{3·6}$$

Next we shall consider the diagrams appearing in $z_{\alpha\beta}(r_{12})$ (see (2·7)). These diagrams can be grouped together by the number of parts into which the diagrams are divided when particles 1 and 2 are removed. It will be supposed first that particles 1 and 2 are not directly connected. Then the diagrams which are to appear in each part are restricted by restrictions (I), (II) and (III) of (2·5) ; hence the diagrams belong to $w_{\alpha\beta}(r_{12})$. Therefore the contribution, to $z_{\alpha\beta}(r_{12})$, of diagrams not containing $b_{\alpha\beta}(r_{12})$ is expressed symbolically as

$$\tag{3·7f}$$

The reason why the first term is not $w_{\alpha\beta}$ but $x_{\alpha\beta}$ is that the diagrams in $z_{\alpha\beta}(r_{12})$ must not have s-points. In a similar way the contribution, to $z_{\alpha\beta}(r_{12})$, of diagrams containing $b_{\alpha\beta}(r_{12})$ turns out to be expressed symbolically as

$$\tag{3·7′f}$$

The function $z_{\alpha\beta}(r_{12})$ is the sum of contributions (3·7f) and (3·7′f) so that $z_{\alpha\beta}(r_{12})$ is written in the form (see below (3·4f) in I) :

$$z_{\alpha\beta}(r_{12}) = x_{\alpha\beta}(r_{12}) + \frac{1}{2!} w_{\alpha\beta}^2(r_{12}) + \frac{1}{3!} w_{\alpha\beta}^3(r_{12}) + \cdots\cdots$$

$$+ b_{\alpha\beta}(r_{12}) + \frac{1}{1!} b_{\alpha\beta}(r_{12}) w_{\alpha\beta}(r_{12}) + \frac{1}{2!} b_{\alpha\beta}(r_{12}) w_{\alpha\beta}^2(r_{12}) + \cdots\cdots$$

$$= [b_{\alpha\beta}(r_{12}) + 1] e^{w_{\alpha\beta}(r_{12})} - 1 + x_{\alpha\beta}(r_{12}) - w_{\alpha\beta}(r_{12}). \tag{3·7}$$

As in I, it will be shown that the sum $\Sigma'^{(X)}$ appearing in (2·6) can be reduced to a more restricted sum $\Sigma'^{(X')}$ if one uses v-bonds in place of b-bonds. Let a diagram in $\Sigma'^{(X)}$ have a pair of points (Let the particles on the points be particles 3 and 4.) by which the diagram is divided into two parts in the following way. The one is the part that includes particles 1 and 2 and cannot be divided any more by that pair of points. The other part consists of the rest. Diagrams to be included in the latter part are restricted only by restriction (I) of (2·5) where particles 1 and 2 must be replaced by particles 3 and 4. Therefore the latter part can be represented by $v_{\mu\nu}(r_{34})$ where μ and ν are the species of particles 3 and 4, respectively. By replacing the latter part by the $v_{\mu\nu}(r_{34})$-

bond, the original diagram is reduced to a simpler form. Such a reduction can be continued until such a pair of points appears no more. After all, (2·6) is reduced to

$$x_{\alpha\beta}(r_{12}) = \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \int d\{\mathbf{m}\} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(X')} \prod v_{\nu_i \nu_j}(r_{ij}), \qquad (3 \cdot 8)$$

where $\Sigma^{(X')}$ denotes the summation over all diagrams, composed of v-bonds, which are possible under the following restriction as well as (I), (II), (III) and (IV) of (2·5). The additional restriction is that there exists no part which is connected to the rest of the diagrams only by means of two points. As will be seen in the next section, it may be said that the diagrams appearing in (3·8) are those which are constructed by removing one v-bond from the diagrams appearing in the expression for the Helmholtz free energy (see below (4·9)). Some diagrams in $\Sigma^{(X')}$ are shown for a one-component system in Fig. 7 of I.

The set of Eqs. (3·1'), (3·2), (3·6) and (3·7) can be arranged as follows:

$$v_{\alpha\beta}(r) = [b_{\alpha\beta}(r) + 1] e^{w_{\alpha\beta}(r)} - 1 \qquad (3 \cdot 9)$$

$$\rho_\alpha \rho_\beta V_{\alpha\beta}(k) = -\frac{1+\delta_{\alpha\beta}}{2} \frac{\partial \log D(k)}{\partial Z_{\alpha\beta}} - \rho_\alpha \delta_{\alpha\beta} \qquad (3 \cdot 10)$$

$$w_{\alpha\beta}(r) = x_{\alpha\beta}(r) + v_{\alpha\beta}(r) - z_{\alpha\beta}(r). \qquad (3 \cdot 11)$$

It is to be remembered that $Z_{\alpha\beta}(k)$ and $V_{\alpha\beta}(k)$ are the Fourier transforms of $z_{\alpha\beta}(r)$ and $v_{\alpha\beta}(r)$ respectively and that $D(k)$ is the determinant which has been defined by (3·3) or (3·3'). The function $v_{\alpha\beta}(r)$ is related to the pair distribution function $g_{\alpha\beta}(r)$ by

$$v_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1, \qquad (3 \cdot 12)$$

which is readily confirmed with the aid of (2·2), (2·3) and (3·9). The set of Eqs. (3·8)—(3·11) determines in principle the functions $v_{\alpha\beta}(r)$, $w_{\alpha\beta}(r)$, $z_{\alpha\beta}(r)$ and $x_{\alpha\beta}(r)$, and so the pair distribution function $g_{\alpha\beta}(r)$. Therefore we may say that this set of equations is an integral equation for the pair distribution function. It is to be noted that this integral equation is an exact one as far as the original density expansions (2·4), (2·6), (2·7) and (2·8) or their analytical continuations, if exist, are valid.

The above set of equations is reduced to the one which has been derived in I, if the system under consideration is a one-component system. As a matter of fact, the determinant $D(k)$ is reduced, in such a case, to $1 - \rho Z(k)$ so that Eq. (3·10) is reduced to

$$\rho V(k) = \frac{1}{1 - \rho Z(k)} - 1,$$

which is equivalent to (3·7) in I.

As in I, the zeroth approximation to solve the above integral equation will

be given by putting $x_{\alpha\beta}(r)$ to be zero. Then the set of equations is reduced to

$$z_{\alpha\beta}(r) = [b_{\alpha\beta}(r)+1]e^{w_{\alpha\beta}(r)} - 1 - w_{\alpha\beta}(r)$$

and

$$\rho_{\alpha}\rho_{\beta}W_{\alpha\beta}(k) = -\rho_{\alpha}\rho_{\beta}Z_{\alpha\beta}(k) - \frac{1+\delta_{\alpha\beta}}{2}\frac{\partial \log D(k)}{\partial Z_{\alpha\beta}} - \rho_{\alpha}\delta_{\alpha\beta},$$

$$(3\cdot13)$$

which are to be called the equations in the hyper-netted chain approximation,[8] though they have not been written in an explicit form in reference 8). The next approximation will be to approximate $x_{\alpha\beta}(r)$ by the contributions arising from the diagrams $\overset{\mu}{\underset{\alpha}{\bullet}}\!\!\bowtie\!\!\overset{\nu}{\underset{\beta}{\bullet}}$ $(\mu, \nu=1, 2, \cdots, \sigma)$ where the bold lines represent the v-bonds (see Fig. 7 in I).

§ 4. Expression for the Helmholtz free energy

It is known[10] that the interaction part of the Helmholtz free energy is in general expressed as

$$A_1 = \frac{\Omega}{2}\int_0^1 d\xi \int d\mathbf{r} \sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_{\alpha}\rho_{\beta}\phi_{\alpha\beta}(r)g_{\alpha\beta}(r;\xi), \qquad (4\cdot1)$$

where $g_{\alpha\beta}(r;\xi)$ is the pair distribution function for the case that all the pair interaction potentials are $\xi\phi_{\mu\nu}(r)$ $(\mu, \nu=1, 2, \cdots, \sigma)$. In such a case the functions $b_{\alpha\beta}(r)$, $w_{\alpha\beta}(r)$, and so on, are also dependent on ξ. In particular, $b_{\alpha\beta}(r)$ is of the form

$$b_{\alpha\beta}(r;\xi) = e^{-\xi\phi_{\alpha\beta}(r)/kT} - 1. \qquad (4\cdot2)$$

By taking notice of (2·3) and (4·2), expression (4·1) can be rewritten as

$$\frac{A_1}{\Omega kT} = -\frac{1}{2}\int_0^1 d\xi \int d\mathbf{r} \sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_{\alpha}\rho_{\beta}\frac{\partial b_{\alpha\beta}(r;\xi)}{\partial\xi}e^{w_{\alpha\beta}(r;\xi)}. \qquad (4\cdot1')$$

In the following, the ξ-dependence of $b_{\alpha\beta}(r)$, $w_{\alpha\beta}(r)$, and so on, will not be explicitly written, for no confusion will arise.

Differentiating (3·9) with respect to ξ, we get

$$\frac{\partial b_{\alpha\beta}(r)}{\partial\xi}e^{w_{\alpha\beta}(r)} = \frac{\partial v_{\alpha\beta}(r)}{\partial\xi} - \frac{\partial w_{\alpha\beta}(r)}{\partial\xi} - v_{\alpha\beta}(r)\frac{\partial w_{\alpha\beta}(r)}{\partial\xi},$$

which is transformed, by the use of (3·11), into

$$\frac{\partial b_{\alpha\beta}(r)}{\partial\xi}e^{w_{\alpha\beta}(r)} = \frac{\partial}{\partial\xi}\left[v_{\alpha\beta}(r) - w_{\alpha\beta}(r) - w_{\alpha\beta}(r)v_{\alpha\beta}(r) + \frac{1}{2}v_{\alpha\beta}^2(r)\right.$$

$$\left. - v_{\alpha\beta}(r)z_{\alpha\beta}(r)\right] + v_{\alpha\beta}(r)\frac{\partial z_{\alpha\beta}(r)}{\partial\xi} + x_{\alpha\beta}(r)\frac{\partial v_{\alpha\beta}(r)}{\partial\xi}. \qquad (4\cdot3)$$

When this expression is introduced into (4·1′) and use is made of the property of Fourier transforms, the interaction part of the free energy is written in the form

$$\frac{A_1}{\Omega kT} = -\frac{1}{2}\int dr \sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\int_0^1 d\xi\frac{\partial}{\partial\xi}\Big[\,v_{\alpha\beta}(r)-w_{\alpha\beta}(r)-w_{\alpha\beta}(r)v_{\alpha\beta}(r)$$

$$+\frac{1}{2}v_{\alpha\beta}^2(r)-v_{\alpha\beta}(r)z_{\alpha\beta}(r)\,\Big]-\frac{1}{2}\frac{1}{\Omega}\sum_k\int_0^1 d\xi\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\,V_{\alpha\beta}(k)$$

$$\times\frac{\partial Z_{\alpha\beta}(k)}{\partial\xi}+\frac{A_1'}{\Omega kT}, \tag{4·4}$$

where

$$\frac{A_1'}{\Omega kT}=-\frac{1}{2}\int_0^1 d\xi\int dr\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\,x_{\alpha\beta}(r)\,\frac{\partial v_{\alpha\beta}(r)}{\partial\xi}. \tag{4·5}$$

The integration with respect to ξ is readily performed in the first term on the right-hand side of (4·4). By the use of the fact that $v_{\alpha\beta}$, $w_{\alpha\beta}$ and $z_{\alpha\beta}$ vanish at $\xi=0$, it turns out that the first term is written as

$$-\frac{1}{2}\int dr\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\Big[\,v_{\alpha\beta}(r)-w_{\alpha\beta}(r)-w_{\alpha\beta}(r)v_{\alpha\beta}(r)$$

$$+\frac{1}{2}v_{\alpha\beta}^2(r)-v_{\alpha\beta}(r)z_{\alpha\beta}(r)\,\Big], \tag{4·6}$$

where the values of $v_{\alpha\beta}$, $w_{\alpha\beta}$ and $z_{\alpha\beta}$ are those at $\xi=1$. The integration over ξ is carried out also in the second term as follows:

$$-\frac{1}{2}\frac{1}{\Omega}\sum_k\int_0^1 d\xi\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\,V_{\alpha\beta}(k)\,\frac{\partial Z_{\alpha\beta}(k)}{\partial\xi}$$

$$=+\frac{1}{2}\frac{1}{\Omega}\sum_k\int_0^1 d\xi\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\Big[\frac{1+\delta_{\alpha\beta}}{2}\frac{\partial\log D(k)}{\partial Z_{\alpha\beta}}+\rho_\alpha\delta_{\alpha\beta}\Big]\frac{\partial Z_{\alpha\beta}(k)}{\partial\xi}$$

$$=+\frac{1}{2}\frac{1}{\Omega}\sum_k\int_0^1 d\xi\frac{\partial}{\partial\xi}\Big[\log D(k)+\sum_{\alpha=1}^{\sigma}\rho_\alpha Z_{\alpha\alpha}(k)\Big]$$

$$=+\frac{1}{2}\frac{1}{\Omega}\sum_k\Big[\log D(k)+\sum_{\alpha=1}^{\sigma}\rho_\alpha Z_{\alpha\alpha}(k)\Big]. \tag{4·7}$$

In the last expression of (4·7), the values of $D(k)$ and $Z_{\alpha\alpha}(k)$ are those at $\xi=1$. In transforming the first expression of (4·7) into the second one, use has been made of (3·10). In transforming the second expression into the third one, the following relation has been used:

$$\frac{\partial \log D(k)}{\partial \xi} = \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \frac{1+\delta_{\alpha\beta}}{2} \frac{\partial \log D(k)}{\partial Z_{\alpha\beta}} \frac{\partial Z_{\alpha\beta}(k)}{\partial \xi}, \qquad (4\cdot8)$$

which can be readily proved with the aid of the fact that the determinant $D(k)$ is dependent on ξ through $Z_{\alpha\beta}(k)$'s alone (see $(3\cdot3)$). We can prove that the last term of $(4\cdot4)$, which is defined by $(4\cdot5)$, is expressed in a form

$$\frac{A_1'}{\Omega kT} = - \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \frac{1}{\Omega} \int d\{\mathbf{m}\} \sum_{\mathbf{m} \geq i > j \geq 1}^{(A')} \prod v_{\nu_i \nu_j}(r_{ij}), \qquad (4\cdot9)$$

where $\Sigma^{(A')}$ denotes the summation over the diagrams which are obtained by introducing the $v_{\alpha\beta}(r_{12})$-bond into the diagrams appearing in $\Sigma^{(X')}$. If one takes notice of the restrictions which are imposed on the diagrams in $\Sigma^{(X')}$ (see below $(3\cdot8)$), it can be verified that $\Sigma^{(A')}$ may be said to be the summation over all diagrams which are *more than doubly connected*, though the proof will be omitted here.

The proof of $(4\cdot9)$ is as follows. Let us consider the integral

$$\int d\{\mathbf{m}+2\} \frac{\partial v_{\alpha\beta}(r_{12})}{\partial \xi} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(X')} \prod v_{\nu_i \nu_j}(r_{ij}).$$

This integral can be transformed, with the aid of the definition of $\Sigma^{(A')}$, into the form

$$\frac{1+\delta_{\alpha\beta}}{(m_\alpha+1)(m_\beta+1+\delta_{\alpha\beta})} \frac{\partial}{\partial \xi} \int d\{\mathbf{m}+2\} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(A')} \prod v_{\nu_i \nu_j}(r_{ij}).$$

The factor $(1+\delta_{\alpha\beta})/(m_\alpha+1)(m_\beta+1+\delta_{\alpha\beta})$ enters because the total of diagrams appearing in $\Sigma^{(X')}$ is symmetrical in $\mathbf{m}$ particles while the total of diagrams appearing in $\Sigma^{(A')}$ is symmetrical in $(\mathbf{m}+2)$ particles which are $\mathbf{m}$ particles plus particles $1(\alpha$-species) and $2(\beta$-species). By the use of the above transformation, $(4\cdot5)$ is transformed in the following way (see $(3\cdot8)$).

$$\frac{A_1'}{\Omega kT} = -\frac{1}{2} \int_0^1 d\xi \frac{1}{\Omega} \iint d\mathbf{r}_1 d\mathbf{r}_2 \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \frac{\partial v_{\alpha\beta}(r_{12})}{\partial \xi} x_{\alpha\beta}(r_{12})$$

$$= -\frac{1}{2} \int_0^1 d\xi \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \frac{1}{\Omega} \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \int d\{\mathbf{m}+2\} \frac{\partial v_{\alpha\beta}(r_{12})}{\partial \xi} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(X')} \prod v_{\nu_i \nu_j}(r_{ij})$$

$$= -\frac{1}{2} \int_0^1 d\xi \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \frac{1}{\Omega} \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \frac{1+\delta_{\alpha\beta}}{(m_\alpha+1)(m_\beta+1+\delta_{\alpha\beta})}$$

$$\times \frac{\partial}{\partial \xi} \int d\{\mathbf{m}+2\} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(A')} \prod v_{\nu_i \nu_j}(r_{ij})$$

$$= -\frac{1}{2} \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \frac{1}{\Omega} \sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \frac{1+\delta_{\alpha\beta}}{(m_\alpha+1)(m_\beta+1+\delta_{\alpha\beta})}$$

$$\times \int d\{\mathbf{m}+2\} \sum_{\mathbf{m}+2 \geq i > j \geq 1}^{(A')} \prod v_{\nu_i \nu_j}(r_{ij})$$

$$= -\sum_{\mathbf{m}} \frac{\rho^{\mathbf{m}}}{\mathbf{m}!} \frac{1}{\Omega} \int d\{\mathbf{m}\} \sum_{\mathbf{m}\geq i>j\geq 1}^{(A')} \prod v_{\nu_i \nu_j}(r_{ij}).$$

The last expression is the one to be proved, and, consequently, the proof of (4·9) has been completed.

As a result of (4·6) and (4·7), the interaction part of the free energy is written in the form

$$\frac{A_1}{\Omega kT} = -\frac{1}{2} \int dr \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \left[v_{\alpha\beta}(r) - w_{\alpha\beta}(r) - w_{\alpha\beta}(r) v_{\alpha\beta}(r) \right.$$
$$\left. + \frac{1}{2} v_{\alpha\beta}^2(r) - v_{\alpha\beta}(r) z_{\alpha\beta}(r) \right]$$
$$+ \frac{1}{2} \frac{1}{\Omega} \sum_k \left[\log D(k) + \sum_{\alpha=1}^{\sigma} \rho_\alpha Z_{\alpha\alpha}(k) \right] + \frac{A_1'}{\Omega kT}, \qquad (4·10)$$

where $A_1'/\Omega kT$ is given by (4·9). Expression (4·10) is rewritten, by the use of (3·9), as follows:

$$\frac{A_1}{\Omega kT} = -\frac{1}{2} \int dr \sum_{\alpha=1}^{\sigma} \sum_{\beta=1}^{\sigma} \rho_\alpha \rho_\beta \left[\{b_{\alpha\beta}(r) + 1\} e^{w_{\alpha\beta}(r)} - 1 - w_{\alpha\beta}(r) \right.$$
$$\left. - w_{\alpha\beta}(r) v_{\alpha\beta}(r) + \frac{1}{2} v_{\alpha\beta}^2(r) - v_{\alpha\beta}(r) z_{\alpha\beta}(r) \right]$$
$$+ \frac{1}{2} \frac{1}{\Omega} \sum_k \left[\log D(k) + \sum_{\alpha=1}^{\sigma} \rho_\alpha Z_{\alpha\alpha}(k) \right] + \frac{A_1'}{\Omega kT}, \qquad (4·11)$$

which will be more conveniently used than (4·10) in the following.

It can be easily seen that the above expression (4·11) is reduced to (4·11) in I if one considers a one-component system. It can also be seen that (4·10) is reduced to the expression in the hyper-netted chain approximation if one omits $A_1'/\Omega kT$ from (4·10), though in reference 8) $D(k)$ (which is identical to L in reference 8)) is not expressed explicitly in the form of determinant.

The expression for the free energy in a one-component system has been shown to have a stationary character.[1] It will be shown here that expression (4·11) also has the same character. The following relation is necessary to show it:

$$\frac{\delta}{\delta v_{\alpha\beta}(r)} \left(\frac{A_1'}{\Omega kT} \right) = -\frac{\rho_\alpha \rho_\beta}{1 + \delta_{\alpha\beta}} x_{\alpha\beta}(r), \qquad (4·12)$$

where the left-hand side denotes the functional derivative of $A_1'/\Omega kT$ with respect to $v_{\alpha\beta}(r)$.* The proof of (4·12) can be done by reversing the reasoning which

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* The functional derivative is in general defined as follows. Let P be a functional of $\alpha(r)$. When $\alpha(r)$ is varied by $\delta\alpha(r)$, the corresponding first order variation of P is denoted by δP. Then the functional derivative $\delta P/\delta\alpha(r)$ is defined by[1],[11]

$$\delta P = \int dr \frac{\delta P}{\delta\alpha(r)} \delta\alpha(r).$$

was used in the derivation of (4·9) from (4·5), though the proof is omitted here. The first order variation of the free energy when in (4·11) the functions $w_{\alpha\beta}$, $v_{\alpha\beta}$ and $z_{\alpha\beta}$ are varied *independently* of each other, is shown to be, with the aid of (4·12) and (3·3),

$$
\delta\left(\frac{A_1}{\Omega kT}\right) = -\frac{1}{2}\int d\boldsymbol{r}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\Big[\{b_{\alpha\beta}(r)+1\}e^{w_{\alpha\beta}(r)}-1-v_{\alpha\beta}(r)\Big]\delta w_{\alpha\beta}(r)
$$

$$
-\frac{1}{2}\int d\boldsymbol{r}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\Big[v_{\alpha\beta}(r)-w_{\alpha\beta}(r)-z_{\alpha\beta}(r)+x_{\alpha\beta}(r)\Big]\delta v_{\alpha\beta}(r)
$$

$$
+\frac{1}{2}\frac{1}{\Omega}\sum_{k}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\Big[\frac{1+\delta_{\alpha\beta}}{2}\frac{\partial\log D(k)}{\partial Z_{\alpha\beta}}+\rho_\alpha\rho_\beta V_{\alpha\beta}(k)+\rho_\alpha\delta_{\alpha\beta}\Big]\delta Z_{\alpha\beta}(k).
$$

$$(4\cdot13)$$

The coefficients of $\delta w_{\alpha\beta}(r)$, $\delta v_{\alpha\beta}(r)$ and $\delta Z_{\alpha\beta}(k)$ in the above expression are seen to vanish if there exist relations (3·9), (3·11) and (3·10) among $w_{\alpha\beta}$, $v_{\alpha\beta}$ and $z_{\alpha\beta}$. In other words, it has been proved that the free energy (4·11) is stationary with respect to the functions satisfying (3·9), (3·10) and (3·11). Conversely, it may be said that the set of Eqs. (3·9), (3·10) and (3·11) can be derived by means of such a variational principle that the free energy (4·11) is to be stationary with respect to the variations of $w_{\alpha\beta}$, $v_{\alpha\beta}$ and $z_{\alpha\beta}$.

The stationary character of (4·11) is useful in deriving the expressions for the pressure and the internal energy by means of thermodynamical relations, because in such cases the dependence of $w_{\alpha\beta}$, $v_{\alpha\beta}$ and $z_{\alpha\beta}$ on density and temperature can be neglected. It may be useful also in determining the approximate forms of $w_{\alpha\beta}$, $v_{\alpha\beta}$ and $z_{\alpha\beta}$, hence of the pair distribution function.

It is known that the pair distribution function is related to the free energy by[11],[8]

$$
\rho_\alpha\rho_\beta g_{\alpha\beta}(r) = \frac{1+\delta_{\alpha\beta}}{\Omega}\frac{\delta A_1}{\delta\phi_{\alpha\beta}(r)}.
$$

$$(4\cdot14)$$

It can be readily verified, by the use of (4·11), that this relation is valid in our case as it should be.

§ 5.   Summary and concluding remarks

The results which have been obtained can be summarized as follows. The interaction part of the Helmholtz free energy in a σ-component fluid system (the volume Ω, the temperature T and the number densities $\rho_1, \rho_2, \cdots, \rho_\sigma$) is written in the form

$$
\frac{A_1}{\Omega kT} = -\frac{1}{2}\int d\boldsymbol{r}\sum_{\alpha=1}^{\sigma}\sum_{\beta=1}^{\sigma}\rho_\alpha\rho_\beta\Big[\{b_{\alpha\beta}(r)+1\}e^{w_{\alpha\beta}(r)}-1-w_{\alpha\beta}(r)
$$

$$
-w_{\alpha\beta}(r)v_{\alpha\beta}(r)+\frac{1}{2}v_{\alpha\beta}^2(r)-v_{\alpha\beta}(r)z_{\alpha\beta}(r)\Big]
$$

$$+\frac{1}{2}\frac{1}{\varOmega}\sum_{k}\left[\log D(k)+\sum_{\alpha=1}^{\sigma}\rho_{\alpha}Z_{\alpha\alpha}(k)\right]$$

$$-\sum_{m}\frac{\rho^{m}}{m!}\frac{1}{\varOmega}\int d\{\mathbf{m}\}\sum_{\mathbf{m}\geq i>j\geq1}\varPi\,v_{\nu_{i}\nu_{j}}(r_{ij}),\qquad(5\cdot1)$$

All products which are
more than doubly connected.

where $b_{\alpha\beta}(r)$ is defined in terms of the pair interaction potential $\phi_{\alpha\beta}(r)$ by

$$b_{\alpha\beta}(r)=e^{-\phi_{\alpha\beta}(r)/kT}-1\qquad(5\cdot2)$$

and $D(k)$ is a determinant

$$D(k)=\begin{vmatrix}1-\rho_{1}Z_{11}(k) & -\rho_{1}Z_{12}(k) & \cdots\cdots & -\rho_{1}Z_{1\sigma}(k)\\ -\rho_{2}Z_{21}(k) & 1-\rho_{2}Z_{22}(k) & \cdots\cdots & -\rho_{2}Z_{2\sigma}(k)\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\ -\rho_{\sigma}Z_{\sigma1}(k) & -\rho_{\sigma}Z_{\sigma2}(k) & \cdots\cdots & 1-\rho_{\sigma}Z_{\sigma\sigma}(k)\end{vmatrix}.\qquad(5\cdot3)$$

Mayer's notation is adopted in the last term on the right-hand side of (5·1). The functions $w_{\alpha\beta}(r)$, $v_{\alpha\beta}(r)$ and $z_{\alpha\beta}(r)$ which are symmetric in α and β ($V_{\alpha\beta}(k)$ and $Z_{\alpha\beta}(k)$ denote the Fourier transforms of $v_{\alpha\beta}(r)$ and $z_{\alpha\beta}(r)$, respectively.) are to be determined in such a way that (5·1) is stationary with respect to the variations of these functions. Namely they must satisfy the set of equations:

$$v_{\alpha\beta}(r)=[b_{\alpha\beta}(r)+1]e^{w_{\alpha\beta}(r)}-1,\qquad(5\cdot4)$$

$$\rho_{\alpha}\rho_{\beta}V_{\alpha\beta}(k)=-\frac{1+\delta_{\alpha\beta}}{2}\frac{\partial\log D(k)}{\partial Z_{\alpha\beta}}-\rho_{\alpha}\delta_{\alpha\beta},\qquad(5\cdot5)$$

and

$$w_{\alpha\beta}(r)=x_{\alpha\beta}(r)+v_{\alpha\beta}(r)-z_{\alpha\beta}(r).\qquad(5\cdot6)$$

The function $x_{\alpha\beta}(r)$ is defined by

$$x_{\alpha\beta}(r_{12})=\sum_{m}\frac{\rho^{m}}{m!}\int d\{\mathbf{m}\}\sum_{m+2\geq i>j\geq1}^{(X')}\varPi\,v_{\nu_{i}\nu_{j}}(r_{ij}),\qquad(5\cdot7)$$

where $\Sigma'^{(X')}$ denotes the summation over all the different diagrams which are to be constructed if one removes one bond $v_{\alpha\beta}(r_{12})$ from the diagrams appearing in the last term on the right-hand side of (5·1). The pair distribution function $g_{\alpha\beta}(r)$ is related to $v_{\alpha\beta}(r)$ by

$$g_{\alpha\beta}(r)=v_{\alpha\beta}(r)+1.\qquad(5\cdot8)$$

In some cases the above results may be exact ones as far as the expressions themselves are well determined, irrespective as to whether the original density expansions (2·4), (2·6), (2·7) and (2·8) from which the above results have been obtained are valid or not. For instance, in an ionic solution or a classical plasma, the interaction potentials are of long-range character so that the original

density expansions diverge term by term. There is good reason to expect that the above expressions have definite meanings even in such a case (see references 6), 7), 8) and 12)). An application of the present theory to such a system will be undertaken in a forthcoming paper.

If we restrict ourselves to a system without long-range interactions, the original density expansions converge at low enough densities so that the series appearing in the above expressions converge, perhaps more rapidly than the original expansions,* at such densities. The present author hopes that the series appearing in the above expressions may converge even at the densities which are larger than the maximum density for which the original expansions converge. It is also hoped that the maximum density for which the determinant $D(k)$ does not vanish for any k may be larger than the maximum density for which the original expansions converge.

At the present stage a physical meaning is not clear of the case where $D(k)$ vanishes for some k or where the series appearing in the above expressions diverge. The situation is the same as in I. Such a problem will be investigated in the near future.

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* This may be inferred from the fact that the diagrams appearing in the above series are more restricted ones than the diagrams in the original expansions, though we cannot prove it in general.