Statistical Mechanics of Quantum Mixtures II

——Cluster Expansion for the chemical Potential——

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Cluster expansion formula for the chemical potential of each component of the binary quantum mixture is derived. The canonical ensemble formalism is adopted in contrast to the grand canonical ensemble formalism used in the previous paper. This formalism enables us to simplify the process of the calculation.

1. Introduction

In the previous paper[1] *, K. Shimojima and the present auther have proposed a cluster expansion formalism for the statistical mechanics of the two component systems in which both dynamical and statistical quantum effects play important roles (quantum mixtures). In their formalism the chemical potential of the actual component system appears in the Bose or Fermi distribution function through which the effect of the quantum statistics is taken into account. Hence the determination of the chemical potentials in terms of the density and the temperature requires somewhat tedious processes. In the present paper, the method based on the canonical ensemble is adopted in contrast to the grand canonical ensemble method used in the paper [I]. One of the characteristic features of present method is that the chemical potential of the corresponding ideal system appears in the quantum distribution function instead of the chemical potential of the actual system. Consequently, the cluster expansion formula for the chemical potential can be derived fairly easily. The flow line of the method developed in the present paper is an straightforward extention of the procedure developed for the single component system[2]. So, only the crucial points will be described in the following sections. The results of the present paper have been applied to the theory of the surface tension of ^{3}He-^{4}He liquid mixtures. It will be given in another paper.

* This will be refered as the paper [I] hereafter.

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2. Cluster decomposition of the partition function.

As has been said in the introduction, the main purpose of the present paper is to derive the cluster expansion formulae for the chemical potentials. In the course of their derivation, however, the cluster decomposition formula for the partition function will be required.

Now we consider a two component system of N_A particles of mass m_A and N_B particles of mass m_B in the volume V. The Hamiltonian $\mathcal{H}_{N_A N_B}$ of the system is given by

$$\mathcal{H}_{N_A N_B} = \mathcal{H}_{N_A} + \mathcal{H}_{N_B} + \Phi_{N_A N_B},$$

$$\mathcal{H}_{N_A}=\mathcal{H}_{N_A}{}^0+\Phi_{N_A N_A},\quad \mathcal{H}_{N_B}=\mathcal{H}_{N_B}{}^0+\Phi_{N_B N_B},$$
$$\mathcal{H}_{N_X}{}^0=-\frac{\hbar^2}{2m_X}\sum_{i=1}^{N_X}\Delta_{X_i}{}^2$$
$$\Phi_{N_X N_Y}=\sum\phi_{XY}(i,j)\qquad (X, Y=A, B) \tag{2.1}$$

, where $\phi_{XY}(i,j)$ is the interaction potential between the i -th particle of X. and j -th particle of Y.

The partition function $Z_{N_A N_B}$ of the system will be given by

$$Z_{N_A N_B}=\int(\prod_{l_A}^{N_A})\int(\prod_{i_B}^{N_B})(l_A', \cdots, N_B'; l_B', \cdots,$$
$$N_B'|\rho_{N_A N_B}|l_A, \cdots, N_A; l_B\cdots, N_B)$$
$$\rho_{N_A N}=e^{-\beta\mathcal{H}_{N_A N_B}},\quad \beta=l/kT \tag{2.2}$$

Here $(\cdots\cdots|\rho_{N_A N_B}|\cdots\cdots)$ means the matrix element of the density matrix operator $\rho_{N_A N_B}$ on the basis of the properly symmetrized wave function, $i_A=(r_{Ai}, \xi_{Ai})$ is the abreviation of the particle coordinate r_{Ai} together with the spin ξ_{Ai}, and $\int(\prod_{l_A}^{N_A})$ means to take trace with respect to the coordinates $l_A, \cdots\cdots, N_A$.

We define the operator $W_{N_A N_B}$ by the relations

$$e^{-\beta\mathcal{H}_{N_A N_B}}=W_{N_A N_B}e^{-\beta\mathcal{H}^0{}_{N_A N_B}}$$
$$\mathcal{H}^0{}_{N_A N_B}=\mathcal{H}^0{}_{N_A}+\mathcal{H}^0{}_{N_B} \tag{2.3}$$

and start from the expression

$$Z_{N_A N_B}=\int(\prod_{l_A}^{N_A})\int(\prod_{l_B}^{N_B})(x'^{N_A}, y'^{N_B}|W_{N_A N_B}\rho_{N_A N_B}{}^{(0)}|$$
$$x^{N_A}, y^{N_B})\qquad \rho_{N_A N_B}{}^{(0)}=e^{-\beta\mathcal{H}^0{}_{N_A N_B}} \tag{2.4}$$

where further abbreviations such as $l_A', \cdots N'_A \rightarrow X_A'$ are used. Following the Ursell-Mayer cluster decomposition technique, we define from the operators $W_{N_A N_B}$ the $U_{l,p}$ operators by the relations

$$W_{N_A N_B}=\sum_{\{m_l\}}\sum_{\{n_p\}}S_A S_B\prod_l\prod_p \underbrace{U_{l,p}\cdots U_{l,p}}_{m_l n_p \text{ factars}}$$
$$(\sum l m_l=N_A,\quad \sum p n_p=N_B) \tag{2.5}$$

$$W_{0,0}=1=U_{0,0}$$
$$W_{1,0}=W_{0,1}=1=U_{1,0}=U_{0,1}$$

Here $\sum_{\{m_l\}}\sum_{\{n_p\}}$ means to sum over all possible values of m_l and n_p under the conditions given in the bracket, and $S_A(S_B)$ means to symmetrize the product of $U_{l,p}$ with respect to the coordinates of A (B) particles. The beginning several relations are shown in the appendix Al.

From these $U_{l,p}$ operators we define $w_{m,n}$ operators by

$$w_{m,n}=\sum_{\{m_l\}}\sum_{\{n_p\}}S_{AB}S\prod_l\prod_p \underbrace{U_{l,p}\cdots U_{l,p}}_{m_l n_p \text{ factors}}$$
$$(\sum l m_l=m,\quad \sum p n_p=n;\ l+p\geqq 2\ m+n\geqq 2) \tag{2.6}$$

$$w_{0,0}=1,\quad w_{1,0}=w=_{0,1}=0$$

Beginning relations are also shown in the appendix A 1.

Then we have

$$W_{N_A N_B}=\sum\ \sum(w_{m,n}{}^{(1)}+\cdots+w_{m,n}{}^{(M)})$$
$$M=\binom{N_A}{m}\binom{N_B}{n} \tag{2.7}$$

Here M is the number of all possible different $w_{m,n}$ (See [1]).

Substituting (2.7) into (2.4) and utilizing the symmetry characters of the term in the trace calculations, we can carry out the following transformations.

$$Z_{N_A N_B}=\int(\prod_1^{N_A})\int(\prod_1^{N_B})\sum_{m=0}^{N_A}\sum_{n=0}^{N_B}(w^{(1)}{}_{m,n}+\cdots+w_{m,n}{}^{(M)})$$
$$\times\rho_{N_A N_B}{}^{(0)}$$
$$=\int(\prod_1^{N_A})\int(\prod_1^{N_B})\sum_{m=0}^{N_A}\sum_{n=0}^{N_B}\binom{N_A}{m}\binom{N_B}{n}w_{m,n}\rho_{N_A N_B}{}^{(0)}$$
$$=\sum_{m=0}^{N_A}\sum_{n=0}^{N_B}\frac{N_A!}{m!(N_A-m)!}\ \frac{N_B!}{n!(N_B-n)!}$$
$$\times\int(\prod_1^m)\int(\prod_1^n)w_{m,n}\int(\prod_{m+1}^{N_A})\int(\prod_{n+1}^{N_B})\rho_{N_A N_B}{}^{(0)}$$
$$=Z_{N_A N_B}{}^{(0)}\cdot\sum_{m=0}^{N_A}\sum_{n=0}^{N_B}\frac{1}{m!n!}\int(\prod_1^m)\int(\prod_1^n)w_{m,n}$$
$$\times\rho_{N_{Am};N_{Bn}}{}^{(0)} \tag{2.8}$$

where we have used the notations

$$Z_{N_AN_B}{}^{(0)}=Z_{N_A}{}^{(0)}Z_{N_B}{}^{(0)},\quad \rho_{N_AN_B}{}^{(0)}=e^{-\beta(\mathcal{H}_A{}^0+\mathcal{H}_B{}^0)}$$
$$=\rho_{N_AN_B}{}^{(0)}\cdot\rho_{N_B}{}^{(0)}$$
$$\rho_{N_A}{}^{(0)}=e^{-\beta\mathcal{H}_{N_A}{}^0}$$
$$Z_{N_A}{}^{(0)}=\int(\prod_1^{N_A})\rho_{N_A}{}^{(0)},\quad \text{etc.}$$
$$\rho_{N_Am}{}^{(0)}=\frac{N_A!}{(N_A-m)!}\int(\prod_{m+1}^{N_A})\rho_{N_A}{}^{(0)}/Z_{N_A}{}^{(0)},$$
$$\rho_{N_Am;\,N_Bn}{}^{(0)}=\rho_{N_Am}{}^{(0)}\rho_{N_Bn}{}^{(0)} \tag{2.9}$$

$\rho_{N_Am}{}^{(0)}$ is the m-particle reduced density matrix of the corresponding single component ideal system.

Further, defining $R_{N_A,m;\,N_B,n}$ and $\tilde{w}_{m,n}$ by

$$V^mV^n\int(\prod_{m+1}^{N_A})\int(\prod_{n+1}^{N_B})\rho_{N_AN_B}{}^{(0)}=R_{N_Am;\,N_Bn}$$
$$=V^mV^n\frac{(N_A-m)!}{N_A!}\;\frac{(N_B-n)!}{N_B!}\rho_{N_Am;\,N_Bn}{}^{(0)} \tag{2.10}$$
$$\tilde{w}_{m,n}=w_{m,n}R_{N_Am;\,N_Bn} \tag{2.11}$$

we obtain

$$Z_{N_AN_B}=Z_{N_AN_B}{}^{(0)}\sum_{m=0}^{N_A}\sum_{n=0}^{N_B}\binom{N_A}{m}\binom{N_B}{n}\frac{1}{V^{m+n}}$$
$$\times\int(\prod_1^m)\int(\prod_1^n)(x'^m,y'^n\,|\,\tilde{w}_{m,n}\,|\,x^m,y^n) \tag{2.12}$$

This is equivalent to

$$Z_{N_AN_B}=Z_{N_AN_B}{}^{(0)}Y_{N_AN_B}$$
$$Y_{N_AN_B}=\frac{1}{V^{N_A+N_B}}\int(\prod_1^{N_A})\int(\prod_1^{N_B})(x'^{N_A},y'^{N_B}\,|\,\tilde{w}_{m,n}{}^{(1)}$$
$$+\cdots+\tilde{w}_{m,n}{}^{(N)}\,|\,x^{M_A},y^{N_B}) \tag{2.13}$$

as may be seen easilv. Now we introduce $\tilde{U}_{l,p}$ operators using the relations which correspond to (2.6)

$$\tilde{w}_{m,n}=\sum_{\{m_l\}}\sum_{\{n_p\}}S_AS_B\prod_l\prod_p\underbrace{\tilde{U}_{l,p}\cdots\tilde{U}_{l,p}}_{m_ln_p\ \text{faetors}} \tag{2.14}$$
$$(\textstyle\sum lm_l=m,\ \sum pn_p=n;\ l=p\geqq2,\ m+n\geqq2)$$

and complement the relations $U_{0,0}=1$, $U_{1,0}=U_{0,1}=1$. Then we can define the operator $\tilde{W}_{N_AN_B}$ by

$$\tilde{W}_{N_AN_B}=\sum_{\{m_l\}}\sum_{\{n_p\}}S_AS_B\prod_l\prod_p\underbrace{\tilde{U}_{l,p}\cdots\tilde{U}_{l,p}}_{m_ln_p\ \text{factors}} \tag{2.15}$$
$$(\textstyle\sum lm_l=N_A,\ \sum pn_p=N_B)$$

which corresponds to (2.5) and get

$$Z_{N_AN_B}=Z_{N_AN_B}{}^{(0)}Y_{N_AN_B}$$
$$Y_{N_AN_B}=\frac{1}{V^{N_A+N_B}}\int(\prod_1^{N_A})\int(\prod_1^{N_B})(x'^{N_A},y'^{N_B}\,|\,\tilde{W}_{N_AN_B}\,|$$
$$x^{N_A},y^{N_B} \tag{2.16}$$

The procedure which have led us from (2.11) to (2.16) corresponds to the steps from (2.4) to (2.8) in backward direction.

The formula (2.16) is the cluster decomposition formula for the partition function $Z_{N_AN_B}$ of our quantum mixtures. As may be seen easily the effects of the quantum statistics are taken into consideration through $Z_{N_AN_B}{}^{(0)}$ and $R_{N_Am;\,N_Bn}$. From the formula (2.16), we can proceed completely in the same way as in the usual cluster expansion theory for the classical system, using the newly defined cluster integral $\tilde{b}_{l,p}$

$$Vl!p!\tilde{b}_{l,p}=\int(\prod_1^l)\int(\prod_1^p)(x^{l\prime},y^{p\prime}\,|\,\tilde{U}_{l,p}\,|\,x^l,y^p) \tag{2.17}$$

3. Cluster decomposition of the reduced density matrix.

Now we go to the cluster decomposition of the reduced density matrix-the correlation function-.

(h,k)-particle reduced density matrix based on the canonical distribution is defined by

$$(1_A'\cdots h_A',1_B'\cdots k_B'\,|\,\rho_{N_AN_B}{}^{(h,k)}\,|\,1_A\cdots h_A,1_B\cdots k_B)$$
$$=\rho_{N_AN_B}{}^{(h,k)}((h);(k))$$
$$=\frac{N_A!N_B!}{Z_{N_AN_B}(N_A-h)!(N_B-k)!}\int(\prod_{h+1}^{N_A})\int(\prod_{k+1}^{N_B})$$
$$\times(1_A'\cdots h_A',(h+1)_A',\cdots N_A';1_B'\cdots k_B'\cdots k_B',$$
$$(k+1)_B',\cdots N_B'\,|\,W_{N_AN_B}\rho_{N_AN_B}{}^{(0)}\,|\,1_A\cdots h_A,$$
$$(h+1)_A,\cdots N_A;1_B\cdots k_B,(k+1)_B,\cdots N_B)$$

(3.1)

From now on we use the abbreviated notations for the matrix elements. For instance, we write $W_{N_AN_B}\rho_{N_AN_B}{}^{(0)}((h), h+1, \cdots N_A; (k), k+1, \cdots N_B)$ or $W_{N_AN_B}\rho_{N_AN_B}{}^{(0)}$ in place of the full expression is (3.1).

As in the paper [1], we introduce $U_{l,p}{}^{(g,k)}$ operators with (h, k) reserved coordinates.

$$W_{N_AN_B}(1, \cdots, N_A; 1, \cdots, N_B)$$
$$=\sum_{\{l_i\}}\sum_{\{p_j\}} S_AS_BU_{l_1,p_1}{}^{(h,k)}((h), h+1, \cdots l_1; (k), k+1, \cdots, p_1)$$
$$\times \Pi\Pi U_{l_i,p_j}(r_1\cdots r_{l_i}; s_1\cdots s_{p_j}) \quad (3.2)$$
$$(\sum l_i=N_A, \sum p_j=N_B, l_1\geqq h, p_1\geqq k)$$

Notations are quite similar to that of (2.5) Several beginning equations are given in the appendix A 2. With these $U_{l,p}{}^{(h,k)}$, we define $w_{h+m,k+n}{}^{(h,k)}$ operators by

$$w_{h+m,k+m}{}^{(h,k)}((h)h+1, \cdots h\cdots m; (k), k+1, \cdots k+n)$$
$$=\sum\sum S_AS_BU_{h+l_1,k+p_1}{}^{(h,k)}((h), h+1, \cdots h+l_1; (k), k+1\cdots k+p_1)\times\Pi\Pi U_{l_i,p_j} \quad (3.3)$$
$$(\sum l_i=m, \sum p_j=n, \ l_1\geqq 0, p_1\geqq 0)$$
$$(l_i+p_j\geqq 2, \ i, j\geqq 2)$$

and we have

$$W_{N_AN_B}$$
$$=\sum_{n=0}^{N_A-h}\sum_{m=0}^{N_B-k}(\underbrace{w_{h+m,k+n}{}^{(h,k)}+\cdots+w_{h+m,k+n}{}^{(h,k)}}_{\binom{N_A-h}{m}\times\binom{N_B-k}{n}\text{ terms}}) \quad (3.4)$$

Putting (3.4) into (3.1), we get

$$\rho_{N_AN_B}{}^{(h,k)}((h)(k))$$
$$=\frac{N_A!N_B!}{Z_{N_AN_B}(N_A-h)!(N_B-k)!}\sum_{m=0}^{N_A-h}\sum_{n=0}^{N_B-h}\binom{N_A-h}{m}\times\binom{N_B-k}{n}\int\overset{h+k}{\underset{h+1}{(\Pi)}}\int\underset{k+1}{(\Pi)}w_{h+m,k+n}{}^{(h,k)}((h),$$
$$h+1, \cdots h+m; (k), k+1, \cdots k+n)\int\overset{N_A}{\underset{h+m+1}{(\Pi)}}\int\overset{N_B}{\underset{k+n+1}{(\Pi)}}$$

$$\rho_{N_AN_B}{}^{(0)}=\frac{Z_{N_AN_B}{}^{(0)}}{Z_{N_AN_B}}\sum_{m=0}^{N_A-h}\sum_{n=0}^{N_B-k}\frac{1}{m!n!}\int\overset{h+m}{\underset{h+1}{(\Pi)}}\int\overset{k+n}{\underset{k+1}{(\Pi)}}$$
$$\times w_{h+m,k+n}{}^{(h,k)}((h), h+1, \cdots h+m; (k), k+1, \cdots k+n)\rho^{(0)}{}_{N_Ah+m; N_Bk+n} \quad (3.5)$$

where we have used the definition of the $(h+m, k+n)$-particle reduced density matrix of the ideal system given in (2.9). We introduce $\tilde{w}_{h+m,k+n}{}^{(h,k)}$ operators by

$$\tilde{w}_{h+m,k+n}{}^{(h,k)}=w_{h+m,k+n}{}^{(h,k)}R_{N_Ah+m; N_Bk+n} \quad (3.6)$$

$R_{N_Ah+m; N_Bk+n}$ is defined in (2.10). So we obtain,

$$\rho_{N_AN_B}{}^{(h,k)}=\frac{Z_{N_AN_B}{}^{(0)}}{Z_{N_AN_B}}\frac{N_A!\,N_B!}{(N_A-h)!(N_B-k)!}$$
$$\sum_{m=0}^{N_A-h}\sum_{n=0}^{N_B-k}\frac{(N_A-h)!(N_B-k_B)!}{(N_A-h-m)!m!(N_B-k-n)!n!}$$
$$\frac{1}{V^{h+m}V^{k+m}}\times\int\overset{k+m}{\underset{k+1}{(\Pi)}}\int\overset{k+n}{\underset{k+1}{(\Pi)}}\tilde{w}_{h+m,k+n}{}^{(h,k)}((h)h+1, \cdots h+m; (k), k+1, \cdots k+n) \quad (3.7)$$

Now we decompose $\tilde{w}_{h+m,k+n}{}^{(h,k)}$ by the following scheme, i. e. the successive definition of the operators $\tilde{U}_{l,p}{}^{(h,k)}$ by $\tilde{w}_{h+m,k+n}{}^{(h,k)}$ and $\tilde{U}_{l,p}$.

$$\tilde{w}_{h,k}{}^{(h,k)}((h); (k))=\tilde{U}_{h,k}{}^{(h,k)}((h); (k)) \quad (3.8)$$
$$\tilde{w}_{h+1,k}{}^{(h,k)}((h), h+1; (k))=\tilde{U}_{h+1,k}{}^{(h,k)}((h), h+1; (k)) \quad (3.9)$$
$$\tilde{w}_{h+2,k}{}^{(h,k)}((h), h+1, h+2; (k))=\tilde{U}_{h+2,k}{}^{(h,k)}((h), h+1, h+2; (k))+\tilde{U}_{h,k}{}^{(h,k)}((h); (k))U_2(h+1, h+2) \quad (3.10)$$

$$\tilde{w}_{h+m,k}{}^{(h,k)}((h), h+1, \cdots h+m; (k))=\tilde{U}_{h+m,k}{}^{(h,k)}((h), h+1, \cdots h+m; (k))+[\tilde{U}_{h+m-2,k}{}^{(h,k)}((h)h+1, \cdots h+m-2; (k))\tilde{U}_2(h+m-1, h+m)+\cdots \binom{m}{2}\text{ terms}]+[\tilde{U}_{h+m-3,k}{}^{(h,k)}((h), h+1, \cdots h+m-3; (k))\tilde{U}_3(h+m-2, h+m-1, h+m)+\cdots \binom{m}{3}\text{ terms}]+[\tilde{U}_{h+m-4,k}{}^{(h,k)}((h), h+1, \cdots h+m-4; (k))\times\{\tilde{U}_4(h+m-3, h+m-2, h+m-1,$$

$h+m)+\tilde{U}_2(h+m-3,h+m-2)\tilde{U}_2(h+m-1, h+m)+\tilde{U}_2(h+m-3,h+m-1)\tilde{U}(h+m-2,h+m)+\tilde{U}_2(h+m-3,h+m)\tilde{U}_2(h+m-2,h+m-1)\}+\cdots\binom{m}{4}$ terms$]$ $+\cdots[\tilde{U}_{h+1,k}{}^{(h,k)}((h),h+1;(k))\times\{\tilde{U}_{m-1}(h+2,\cdots h+m)+\tilde{U}_{m-2}(h+1,\cdots h+m-2)\tilde{U}_2(h+m-1,h+m)\}+\cdots\binom{m}{m-1}$ terms$]+\tilde{U}_{h,k}{}^{(h,k)}((h);(k))\times\{\tilde{U}_m(h+1,\cdots h+m)+\tilde{U}_{m-2}(h+1,\cdots h+m-2)\tilde{U}(h+m-1,h+m)+\cdots\},\cdots$ (3.11)

The general relation is given in the paper [I] (1930 p Equ. (A 19)). As may be seen from the relation of $\tilde{w}_{m,n}$, $\tilde{U}_{l,p}$ in (2.14), the curly bracketed factors in (3.11) can be replaced by $\tilde{w}_{m-l_1,n-p_1}$. Then we have

$$\tilde{w}_{h+m,k+n}{}^{(h,k)}=\sum_{l_1=0}^{m}\sum_{p_1=0}^{n}S_AS_B\tilde{U}_{h+l_1,k+p_1}{}^{(h,k)}\tilde{w}_{m-l_1,n-p_1} \tag{3.12}$$

(See [I] (A 20)). If we put the decomposition (3.12) into (3.7), we can proceed to get the formula for $\rho_{N_AN_B}{}^{(h,k)}$. For the purpose of the present paper, however, only the formula for the special cases $\rho_{N_AN_B}{}^{(1,0)}$ and $\rho_{N_AN_B}{}^{(0,1)}$ will be sufficient. Hence, we wil work with them hereafter.

We can show that the formula

$$\rho_{N_AN_B}{}^{(1,0)}=\frac{Z_{N_AN_B}{}^{(0)}}{Z_{N_AN_B}}\frac{N_A!\ N_B!}{(N_A-1)!\ N_B!}\frac{(N_A-1)!\ N_B!}{(N_A-1-m)!m!(N_B-n)!n!}\frac{1}{V^{1+m}V^n}\times\int(\prod_2^{1+m})\int(\prod_1^{n})\tilde{w}_{1+m,n}{}^{(1,0)}((1),2,\cdots 1+m;1,\cdots n)$$

$$\tilde{w}_{1+m,n}{}^{(1,0)}\sum_{l_1=0}^{m}\sum_{p_1=0}^{n}S_AS_B\tilde{U}_{1+l_1,p_1}{}^{(1,0)}\tilde{w}_{m-l_1,n-p_1}. \tag{3.13}$$

can be transformed into the form given (3.17) below. We exchange the order of the summations and replace m by m' $(m=l_1+m')$, that is

$$\sum_{m=0}^{N_A-1}\sum_{l_1=0}^{m}\frac{1}{(N_A-1-m)!m!}\to$$

$$\sum_{l_1=0}^{N_A-1}\sum_{m=l_1}^{N_A-1}\frac{1}{(N_A-1-m)!m!}\to$$

$$\sum_{l_1=0}^{N_A-1}\sum_{m=0'}^{N_A-1-l_1}\frac{1}{(N_A-1-l_1-m')!(l_1+m')!}$$

and similarly

$$\sum_{n=0}^{N_B}\sum_{p_1=0}^{n}\frac{1}{(N_B-n)!n!}\to$$

$$\sum_{p_1=0}^{N_B}\sum_{n'=0}^{N_B-p_1}\frac{1}{(N_B-p_1-n)!n!}$$

So we obtain

$$\rho_{N_AN_B)}{}^{1,0)}=\frac{Z_{N_AN_B}{}^{(0)}}{Z_{N_AN_B}}$$

$$\frac{N_A!N_B!}{(N_A-1)!N_B!}\sum_{l_1=0}^{N_A-1}\sum_{m'=0}^{N_A-1-l_1}\sum_{p_1=0}^{N_B}\sum_{n'=0}^{N_B-p_1}$$

$$\frac{(N_A-1)!\quad N_B!}{(N_A-1-l_1-m')!(l_1+m')!\,(N_B-p_1-n')!(p_1+n')!}$$

$$\frac{1}{V^{1+l_1+m'}V^{p_1+n'}}\times\int(\prod_2^{1+m})\int(\prod_1^{2})S_AS_B\tilde{U}_{1+l_1,p_1}{}^{(1,0)}$$

$$((1),2,\cdots 1+l_1;1,\cdots p_1)$$

$$\times\tilde{w}_{m'n'}(1+l_1+1,\cdots 1+l_1+m';p_1+1,\cdots p_1+n')$$

$$=\sum_{l_1=0}^{N_A-1}\sum_{p_1=0}^{N_B}\frac{Z_{N_AN_B}{}^{(0)}}{Z_{N_AN_B}}\frac{N_A!\ N_B!}{(N_A-1-l_1)!\ (N_B-p_1)!}$$

$$\times\frac{1}{V^{1+l_1}\Lambda^{p_1}}\frac{1}{l_1!p!}\int(\prod_2^{1+l_1})\int(\prod_1^{p_1})\tilde{U}_{1+l_1,p_1}{}^{(1,0)}$$

$$((1),2,\cdots 1+l_1;1,\cdots p_1)$$

$$\times\Bigg[\sum_{m'=0}^{N_A-1-l_1}\sum_{n'=0}^{N_B-p_1}\binom{N_A-1-l_1}{m'}\binom{N_B-p_1}{n'}\frac{1}{V^{m'}V^{n'}}$$

$$\int(\prod_{1+l_1+1}^{1+l_1+m'})\int(\prod_{p_1+1}^{p_1+n'})\tilde{w}_{m'n'}(1+l_1+1,\cdots 1+l_1+m';$$

$$p_1+1,\cdots p_1+n')\Bigg] \tag{3.14}$$

The factor in the large [ ] bracket of the above equation is nothing but the decomposition of $Z_{N_A-1-l_1,N_B-p_1}/Z^{(0)}{}_{N_A-1-l_1,N_B-p_1}$, as may be seen from (2.12). Here we replace l_1 by $l_1'=l_1-1$. So we get

$$\rho_{N_A N_B}{}^{(1,0)}=\sum_{l_1'=1}^{N_A}\sum_{p_1=0}^{N_B}\frac{1}{V^{1+l_1'-1}V^{p_1}}\frac{l_1'}{l_1'!p_1!}$$

$$\times\int(\prod_2^{1+l_1'-1})\int(\prod_1^{p_1})\,\tilde{U}_{1+l_1'-1,p_1}{}^{(1,0)})(1),2,\cdots 1+l_1'$$

$$\times\frac{Z_{N_A N_B}{}^{(0)}}{Z^{(0)}{}_{N_A-1-l_1'+1,N_B-p_1}}\frac{Z_{N_A-1-+1,N_B-p_1}}{Z_{N_A N_B}}$$

$$\frac{N_A!N_B!}{(N_A-1-l_1'+1)!(N_B-p_1)!} \tag{3.15}$$

Defining the cluster integral $\tilde{b}_{l,p}{}^{(1,0)}$ by

$$l!p!\tilde{b}_{l,p}{}^{(1,0)}=\int(\prod_1^l)\int(\prod_1^p)\tilde{U}_{l,p}{}^{(1,0)}((1),2,\cdots l;$$

$$1,\cdots p) \tag{3.16}$$

we have

$$\rho_{N_A N_B}{}^{(1,0)}=\sum_{l=1}^{N_A}\sum_{p=0}^{N_B}\tilde{b}_{l,p}{}^{(1,0)}\frac{Z_{N_A N_B}{}^{(0)}}{Z_{N_A-l,N_B-p}{}^{(0)}}$$

$$\frac{V^{N_A-l}V^{N_B{}^2p}}{(N_A-l)!(N_B-p)!}\frac{1}{\dfrac{V^{N_A}V^{N_B}}{N_A!N_B!}} \tag{3.17}$$

where we have written l,p in place of l_1',p_1. This is the end of our straightforward calculation. At this point we make a limitting step which will be allowed for $N\to\infty$, $V\to\infty$ $N/V=\rho=$const., Let $\mu_A(\mu_A{}^{(0)})$ be the chemical potential of the component A and $z_A=e^{\beta\mu_A}$ $(z_A{}^{(0)}=e^{\beta\mu_A{}^{(0)}})$, then we have from the definition of the chemical potential $(\mu_A=-(\partial kT\log Z_{N_A N_B}/\partial N_A)_{N_B,T,V})$,

$$\frac{Z_{N_A}{}^{(0)}}{Z_{N_A-1}{}^{(0)}}\frac{Z_{N_A-1}}{Z_{N_A}}\frac{V^{N_A-1}(N_A-1)!}{V^{N_A}N_A!}\to\rho_A\frac{z_A}{z_A{}^{(0)}} \tag{3.18}$$

We use this limitting relation repeatedly for each term of (3.17). For instance,

$$\frac{Z_{N_A N_B}{}^{(0)}}{Z_{N_A-2,N_B}{}^{(0)}}\frac{Z_{N_A-2,N_B}}{Z_{N_A N_B}}\frac{V^{N_A-2}V^{N_B}}{(N_A-2)!N_B!}\frac{V^{N_A}V^{N_B}}{N_A!N_B!}$$

$$=\frac{Z_{N_A N_B}{}^{(0)}}{Z_{N_A-1,N_B}{}^{(0)}}\frac{Z_{N_A-1,N_B}{}^{(0)}}{Z_{N_A-2,N_B}{}^{(0)}}\cdots\cdots\frac{V^{N_A-2}V^{N_B}}{(N_A-2)!N_B!}$$

$$\frac{V^{N_A}V^{N_B}}{N_A!N_B!}\to\rho_A{}^2\frac{z_A{}^2}{z_A{}^{(0)2}}$$

$$\frac{Z_{N_A N_B}{}^{(0)}}{Z_{N_A-,N_B-1}{}^{(0)}}\frac{Z_{N_A-1,N_B-1}}{Z_{N_A N_B}}\frac{V^{N_A-1}V^{N_B-1}}{(N_A-1)!(N_B-1)!}$$

$$\frac{V^{N_A}V^{N_B}}{N_A!N_B!}=\frac{Z_{N_A N_B}{}^{(0)}}{Z_{N_A-1,N_B}{}^{(0)}}\frac{Z_{N_A-1,N_B}{}^{(0)}}{Z_{N_A-1,N_B-1}{}^{(0)}}\frac{Z_{N_A-1,N_B}}{Z_{N_A-1,N_B-1}}$$

$$\frac{Z_{N_A-1,N_B}}{Z_{N_A,NB}}\frac{V^{N_A-1}V^{N_B-1}}{(N_A-1)!(N_B-1)!}\frac{V^{N_A}V^{N_B}}{N_A!N_B!}$$

$$\to\rho_A\rho_B\frac{z_A z_B}{z_A{}^{(0)}z_B{}^{(0)}}$$

Introducing the new notations such as $\tilde{z}_A=\rho_A z_A/z_A{}^{(0)}$, we have finally

$$\rho_{N_A N_B}{}^{(1,0)}=\tilde{b}_{1,0}{}^{(1,0)}\tilde{z}_A+2\,\tilde{b}_{2,0}{}^{(1,0)}\tilde{z}_A{}^2+\tilde{b}_{1,1}{}^{(1,0)}\tilde{z}_A\tilde{z}_B+\cdots$$

$$=\sum_{l=1}^{N_A}\sum_{p=1}^{N_B}l\tilde{b}_{l,p}{}^{(1,))}\tilde{z}_A{}^l\tilde{z}_B{}^p \tag{3.19}$$

By the similar procedure we get

$$\rho_{N_A N_B}{}^{(0,1)}=\sum_{l=0}^{N_A}\sum_{p=1}^{N_B}p\tilde{b}_{l,p}{}^{(0,1)}\tilde{z}_A{}^l\tilde{z}_B{}^p \tag{3.20}$$

These formulae have formal resemblance to the fugacity expansion of the correlation functions in the theory of classical system.

4. Formulae for the chemical potentials.

Carrying out the trace calculation with respect to the coordinates in $\rho_{N_A N_B}{}^{(1,0)}$ and $\rho_{N_A N_B}{}^{(0,1)}$, we obtain

$$\rho_A=\frac{N_A}{V}=\sum_{l=1}^{N_A}\sum_{p=0}^{N_B}l\tilde{b}_{l,p}\tilde{z}_A{}^l\tilde{z}_B{}^p \tag{4.1}$$

$$\rho_B=\frac{N_B}{V}=\sum_{l=0}^{N_A}\sum_{p=1}^{N_B}p\tilde{b}_{l,p}\tilde{z}_A{}^l\tilde{z}_B{}^p \tag{4.2}$$

where the relation

$$\int(\prod_1)\tilde{b}_{l,p}{}^{(1,0)}=V\tilde{b}_{l,p} \tag{4.3}$$

is used. The cluster integral $\tilde{b}_{l,p}$ in our case, depends on ρ_A and ρ_B through the Fermi or Bose distribution function which appear in the reduced density matrices for the reference ideal system, the appearance of which is the characteristic feature of our formalism. Here, however, we disregard these ρ_A and ρ_B dependence and make the formal inversion of the series in (4.1) and (4.2). We put

$$\tilde{z}_A = \rho_A \exp(-\sum_{\substack{k \ q \\ (k=q=0)'}}\sum \beta_{k,q}{}^{(A)} \rho_A{}^k \rho_B{}^q) \quad (4.4)$$

$$\tilde{z}_B = \rho_B \exp(-\sum_{\substack{k \ q \\ (k=q=0)'}}\sum \beta_{k,q}{}^{(B)} \rho_A{}^k \rho_B{}^q) \quad (4.5)$$

and determine successively $\beta_{k,q}{}^{(A)}$ and $\beta_{k,q}{}^{(B)}$, substituting (4. 4), (4. 5) in (4. 1), (4. 2). This is the process which is quite well known in the theory of the classical impertect gases. Now we obtain

$$\beta_{1,0}{}^{(A)} = 2\,\tilde{b}_{2,0}\,, \quad \beta_{0,1}{}^{(B)} = 2\,\tilde{b}_{0,2}$$
$$\beta_{0,1}{}^{(A)} = \tilde{b}_{1,1} = \beta_{1,0}{}^{(B)}$$
$$\beta_{1,1}{}^{(A)} = 4\,\tilde{b}_{1,1}\tilde{b}_{2,0}\,, \quad \beta_{1,1}{}^{(B)} = 4\,\tilde{b}_{1,1}\tilde{b}_{0,2}$$
$$\beta_{0,2}{}^{(A)} = 2\,\tilde{b}_{0,2}\frac{1}{2}(\tilde{b}_{1,1})^2$$
$$\beta_{2,0}{}^{(B)} = 2\,\tilde{b}_{2,0}\frac{1}{2}(\tilde{b}_{1,1})^2$$
$$\cdots\cdots\cdots\cdots \quad (4.6)$$

From (4. 4) and (4. 5) we have

$$\beta(\mu_A - \mu_A{}^{(0)}) = -\sum_{\substack{k \ q \\ (k=q=00)'}}\sum \beta_{k,q}{}^{(A)} \rho_A{}^k \rho_B{}^q$$
$$= -2\,\tilde{b}_{2,0}\rho_A - \tilde{b}_{1,1}\rho_B - 4\,\tilde{b}_{2,0}\tilde{b}_{1,1}\rho_A\rho_B - \left(2\,\tilde{b}_{0,2} - \frac{1}{2}(\tilde{b}_{1,1})^2\right)\rho_B{}^2 \cdots \quad (4.7)$$

$$\beta(\mu_B - \mu_B{}^{(0)}) = -\sum_{\substack{k \ q \\ (k=q=0)'}}\sum \beta_{k,q}{}^{(B)} \rho_A{}^k \rho_B{}^q$$
$$= -2\tilde{b}_{0,2}\rho_B - \tilde{b}_{1,1}\rho_A - 4\,\tilde{b}_{0,2}\tilde{b}_{1,1}\rho_A\rho_B - \left(2\,\tilde{b}_{2,0} - \frac{1}{2}(\tilde{b}_{1,1})^2\right)\rho_A{}^2 \cdots \quad (4.8)$$

In the aboves, $(k=q=0)'$ below the summation sign means to omit the term $k=q=0$.

$\mu_A{}^{(0)}(\mu_B{}^{(0)})$ is the chemical potential of the reference ideal system of the component A (B) which has the same T, V, and $N_A(N_B)$. This is determined from the well known formula

$$\sum_k f_k{}^{(A)} = N_A \quad (4.9)$$

where $f_k{}^{(A)}$ is the Fermi or Bose distribution function corresponding to the statistics of the particle A.

The formulae derived here have already been applied to the theory of the surface tension of the liquid ^3He-^4He system. For the details of the cluster integrals see the paper [I].

A 1.

$$W_{1,1} = U_{1,1} + U_{1,0}\tilde{U}_{0,1}\,, \quad W_{1,0} = U_{1,0}\,, \quad W_{0,} = U_{0,1}\,,$$
$$W_{2,0} = U_{2,0} + U_{1,0}U_{1,0}\,,$$
$$W_{3,0} = U_{3,0} + U_{2,0}U_{1,0} + U_{1,0}U_{1,0}U_{1,0}\,,$$
$$W_{2,1} = U_{2,1} + U_{2,0}U_{0,1} + U_{1,0}U_{1,1} + U_{1,0}U_{1,1} + U_{1,0}U_{1,0}U_{0,1}\,,$$
$$\cdots\cdots\cdots\cdots$$

$$w_{1,1} = U_{1,1}\,,$$
$$w_{2,0} = U_{2,0}\,, \quad w_{0,2} = U_{0,2}\,,$$
$$w_{3,0} = U_{3,0}\,,$$
$$w_{2,1} = U_{2,1}\,, \quad w_{1,2} = U_{1,2}\,,$$
$$w_{2,2} = U_{2,2} + U_{2,0}U_{0,2} + U_{1,1}U_{1,1} + U_{1,1}U_{1,1}\,,$$
$$\cdots\cdots\cdots\cdots$$

A 2.

$$W_{1,0} = U_{1,0}{}^{(1,0)},$$
$$W_{1,1} = U_{1,1}{}^{(1,0)} + U_{1,0}{}^{(1,0)}U_{0,1}\,,$$
$$W_{2,0} = U_{2,0}{}^{(1,0)} + U_{1,0}{}^{(1,0)}U_{1,0}\,,$$
$$W_{1,2} = U_{1,2}{}^{(1,0)} + U_{1,1}{}^{(1,0)}U_{1,1} + U_{1,1}{}^{(1,0)}U_{0,1} + U_{1,0}{}^{(1,0)}U_{0,2} + U_{1,0}{}^{(1,0)}U_{0,1}U_{0,1}\,,$$
$$W_{2,1} = U_{2,1}{}^{(1,0)} + U_{2,0}{}^{(1,0)}U_{0,1} + U_{1,1}{}^{(1,0)}U_{1,0} + U_{1,0}{}^{(1,0)}U_{1,1}$$
$$\cdots\cdots\cdots\cdots$$

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