

STATISTICAL-MECHANICAL THEORY OF MIXTURES IN THE  
ONE-CHAIN APPROXIMATION. I. BINARY SYSTEMS

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The free energy, pressure, chemical potentials, and radial distribution functions are calculated for a macroscopic system composed of two different species, in the one-chain approximation. This approximation, which consists in retaining the simplest infinite subset of terms of the virial expansion, was proved recently to be able to predict the existence of first-order phase transitions and to describe qualitatively the condensed phases in one-component systems.

*1. Introduction*

Very little has been hitherto done in the microscopic description of many-component fluids. The generalization of the Ursell-Mayer virial expansion method [1, 2] to many-component system has been given long ago (*cf. e.g.* [1, 3, 4] and references quoted there). The formal method of generating subsequent virial coefficients of the density expansion of macroscopic properties (partition function and equation of state), as well as the distribution functions, is thus known for such systems. However, the actual calculation of the terms of the virial expansion, for systems composed of different species of particles, is fairly complicated because the labeling of the points of corresponding graphs contains now not only the running numbers of particles, but also the identification of the species. So far, only some very simplified models of binary mixtures have been considered, as, *e.g.*, the Ising model description examined by Heims [5], and the model of Gaussian molecules with interactions only between different species, developed by Helfland and Stillinger [6]. A semi-guessed equation of state for mixtures of hard spheres has been proposed by Boublik [7] on the basis of the similar equation of Carnahan and Starling for a one-component system [8]. Besides, some progress has been also achieved in the theory of two-component quantum fluids (*cf. e.g.* [9]).

We have recently proposed the so-called one-chain (OC) approximation for the equation of state and radial distribution function for one-component fluid, which proved to be able to predict the existence of phase transitions, and to describe qualitatively the structure of condensed phases [10]. This approximation consists in the summation to a closed form

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of some simple infinite subset of graphs (built of one chain only) of the Ursell-Mayer virial expansion of the properties of the one-component system. It turns out that the same method may be also applied, without any additional approximations, to many-component systems. It seems thus worthwhile to perform such calculations, the more that the OC approximation for one-component system may be considered as some approximate solution of the Percus-Yevick (PY) [11, 12] and hypernetted chain (HNC) [13, 14] approximations, which are now known to yield quantitatively correct results (*cf. e.g.* [15÷17]).

Because both the calculations and the resulting formulae are somewhat complicated and lengthy, we shall restrict ourselves in this paper to the case of binary (two-component) systems, in order to explain better the details of the involved calculations. A further generalization to  $n$ -component system ( $n$  arbitrary) will be presented in the second part of this work.

## 2. Radial distribution functions

We begin with the calculation of the radial distribution functions, which presents a simpler task than the analogous calculation of the partition function, or the free energy.

Consider the system composed of  $N_\alpha$  particles of the species  $\alpha$ ,  $N_\beta$  particles of the species  $\beta$ , ( $N = N_\alpha + N_\beta$ ), contained in the volume  $\Omega$ , and kept at temperature  $T$ . The particles interact with each other through the pair potentials  $V_{ab}(r)$  ( $a, b = \alpha, \beta$  denote the species, and  $V_{ab} = V_{ba}$ ), which are assumed to be dependent only on the relative distance  $r$  between a given pair of particles. It is also assumed that the quantum effects are negligible, and the thermodynamical limit

$$N = N_\alpha + N_\beta \rightarrow \infty, \quad \Omega \rightarrow \infty, \quad \varrho = \frac{1}{v} = \frac{N}{\Omega} = \text{finite} \quad (2.1)$$

is considered. We introduce also the notion of mole (or number) fractions,

$$x_a = N_a/N, \quad a = \alpha, \beta, \quad x_\alpha + x_\beta = 1. \quad (2.2)$$

$N$ ,  $\varrho$ , and  $v$  denote the overall number of particles, overall number density, and overall specific volume of the system, respectively. The respective species parameters may thus be obtained by multiplying (or dividing, in the case of  $v$ ) these quantities by the mole fraction of a given species. The radial distribution function  $g_{ab}(r)$ , which describes the spatial arrangement of particles  $b$  with respect to the particle  $a$  placed at the origin of the coordinate system, may be formally written in the form of the virial series (*i.e.*, the series of the powers of  $\varrho$ ):

$$\ln \{g_{ab}(r)\} = -\frac{1}{kT} V_{ab}(r) + \sum_{m=1}^{\infty} d_{m,ab}(r) \varrho^m, \quad a, b = \alpha, \beta \quad (2.3)$$

where the virial coefficients  $d_{m,ab} = d_{m,ab}(r; T, x_\alpha, x_\beta)$ , may be calculated according to the following prescriptions (*cf.* [2]),

(i)  $d_{m,ab}$  is represented by all topologically different,  $m$ -point, non-parallel, biconnected, labeled linear graphs;

(ii)  $m$ -point linear graph is constructed by drawing two rootpoints (representing particles  $a$  and  $b$ ), and  $m$  internal points (representing integration variables), and linking these points by lines in any possible way, with one exception that the rootpoints must not be linked directly with each other;

(iii) the given graph is biconnected (*i.e.*, is a "star" graph [2]), if (after drawing the completing direct line between two root-points) it may be made disconnected by removing at least two of its lines;

(iv) the given graph is non-parallel, if it cannot be made disconnected after erasing both root-points;

(v) every internal point is labeled by the number  $j$  ( $j = 1, 2, \dots, m$ ), identifying the integration variable ascribed to the point (these numbers must be different for different points), and by the label  $\lambda$  ( $\lambda = \alpha, \beta$ ), identifying the species; the labels ( $a, b$ ) of the root-points are determined by labels of the function  $\mathcal{G}_{ab}$ ;

(vi) to every internal point of the graph, labeled  $\lambda$ , the factor  $x_\lambda$  is associated;

(vii) to every line of the graph, labeled ( $i\lambda$ ) and ( $j\nu$ ) (including the root-points  $a, b$ ), the factor:

$$f_{\lambda\nu}(r_{ij}) = \exp \{-V_{\lambda\nu}(r_{ij})/kT\} - 1, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \quad (2.4)$$

is associated;

(viii) the value of the  $m$ -th virial coefficient  $d_{m,ab}$  is obtained by collecting the contributions from all the relevant graphs (multiplied by  $1/m_\alpha! m_\beta!$ , where  $m_\alpha, m_\beta$  denote numbers of  $\alpha$  and  $\beta$  points respectively ( $m_\alpha + m_\beta = m$ ), and integrated over  $\int d\mathbf{r}_1 \dots \int d\mathbf{r}_m$ . An example will be given below.

Now, the OC approximation consists in retaining for every  $d_m$  only one type of graphs, such that all the points of the OC graph are connected into one chain, *i.e.*, every internal point is connected with two other points (internal or root) only. Of course, all possible labelings of such a graph must be taken into account. For the one-component system the calculation of the contributions from such graphs is quite simple (*cf.* [10]), because in this case the contributions do not depend on labeling (the same is true for more complicated one component graphs [2]). This, is, however, not the case for many-component system.

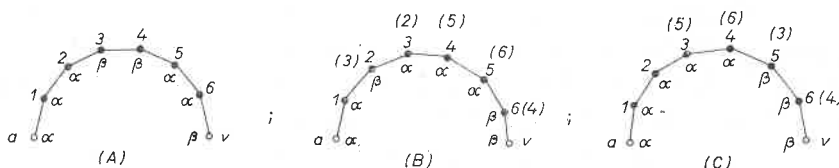


Fig. 1. Examples of differently labeled OC graphs from  $d_{6,\alpha\beta}$

Nevertheless, it turns out that, at least for OC graphs<sup>1</sup>, the contribution from a given graph also does not depend on the detailed arrangement of labels, the only relevant property being the number of different bounds (lines)  $\alpha - \alpha$ ,  $\alpha - \beta$  (or  $\beta - \alpha$ ), and  $\beta - \beta$  and, of course, the number of points  $\alpha$  and points  $\beta$ . We shall demonstrate this on a simple example.

<sup>1</sup> The same property holds true also for the graph of the hypernetted chain type.

Consider two graphs (*A*) and (*B*), from Fig. 1. These two graphs are evidently different with respect to the labels. Write down the contributions to  $d_{6,\alpha\beta}$  from these two graphs, according to the rules stated above:

$$A = \frac{1}{4!2!} x_\alpha^4 x_\beta^2 \int d\mathbf{r}_1 \dots \int d\mathbf{r}_6 f_{\alpha\alpha}(\mathbf{r}_{a1}) f_{\alpha\alpha}(\mathbf{r}_{12}) f_{\alpha\beta}(\mathbf{r}_{23}) f_{\beta\beta}(\mathbf{r}_{34}) \times \\ \times f_{\beta\alpha}(\mathbf{r}_{45}) \cdot f_{\alpha\alpha}(\mathbf{r}_{56}) f_{\alpha\beta}(\mathbf{r}_{6b}), \quad (2.5)$$

$$B = \frac{1}{4!2!} x_\alpha^4 x_\beta^2 \int d\mathbf{r}_1 \dots \int d\mathbf{r}_6 f_{\alpha\alpha}(\mathbf{r}_{a1}) f_{\alpha\beta}(\mathbf{r}_{12}) f_{\beta\alpha}(\mathbf{r}_{23}) f_{\alpha\alpha}(\mathbf{r}_{34}) \times \\ \times f_{\alpha\alpha}(\mathbf{r}_{45}) f_{\alpha\beta}(\mathbf{r}_{56}) f_{\beta\beta}(\mathbf{r}_{6b}). \quad (2.6)$$

Introduce the Fourier transforms  $\gamma(q)$  of the Mayer functions  $f(r)$ :

$$\gamma_{\lambda\nu}(q) = \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} f(r) \quad \lambda, \nu = \alpha, \beta, \quad (2.7).$$

$$i.e., f_{\lambda\nu}(r) = (2\pi)^{-3} \int d\mathbf{q} e^{-i\mathbf{q} \cdot \mathbf{r}} \gamma_{\lambda\nu}(q),$$

$$\gamma_{\alpha,\beta}(q) = \gamma_{\beta,\alpha}(q).$$

With the help of these functions, it is easy to find that the contributions *A* and *B* are identical with each other, and equal (the properties of the Fourier transforms of convolution are used) to:

$$A = B = \frac{1}{4!} \frac{1}{2!} x_\alpha^4 x_\beta^2 (2\pi)^{-3} \int d\mathbf{q} e^{-i\mathbf{q} \cdot (\mathbf{r}_a - \mathbf{r}_b)} [\gamma_{\alpha\alpha}(q)]^3 [\gamma_{\alpha\beta}(q)]^3 \gamma_{\beta\beta}(q). \quad (2.8)$$

On the other hand, the contribution from the graph (*C*) from Fig. 1, calculated in the same way is:

$$C = \frac{1}{4!} \frac{1}{2!} x_\alpha^4 x_\beta^2 (2\pi)^{-3} \int d\mathbf{q} e^{-i\mathbf{q} \cdot (\mathbf{r}_a - \mathbf{r}_b)} [\gamma_{\alpha\alpha}(q)]^4 [\gamma_{\beta\beta}(q)]^2 \gamma_{\alpha\beta}(q) \quad (2.9)$$

*i.e.*,  $C \neq A$ , although the graphs (*A*), (*B*) and (*C*) contain the same number of  $\alpha$ - and  $\beta$ -points. It is also easy to check that any exchange of the numbers 1, ..., 6 (*e.g.*, the numbers in the parentheses in Fig. 1) between the internal points, with the labels  $\alpha, \beta$  unaltered, does not change the values *A, B, C*. According to the above results, we may reformulate the prescriptions (*vii*) and (*viii*), for the OC approximation, as follows:

(*vii*) to every line joining the points  $\lambda$  and  $\nu$ , ( $\lambda, \nu = \alpha, \beta$ ) the factor  $\gamma_{\lambda\nu}(q)$  is associated:

(*viii*) the value of the *m*-th virial coefficient  $d_{m,ab}$  in the OC approximation is obtained by collecting the contributions from all the differently labeled OC graphs multiplying them by the factor  $[(2\pi)^3 m_\alpha! m_\beta!]^{-1} e^{-i\mathbf{q} \cdot (\mathbf{r}_a - \mathbf{r}_b)}$ , and integrating over  $\int d\mathbf{q}$ .

We are now ready for the calculation of the OC approximation for the radial distribution function of the binary system. The method of construction of the OC graphs for this case is presented in Fig. 2 and is self-explaining. We shall calculate directly the OC part of the virial series (2.3) (the formulae for the density-independent virial coefficient  $d_m$  would be much too difficult to write down here, so we include directly the factors  $q^m$  into subsequent

formulae. Let us first calculate the factor  $\Gamma_v(q)$  proceeding from an  $\alpha$ -chain of the graph. According to the prescriptions formulated above, it is:

$$\Gamma_v(q) = x_v \varrho \sum_{k=0}^{\infty} [x_v \varrho \gamma_{vv}(q)]^k = \frac{x_v \varrho}{1 - x_v \varrho \gamma_{vv}(q)}, \quad v = \alpha, \beta. \quad (2.10)$$

The complete contribution to  $g_{\alpha\alpha}(r)$  from all the graphs of the type shown in Fig. 2 may be found as follows: let the number of  $\beta$ -chains in a given graph be  $n$  ( $n = 0, 1, 2, \dots$ ).

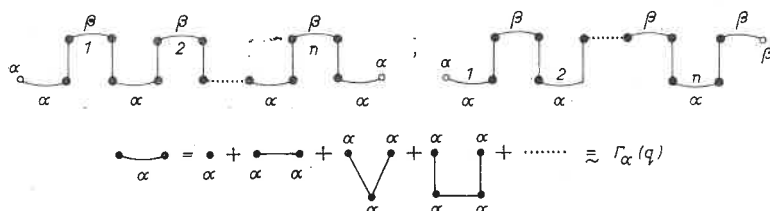


Fig. 2. Construction of the OC graphs for radial distribution function

Thus the number of  $\alpha$ -chains must be  $n+1$ , and the number of bonds  $\alpha-\beta$  (each bringing the factor  $\gamma_{\alpha\beta}$ ) —  $2n$ . The contribution to  $g_{\alpha\alpha}(r)$  will thus be:

$$\sum_{n=0}^{\infty} [\Gamma_\alpha(q)]^{n+1} [\Gamma_\beta(q)]^n [\gamma_{\alpha\beta}(q)]^{2n}. \quad (2.11)$$

Let us note that in the above procedure the root-points have been treated in the same way as other points of the graphs. We must thus subtract the terms  $x_\alpha \varrho [1 + x_\alpha \gamma_{\alpha\alpha}(q)]$ , which proceed from the first two terms of the single  $\alpha$ -chain when there are no  $\beta$ -chains ( $n = 0$ ), because such terms do not exist at all in the original virial series (2.3); next, we must divide the result by  $(x_\alpha \varrho)^2$ , because the factors  $x_v \varrho$  are associated with internal points only. The other distribution functions may be calculated in a similar way, and we get:

$$g_{\lambda\nu}(r) = \exp\left\{-\frac{V_{\lambda\nu}(r)}{kT}\right\} + \Psi_{\lambda\nu}(r), \quad \lambda, \nu = \alpha, \beta \quad (2.12)$$

where

$$\Psi_{\lambda\nu}(r) = (2\pi)^{-3} \int d\mathbf{q} \bar{\Psi}_{\lambda\nu}(q) e^{-i\mathbf{q} \cdot \mathbf{r}}, \quad (2.13)$$

and (we write now the formulae in terms of  $v = 1/\varrho$ )

$$\begin{aligned} \bar{\Psi}_{\alpha\alpha}(q) &= \bar{\Psi}_{\alpha\alpha}(q; T, v, x_\alpha) \\ &= [M(q)]^{-1} [x_\alpha x_\beta \gamma_{\alpha\alpha} (\gamma_{\alpha\beta}^2 - \gamma_{\alpha\alpha} \gamma_{\beta\beta}) + v(x_\beta \gamma_{\alpha\beta}^2 + x_\alpha \gamma_{\alpha\alpha}^2)], \end{aligned} \quad (2.14)$$

$$\bar{\Psi}_{\alpha\beta}(q) = \bar{\Psi}_{\beta\alpha}(q) = [M(q)]^{-1} \gamma_{\alpha\beta} \{ [x_\alpha x_\beta (\gamma_{\alpha\beta}^2 - \gamma_{\alpha\alpha} \gamma_{\beta\beta})] + v(x_\alpha \gamma_{\alpha\alpha} + x_\beta \gamma_{\beta\beta}) \}, \quad (2.15)$$

$$M(q) = (v - x_\alpha \gamma_{\alpha\alpha})(v - x_\beta \gamma_{\beta\beta}) - x_\alpha x_\beta \gamma_{\alpha\beta}^2. \quad (2.16)$$

The explicit indication of the  $q$ -dependence of the  $\gamma$ -functions,  $\gamma_{\lambda\nu} = \gamma_{\lambda\nu}(q)$ , is omitted in the above formulae for the sake of simplicity. The formula for  $\bar{\Psi}_{\beta\beta}(q)$  may be obtained from (2.14) by interchanging the subscripts  $\alpha, \beta$ .

Let us also look for the formulae of the radial distribution functions in an infinitely diluted solution of particles  $\beta$  in particles  $\alpha$  ( $x_\beta \rightarrow 0, x_\alpha \rightarrow 1$ ). We easily get:

$$\begin{aligned}\lim_{x_\beta \rightarrow 0} \bar{\Psi}_{\alpha\alpha} &= \frac{\gamma_{\alpha\alpha}^2}{v - \gamma_{\alpha\alpha}} = \bar{\Psi}_{\alpha\alpha}^0 \\ \lim_{x_\beta \rightarrow 0} \bar{\Psi}_{\beta\beta} &= \frac{\gamma_{\alpha\beta}^2}{v - \gamma_{\alpha\alpha}} = \bar{\Psi}_{\beta\beta}^0 \\ \lim_{x_\beta \rightarrow 0} \bar{\Psi}_{\alpha\beta} &= \frac{\gamma_{\alpha\alpha}\gamma_{\alpha\beta}}{v - \gamma_{\alpha\alpha}} = [\bar{\Psi}_{\alpha\alpha}^0 \cdot \bar{\Psi}_{\beta\beta}^0]^{1/2}.\end{aligned}\quad (2.17)$$

$\bar{\Psi}_{\alpha\alpha}^0$  is identical with the corresponding formula for the one-component system [10]. However, the correlations between the  $\beta$ -particles do not vanish even in an infinitely diluted system.

### 3. Free energy

We are now going to calculate the free energy  $F$  of the system. The virial expansion is usually written for the pressure  $p$ , rather than for  $F$  [1, 2]; however, it is easy to reformulate the theory to yield directly  $F$ , and the series formulae for  $F$  are easier to deal with than those for  $p$ . The virial expansion for  $F$  may thus be written in the form:

$$F = F_{id} - kT \sum_{m=2}^{\infty} C_m \varrho^{m-1}, \quad (3.1)$$

where

$$\begin{aligned}F_{id} &= -kT\{1 + x_\alpha \ln(v/\lambda_\alpha^3) + x_\beta \ln(v/\lambda_\beta^3) - x_\alpha \ln x_\alpha - x_\beta \ln x_\beta\} \\ \lambda_i &= (2\pi\hbar^2/mkT)^{1/2}; \quad i = \alpha, \beta,\end{aligned}\quad (3.2)$$

is the ideal-gas free energy ( $m_i$  — the mass of the particle of the species  $i$ ). Note that we use here the notation in which  $F$  denotes the free energy calculated per one particle, so that the total free energy (the extensive quantity) of the whole system is  $NF$ .

The virial coefficients  $C_m$  are connected with the usual virial coefficients  $B_m$  of the pressure expansion through the relations:

$$B_m = -(m-1)C_m \quad (3.3)$$

(these relations result from the thermodynamical relation between  $F$  and  $p$ , and may be expressed in terms of biconnected graphs in a way similar to that used in the preceding Section for the virial coefficients of the radial distribution functions. The difference is (*cf.* also [2]) that the free-energy (and pressure) graphs do not contain root-points and thus they form closed (directly biconnected) structures (stars [2]). The free-energy graph may thus be obtained from the radial distribution function graph by linking the rootpoints of the latter by a direct line (Mayer function  $f_{\nu\nu}(r_{ab})$  or its Fourier transform  $\gamma_{\nu\nu}(q)$  and treating these points as internal ones<sup>2</sup>, *i.e.*, integrating the graph contribution over  $\int d\mathbf{r}_a \int d\mathbf{r}_b$ . The

<sup>2</sup> The labeling of the points may be interchanged with the labeling of other internal points.

result is to be divided by  $\Omega$  and the limit  $\Omega \rightarrow \infty$  is to be taken [2]. Besides, the graphs containing two points only must be also taken into account (these graphs correspond to the first term of (2.3)).

In order to find the contribution to the free energy from all the OC graphs, we proceed similarly as in the preceding Section. The main difference lies now in the fact that the free-energy OC graphs get some new symmetries [2]. It would be rather difficult to find these symmetries for any single graph of the binary system. However, this task may be easily achieved by considering some subsets of graphs. Consider, for example, the subset

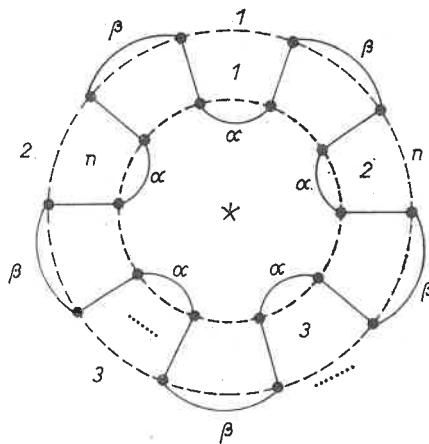


Fig. 3. Construction of the OC graph for free energy. The definition of an arc segment is the same as in Fig. 2. The existence of the  $n$ -fold symmetry axis (marked in the center of the graph) as well as of the symmetry with respect to the right-left inversion (upper and lower sets of labels 1, 2, ...,  $n$ ) is easily visible here

of OC graphs containing  $n$   $\alpha$ -chains (and  $n$   $\beta$ -chains). This subset is represented in Fig. 3. Such a generalized graph possesses an  $n$ -fold symmetry axis (topological invariance with respect to cyclic permutations of the labelings of chains) and also is topologically invariant with respect to the right-left inversion of the sequence of the labelings of chains. The symmetry factor [2] of such a graph is thus  $2n$ , *i. e.* the total number of topologically different labelled graphs is diminished by the factor  $1/2n$ . The procedure analogous to that described in the preceding Section leads finally to the following result for the OC approximation of the energy  $F$  the system (divided by the total number of particles):

$$\begin{aligned} \frac{F-F_{id}}{kT} = & -\frac{1}{2v} [x_{\alpha}^2 \gamma_{\alpha\alpha}(0) + 2x_{\alpha}x_{\beta} \gamma_{\alpha\beta}(0) + x_{\beta}^2 \gamma_{\beta\beta}(0)] + \\ & + \frac{v}{2(2\pi)^3} \int d\mathbf{q} \left\{ \ln |M(\mathbf{q})/v^2| + \frac{1}{v} [x_{\alpha} \gamma_{\alpha\alpha}(\mathbf{q}) + x_{\beta} \gamma_{\beta\beta}(\mathbf{q})] + \right. \\ & \left. + \frac{1}{2v^2} [x_{\alpha}^2 \gamma_{\alpha\alpha}^2(\mathbf{q}) + 2x_{\alpha}x_{\beta} \gamma_{\alpha\beta}^2(\mathbf{q}) + x_{\beta}^2 \gamma_{\beta\beta}^2(\mathbf{q})] \right\}, \end{aligned} \quad (3.4)$$

where  $M(\mathbf{q})$  is given by (2.16). It is easy to check that for  $x_{\beta} = 0$ ,  $x_{\alpha} = 1$ , this formula is identical with the corresponding formula for one-component system.

## 4. Final remarks

Other thermodynamical functions in the OC approximation may be obtained, through the well-known thermodynamical relations, from the formulae (3.4) for free energy. We shall write down some formulae.

The pressure (equation of state) is:

$$\begin{aligned} \frac{P}{kT} = & -\frac{1}{kT} \left( \frac{\partial F}{\partial v} \right)_{T, x_\alpha, N} = \frac{1}{v} - \frac{1}{v^2} [x_\alpha^2 \gamma'_{\alpha\alpha}(0) + 2x_\alpha x_\beta \gamma'_{\alpha\beta}(0) + x_\beta^2 \gamma'_{\beta\beta}(0)] - \\ & - \frac{1}{2(2\pi)^3} \int d\mathbf{q} \left\{ \ln |M(q)/v^2| + \frac{1}{M(q)} [vx_\alpha \gamma'_{\alpha\alpha}(q) + vx_\beta \gamma'_{\beta\beta}(q) + \right. \\ & \quad \left. + 2x_\alpha x_\beta (\gamma'_{\alpha\beta}(q) - \gamma_{\alpha\alpha}(q)\gamma_{\beta\beta}(q))] - \right. \\ & \quad \left. - \frac{1}{2v^2} [x_\alpha^2 \gamma_{\alpha\alpha}^2(q) + 2x_\alpha x_\beta \gamma_{\alpha\beta}^2(q) + x_\beta^2 \gamma_{\beta\beta}^2(q)] \right\}. \end{aligned} \quad (4.1)$$

The next thermodynamical function which may be calculated directly from  $F$  is the entropy  $S$ :

$$\begin{aligned} S = & - \left( \frac{\partial F}{\partial T} \right)_{v, x_\alpha, N}, \\ \frac{S - S_{id}}{kT} = & \frac{1}{2v} [x_\alpha^2 \gamma'_{\alpha\alpha}(0) + 2x_\alpha x_\beta \gamma'_{\alpha\beta}(0) + x_\beta^2 \gamma'_{\beta\beta}(0)] - \\ & - \frac{v}{2(2\pi)^3} \int d\mathbf{q} \left\{ \frac{(\partial M / \partial T)_{v, x_\alpha, N}}{M} + \frac{1}{v} [x_\alpha \gamma'_{\alpha\alpha}(q) + x_\beta \gamma'_{\beta\beta}(q)] + \right. \\ & \quad \left. + \frac{1}{v^2} [x_\alpha^2 \gamma_{\alpha\alpha} \gamma'_{\alpha\alpha} + 2x_\alpha x_\beta \gamma_{\alpha\beta} \gamma'_{\alpha\beta} + x_\beta^2 \gamma_{\beta\beta} \gamma'_{\beta\beta}] \right\}, \end{aligned} \quad (4.2)$$

where

$$\begin{aligned} \frac{\partial M}{\partial T} = & -v(x_\alpha \gamma'_{\alpha\alpha} + x_\beta \gamma'_{\beta\beta}) + x_\alpha x_\beta (\gamma'_{\alpha\alpha} \gamma_{\beta\beta} + \gamma_{\alpha\alpha} \gamma'_{\beta\beta} - 2\gamma'_{\alpha\beta} \gamma_{\alpha\beta}), \\ \gamma'_{\lambda\nu}(q) = & \frac{\partial}{\partial T} \gamma_{\lambda\nu}(q) = \frac{1}{kT^2} \int d\mathbf{r} V(r) e^{-V(r)/kT} e^{i\mathbf{q} \cdot \mathbf{r}}. \end{aligned} \quad (4.3)$$

Other functions, like the internal energy  $U = F + TS$ , Gibbs free energy  $G = F + pv$ , may be found when  $F$ ,  $p$ , and  $S$  are known. Let us note that both pressure and internal energy may be also calculated from the radial distribution functions. We write down the formula for the internal energy of the binary system:

$$u = \frac{3}{2}kT + \frac{1}{2v} \int d\mathbf{r} \{ x_\alpha^2 V_{\alpha\alpha}(r) g_{\alpha\alpha}(r) + 2x_\alpha x_\beta V_{\alpha\beta}(r) g_{\alpha\beta}(r) + x_\beta^2 V_{\beta\beta}(r) g_{\beta\beta}(r) \}, \quad (4.4)$$

being the trivial generalization of the well-known formula for one-component system. The formulae for  $F$ ,  $S$ ,  $U$ , etc. written here give these quantities per one particle, *i. e.*, the corresponding quantities for the whole system are, in fact  $NF$ ,  $NS$ , etc. The chemical potential,



$\mu_\nu$ , of the species  $\nu$ , must be thus calculated by the appropriate differentiation of  $NF$ , and not  $F$  from the formula (3.4) itself:

$$\begin{aligned} \mu_\alpha &= \left( \frac{\partial NF}{\partial N_\alpha} \right)_{T, \Omega, N_\beta} = F + x_\beta \left( \frac{\partial F}{\partial x_\alpha} \right)_{v, T} - v \left( \frac{\partial F}{\partial v} \right)_{x_\alpha, T} \\ \frac{\mu_\alpha - \mu_{\alpha id}}{kT} &= \frac{1}{v} [x_\alpha \gamma_{\alpha\alpha}(0) + x_\beta \gamma_{\beta\beta}(0)] + \frac{v}{2(2\pi)^3} \int d\mathbf{q} \left\{ \frac{x_\beta (\gamma_{\alpha\alpha}(q) \gamma_{\beta\beta}(q) - \gamma_{\beta\beta}^2(q) - v \gamma_{\alpha\alpha}(q))}{M} + \right. \\ &\quad \left. + \frac{\gamma_{\alpha\alpha}(q)}{v} + \frac{1}{v^2} (x_\alpha \gamma_{\alpha\alpha}^2(q) + x_\beta \gamma_{\alpha\beta}^2(q)) \right\}. \end{aligned} \quad (4.5)$$

If we define the standard chemical potential  $\mu_\alpha^0$  and the activity coefficient  $f_\alpha$ , by

$$\mu_\alpha^0 = \lim_{x_\alpha \rightarrow 1} \mu_\alpha, \quad \mu_\alpha = \mu_\alpha^0 + kT \ln(x_\alpha f_\alpha) \quad (4.6)$$

the activity coefficient is:

$$\begin{aligned} f_\alpha &= \frac{1}{x_\alpha} \exp A, \\ A &= \frac{x_\beta}{v} [\gamma_{\alpha\alpha}(0) - \gamma_{\alpha\beta}(0)] + \frac{v}{2(2\pi)^3} \int d\mathbf{q} \left\{ \frac{x_\beta (\gamma_{\alpha\alpha}(q) \gamma_{\beta\beta}(q) - \gamma_{\alpha\beta}^2(q) - v \gamma_{\alpha\alpha}(q))}{M} + \right. \\ &\quad \left. + \frac{\gamma_{\alpha\alpha}(q)}{v - \gamma_{\alpha\alpha}(q)} + \frac{x_\beta}{v^2} [\gamma_{\alpha\beta}^2(q) - \gamma_{\alpha\alpha}^2(q)] \right\}; \end{aligned} \quad (4.7)$$

$$\frac{\mu_\alpha^0 - \mu_{\alpha id}^0}{kT} = -\frac{1}{v} \gamma_{\alpha\alpha}(0) - \frac{1}{v} \frac{1}{2(2\pi)^3} \int d\mathbf{q} \frac{\gamma_{\alpha\alpha}^3(q)}{v - \gamma_{\alpha\alpha}(q)} \quad (4.8)$$

$\mu_\beta$  and  $f_\beta$  may be obtained by interchanging the subscripts  $\alpha$ ,  $\beta$  in the above formulae.

It should be pointed out that the formulae given in this Section have been obtained by interchanging the order of integrations and differentiations. Such a procedure will be correct as long as the integral in the formula (3.4) for the free energy is non-singular. This is the case in the gas region (compare with [10]). In the region of condensed phases, the proper relations are the thermodynamical ones, *i. e.*, the functions  $p$ ,  $S$ ,  $\mu_\nu$ , *etc.* should be in fact calculated by (numerical) differentiations of the (numerical) free energy because in this region the integrals in the formulae (4.1), (4.2), and (4.5) will be probably singular ( $M(q) = 0$  for some values of the integration variable  $q$ ). However, this is not very convenient for numerical computations; on the other hand, these integrals may be calculated in the sense of Cauchy principal values: such a procedure has been successfully applied for the one-component system, leading to qualitatively sensible results [10]. It should be also pointed out that the OC approximation considered in this paper is rather unable to yield quantitatively correct results [10], [18].

In the first Section of this paper, we have mentioned that our OC formulae for mixtures might be considered as the qualitative approximation of the quantitative (but much more

difficult for numerical applications) theories of many-component liquids, like the PY or HNC integral equations [19].

However, it is possible to propose some simpler formal method, which will not require any further enlargement of the theory by summation of intricate sets of hypernetted graphs HNC. Namely, it is well-known that  $-kT \ln g(r)$  may be interpreted as the effective, temperature and density-dependent two-body potential in the many body system. One can make use of this interpretation for iterative correction of the OC approximation: in the first step  $g_{\nu\lambda}^{(1)}(r)$  and  $\gamma_{\nu\lambda}^{(1)}(q)$  are calculated in the first approximation (OC) from the formulae (2.7), (2.12) ÷ (2.16) (with the use of the original pair potentials  $V_{\nu\lambda}(r)$ ). In the second step  $-kT \ln g_{\nu\lambda}^{(1)}(r)$  is introduced into the formula (2.7) in the place of  $V_{\nu\lambda}(r)$ , and the  $\gamma_{\nu\lambda}^{(2)}(q)$ , and  $g_{\nu\lambda}^{(2)}(r)$  are calculated from the same relations. Free energy, and other thermodynamic functions are now calculated from their proper OC formulae with  $\gamma_{\nu\lambda}^{(2)}$  instead of  $\gamma_{\nu\lambda}^{(1)}$ . This procedure may be now repeated as long as convergent results are obtained (assuming this procedure is convergent). From the formal point of view, such an iterative OC approximation with effective potential is equivalent with the retaining of all the HNC graphs, and with additional retaining of some more graphs which either have been already taken into account in the lower approximations, or even do not appear at all in the original virial expansions, which certainly will introduce some errors. However, the PY method neglects many HNC graphs and is considered to be better than the HNC approximation (*cf. e. g.* [14]).

It should be remembered that all these approximations are the formal ones (nevertheless, both HNC and PY method yield quite correct results [15÷17], and have been proposed mainly because of their relative simplicity (the HNC method takes into account only graphs which may be disentangled by means of Fourier transformations). From this point of view, our iterative OC approximation seems worthy to propose because it seems to be sufficiently simple (much simpler than HNC or PY approximation) to deal with.

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