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Configurational Partition Function of Quaternary Systems

Masaji ONODERA

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Abstract

The asymptotic method applied to ternary solutions is extended to quaternary system. The configurational partition function is obtained for the system of particles having spin value 3/2. The method of calculation thereof is based on the assumtion of treating pairs of neighbors as independent entities.

1. Introduction

Recently statistical thermodynamics of ternary systems has been developed[1], however many actual systems involve more than three components. For instance, when we try to treat the system of particles having spin of 3/2, the problem of order-disorder of A and B particles, each of which has spin of 1/2 and ternary solution together with holes, we must solve the problem of quaternary system. So far we have not had any advanced method of describing quaternary systems. In order to study the complex phenomena of multicomponent systems, it is necessary to develop the method of treating quaternary systems.

2. Energy of Configuration

We consider the assembly of particles having a spin value of 3/2 as an example of quaternary systems, which consists of four states. The number of each state is denoted by N_1, N_2, N_3 and N_4 correspondiog to spin components $-3/2$, $-1/2$, $1/2$ and $3/2$ (hereafter, each state is referred to as state 1, 2, 3 and 4). Apparently the total number of particles is $N=N_1+N_2+N_3+N_4$. When we assume that they have potential energies $-N_1x_1$, $-N_2x_2$, $-N_3x_3$ and $-N_4x_4$ in pure states, respectively, the the average energies per pair in each state are $-2x_1/z$, $-2x_2/z$, $-2x_3/z$ and $-2x_4/z$ (z is the coordination number). if we start with particles of state 1, and 2, and interchange an interior particle of state 1 with an interior particle of state 2, the total increase of potential energy is $2w_{12}$. In this process we destroy z pairs of state 1 and z pairs of state 2 and create $2z$ pairs of state 1 and 2. Therefore the average potential energy[2] of a pair of state 1 and 2 is $\phi_{12}=-x_1/z-x_2/z+w_{12}/z$. Similarly the average potential energies of another pair of state i and j are obtained by any selection of two from subscripts 1, 2, 3 and 4.

Now we consider a particular configuration in which the number of pairs of state 1 and 2, 2 and 3, 3 and 1, 1 and 4, 2 and 4, and 3 and 4 are assumed to be zX_{12}, zX_{23}, zX_{31}, zX_{14}, zX_{24} and zX_{34}, respectively. Here the number of pairs of states 1 and 1, 2 and 2, 3 and 3, and 4 and 4 are $(N_1-X_{12}-X_{13}-X_{14})z/2$, $(N_2-X_{23}-X_{24}-X_{12})z/2$, $(N_3-X_{31}-X_{32}-X_{34})z/2$ and $(N_4-X_{41}-X_{42}-X_{43})z/2$, respectively. It

Table 1

Kind of Pairs	Number of pairs	Energies of Pairs
1-1	$(N_1-X_{12}-X_{13}-X_{14})z/2$	$-2x_1/z$
1-2	$X_{12}z/2$	ϕ_{12}
1-3	$X_{13}z/2$	ϕ_{13}
1-4	$X_{14}z/2$	ϕ_{14}
2-1	$X_{21}z/2$	ϕ_{21}
2-2	$(N_2-X_{23}-X_{24}-X_{12})z/2$	$-2x_2/z$
2-3	$X_{23}z/2$	ϕ_{23}
2-4	$X_{24}z/2$	ϕ_{24}
3-1	$X_{31}z/2$	ϕ_{31}
3-2	$X_{32}z/2$	ϕ_{32}
3-3	$(N_3-X_{31}-X_{32}-X_{34})z/2$	$-2x_2/z$
3-4	$X_{34}z/2$	ϕ_{34}
4-1	$X_{41}z/2$	ϕ_{41}
4-2	$X_{42}z/2$	ϕ_{42}
4-3	$X_{43}z/2$	ϕ_{43}
4-4	$(N_4-X_{41}-X_{42}-X_{43})z/2$	$-2x_4/z$

is convenient to display the number of pairs and their energies in the Table 1.

Using this Table, for the particular configuration mentioned above, the total potential energy E is given by

$$E=-N_1x_1-N_2x_2-N_3x_3-N_4x_4+X_{12}w_{12}+X_{23}w_{23}+X_{31}w_{31}+X_{14}w_{14}+X_{24}w_{24}+X_{34}w_{34}. \quad (1)$$

Further the assembly in the magnetic field H has the magnetic energy:

$$E_m=\mu H(3N_1+N_2-N_3-3N_4)$$

in unit 1/2.

3. Configurational Partition Function

Let $g(N_1, N_2, N_3, N_4, X_{12}, X_{23}, X_{31}, X_{14}, X_{24}, X_{34})$ be the number of distinguishable arrangments of N_1, N_2, N_3 and N_4 particles having states 1, 2, 3 and 4, with the specified values of X_{12}, X_{23}, X_{31}, X_{14}, X_{24} and X_{34}, which is abbreviated as $g(\{N_i\}, \{X_{ij}\})$ in the following. Then the configurational partition function is given by

$$Q_c=\sum_{\{X_{ij}\}} g(\{N_i\}, \{X_{ij}\})\exp\left(-\frac{E+E_m}{kT}\right) . \quad (2)$$

In order to obtain the combinatory formula of $g(\{N_i\}, \{X_{ij}\})$ we assume that we may treat pairs of neighbors as independent entities. According to this assumption, from the Table we have

$$g(\{N_i\}, \{X_{ij}\})=\frac{h(N_1, N_2, N_3, N_4)\left\{N\frac{z}{2}\right\}!}{\left\{(N_1-X_{12}-X_{13}-X_{14})\frac{z}{2}\right\}!\left\{(N_2-X_{12}-X_{23}-X_{24})\frac{z}{2}\right\}!\left\{(N_3-X_{31}-X_{32}-X_{34})\frac{z}{2}\right\}!}$$

$$\times\frac{1}{\left\{(N_4-X_{41}-X_{42}-X_{43})\frac{z}{2}\right\}!\left\{\left(X_{12}\frac{z}{2}\right)!\left(X_{23}\frac{z}{2}\right)!\left(X_{31}\frac{z}{2}\right)!\left(X_{14}\frac{z}{2}\right)!\left(X_{24}\frac{z}{2}\right)!\left(X_{34}\frac{z}{2}\right)!\right\}^2} \quad (3)$$

where it is assumed that we can distinguish between the two manners of occupation 1-2 and 2-1, 2-3 and 3-2, 3-1 and 1-3, 1-4 and 4--1 2-4 and 4-2, 3-4 and 4-3. $g(\{N_i\}, \{X_{ij}\})$ has to satisfy the relation:

$$\sum_{\{X_{ij}\}} g(\{N_i\}, \{X_{ij}\}) = \frac{N!}{N_1!\, N_2!\, N_3!\, N_4!} \,. \tag{4}$$

and $h(\{N_i\})$ is a constant to be selected so that $g(\{N_i\}, \{X_{ij}\})$ may satisfy (4). Using the formula: $(\alpha N)! \sim \alpha^{\alpha N}(N!)^{\alpha}$ for large N, we have

$$g(\{N_i\}, \{X_{ij}\}) = h(N_1, N_2, N_3, N_4)\Big[\frac{N!}{(N_1 - X_{12} - X_{13} - X_{14})!\, (N_2 - X_{21} - X_{23} - X_{24})!}$$
$$\times \frac{1}{(N_3 - X_{31} - X_{32} - X_{34})!\, (N_4 - X_{41} - X_{42} - X_{43})!\, (X_{12}!\, X_{23}!\, X_{31}!\, X_{14}!\, X_{24}!\, X_{34}!)^2}\Big]^{z/2} \,. \tag{5}$$

4. Mean Values and Dispersions

In order to obtain the asymptotic exprression of the inner rpart of the bracket of (5), we will start by calculating the following sum with a certain constant c which is given by (18 a) (we have no need of knowing its definite value):

$$\sum_{\{X_{ij}\}} \omega'(\{X_{ij}\}) = \sum_{\{X_{ij}\}} \frac{cN_1!\, N_2!\, N_3!\, N_4!}{(N_1 - X_{12} - X_{13} - X_{14})!\, (N_2 - X_{21} - X_{23} - X_{24})!}$$
$$\times \frac{1}{(N_3 - X_{31} - X_{32} - X_{34})!\, (N_4 - X_{41} - X_{42} - X_{43})!\, (X_{12}!\, X_{23}!\, X_{31}!\, X_{14}!\, X_{24}!\, X_{34}!)^2} \,. \tag{6}$$

The inner part of the blacket (5) is different from $\omega'(\{X_{ij}\})$ of (6) by a certain constant, which is derived from multinomial expansions.

We write down four multinomial expansions in variables x, y, u and v as follows:

$$(x+y+u+v)^{N_1} = \sum \binom{N_1}{N_1 - X_{12} - X_{13} - X_{14}} \binom{X_{12} + X_{13} + X_{14}}{X_{14}} \binom{X_{12} + X_{13}}{X_{13}}$$
$$\times x^{N_1 - X_{12} - X_{13} - X_{14}} y^{X_{12}} u^{X_{13}} v^{X_{14}}, \tag{7}$$

$$(x+y+u+v)^{N_2} = \sum \binom{N_2}{N_1 - X'_{12} - X_{23} - X_{24}} \binom{X'_{12} + X_{23} + X_{24}}{X'_{12}} \binom{X_{23} + X_{24}}{X_{23}}$$
$$\times x^{X'_{12}} y^{N_2 - X'_{12} - X_{23} - X_{24}} u^{X_{23}} v^{X_{24}}, \tag{8}$$

$$(x+y+u+v)^{N_3} = \sum \binom{N_3}{N_3 - X'_{23} - X'_{13} - X_{34}} \binom{X'_{23} + X'_{13} + X_{34}}{X'_{23}} \binom{X'_{13} + X_{34}}{X_{34}}$$
$$\times x^{X'_{13}} y^{X'_{23}} u^{N_3 - X'_{23} - X'_{13} - X_{34}} v^{X_{34}} \tag{9}$$

and

$$(x+y+u+v)^{N_4} = \sum \binom{N_4}{N_4 - X'_{34} - X'_{14} - X'_{24}} \binom{X'_{34} + X'_{14} + X'_{24}}{X'_{34}} \binom{X'_{14} + X'_{24}}{X'_{14}}$$
$$\times x^{X'_{14}} y^{X'_{24}} u^{X'_{34}} v^{N_4 - X'_{34} - X'_{14} - X'_{24}}. \tag{10}$$

Multiplying (7), (8), (9), and (10) side by side, the condition of picking up the term of $x^{N_1} y^{N_2} u^{N_3} v^{N_4}$ is

$$(X_{12} - X'_{12}) + (X_{13} - X'_{13}) + (X_{14} - X'_{14}) = 0 \,, \tag{11}$$
$$(X_{12} - X'_{12}) - (X_{23} - X'_{23}) - (X_{24} - X'_{24}) = 0 \,, \tag{12}$$
$$(X_{23} - X'_{23}) + (X_{13} - X'_{13}) - (X_{34} - X'_{34}) = 0 \tag{13}$$

and

$$(X_{14} - X'_{14}) + (X_{24} - X'_{24}) + (X_{34} - X'_{34}) = 0 \,. \tag{14}$$

These equations are dependent on each other, since we can derive (11) from (12), (13) and (14). In other words, we have only three relations for six variables $(X_{ij} - X'_{ij})$. Therefore we can choose three values among them arbitrarily. After we put

$$X_{12}-X'_{12}=k_1, \quad X_{24}-X'_{24}=k_2 \text{ and } X_{13}-X'_{13}=k_3, \tag{15}$$

we have, on solving (11)~(14),

$$X'_{14}=X_{14}+k_1+k_3, \quad X'_{23}=X_{23}-k_1+k_2 \text{ and } X'_{34}=X_{34}-k_1+k_2-k_3. \tag{16}$$

(15) and (16) are the conditions of picking up the term of $x^{N_1}y^{N_2}u^{N_3}v^{N_4}$. k_1, k_2 and k_3 are the poitive or negtive integer, but (15) and (16) must not constitute any power of (7), (8), (9), and (10) negative when they are put into them. The real role of k_1, k_2 and k_3 is to bound the changing range of variables X'_{12}, X'_{23}, X'_{31}, X'_{14}, X'_{24} and X'_{34}.

Now substituting (15) and (16) into (7), (8), (9), and (10), multiplying them side by side, and comparing the coefficient of the term $x^{N_1}y^{N_2}u^{N_3}v^{N_4}$ of both side, we have

$$\sum_{\{ki,\,Xij\}} PQRS=\frac{N!}{N_1!\,N_2!\,N_3!\,N_4!} \tag{17}$$

together with

$$P=\binom{N_1}{N_1-X_{12}-X_{13}-X_{14}}\binom{X_{12}+X_{13}+X_{14}}{X_{14}}\binom{X_{12}+X_{13}}{X_{13}},$$

$$Q=\binom{N_2}{N_2-X'_{12}-X_{23}-X_{24}}\binom{X'_{12}+X_{23}+X_{24}}{X'_{12}}\binom{X_{23}+X_{24}}{X_{23}},$$

$$R=\binom{N_3}{N_3-X'_{23}-X'_{13}-X_{34}}\binom{X'_{23}+X'_{13}+X_{34}}{X'_{23}}\binom{X'_{13}+X_{34}}{X_{34}}$$

and

$$S=\binom{N_4}{N_4-X'_{34}-X'_{14}-X'_{24}}\binom{X'_{34}+X'_{14}+X'_{24}}{X'_{34}}\binom{X'_{14}+X'_{24}}{X'_{14}}.$$

Using $f(\{k_i\},\{X_{ij}\})$, the abbreviation of the summand on the left hand side of (17), we have

$$\sum_{\{ki,\,Xij\}} f(\{k_i\},\{X_{ij}\})=\frac{N!}{N_1!\,N_2!\,N_3!\,N_4!}. \tag{17a}$$

For the sake of clarity, we write out the left hand side expression of (17a) in full

$$\sum_{\{ki,\,Xij\}}\frac{N_1!\,N_2!\,N_3!\,N_4!}{(N_1-X_{12}-X_{13}-X_{14})!\,(N_2-X_{12}+k_1-X_{23}-X_{24})!\,(X_{12}-k_1)!}$$
$$\times\frac{1}{X_{13}!\,(X_{13}-k_3)!\,X_{14}!\,X_{12}!\,X_{24}!\,X_{23}!\,(N_3-X_{23}+k_1-k_2-X_{13}+k_3-X_{34})!}$$
$$\times\frac{1}{X_{34}!\,(N_4-X_{34}-X_{14}-X_{24})!\,(X_{24}-k_2)!\,(X_{23}-k_1+k_2)!}$$
$$\times\frac{1}{(X_{14}+k_1+k_3)!\,(X_{34}-k_1+k_2-k_3)!}. \tag{18}$$

The special value of (18) having $k_1=k_2=k_3=0$ is a part of the total number of terms $x^{N_1}y^{N_2}u^{N_3}v^{N_4}$ and so we have

$$\sum_{\{ki,\,Xij\}} f(\{k_i\},\{X_{ij}\})=c\sum_{\{Xij\}} f(\{0\},\{X_{ij}\}) \tag{18a}$$
$$\equiv\sum_{\{Xij\}}\omega'(\{X_{ij}\}). \tag{18b}$$

As the right side of (18a) is nothing but (6) and we have the following sum from (18b) and (17):

$$\frac{N!}{N_1!\,N_2!\,N_3!\,N_4!}=\sum_{\{Xij\}}\omega'(X_{ij}). \tag{19}$$

Let us obtain the mean values and dispersions of X_{ij}. As it is shown in appendix 1 that the mean values of X_{ij} through $\omega'(X_{ij})$, namely through $cf(\{0\}, \{X_{ij}\})$ are equal to those through $f(\{k_i\}, \{X_{ij}\})$, we will calculate the mean values and dispersions through $f(\{k_i\}, \{X_{ij}\})$, because it is easier to handle $f(\{k_i\}, \{X_{ij}\})$ by the aid of multinomial formula (7)~(10) than to handle $\omega'(X_{ij})$ itself. The mean values throgh $f(\{k_i\}, \{X_{ij}\})$ is denoted by the bar. First differentiating (7) with respect to y, multiplying it by (8), (9) and (10) side by side, dividing by (17), using the condition (15) and (16), and picking up the coefficient of $x^{N_1}y^{N_2-1}u^{N_3}v^{N_4}$, we have

$$\bar{X}_{12}=N_1N_2/N \tag{20}$$

Next starting with differentiating (7) two times with respect to y and using (20), we have

$$\sigma_{12}^2=\overline{X_{12}^2}-\bar{X}_{12}^2=\frac{N_1N_2\{N_1N_2+(N_3+N_4)N\}}{N^2(N-1)}\ . \tag{21}$$

Similarly we have other mean values and dispersions by a cyclic change of N_1, N_2, N_3 aad N_4. Further we have

$$\bar{k}_i=0\ . \tag{22}$$

5. Asymptotic Expression

The mean values and dispersions are given in the preceding section, and so we can now obtain the asymptotic expression of the following combinatory formula:

$$\omega(\{X_{ij}\})=\frac{N_1!\,N_2!\,N_3!\,N_4!}{N!}\omega'(\{X_{ij}\})\ . \tag{23}$$

For this purpose we carry out the following transformation:

$$t_{ij}=\frac{X_{ij}-\bar{X}_{ij}}{\sigma_{ij}}\ . \tag{24}$$

Then we have

$$X_{12}=\frac{N_1N_2}{N}(1+\beta_{12}t_{12})\ , \tag{25}$$

$$\beta_{12}=\left\{\frac{1+(N_3+N_4)/N_1N_2\,N}{N-1}\right\}^{1/2} \tag{26}$$

and

other variables are obtained by the cyclic change of N_1, N_2, N_3 and N_4. Similarly we have

$$N_1-X_{12}-X_{13}-X_{14}=\frac{N_1^2}{N}\left\{1-\left(\frac{N_2}{N_1}\beta_{12}t_{12}+\frac{N_3}{N_1}\beta_{13}t_{13}+\frac{N_4}{N_1}\beta_{14}t_{14}\right)\right\} \tag{27}$$

and others obtained by the cyclic change of subscripts 1, 2, 3, 4.

When we take the logarithm of both sides of (23), and use Stirling's formula and the following expansion:

$$\log(1+u)=u-\frac{u^2}{2}+\dots\ ,$$

we have

$$-\log\omega(\{X_{ij}\})=-\log c+\frac{9}{2}\log(2\pi)+\log(N_1N_2N_3N_4)^3-8\log N$$
$$+\left[\frac{N_1^2}{N}\left\{1-\left(\frac{N_1}{N_2}\beta_{12}t_{12}+\frac{N_3}{N_1}\beta_{13}t_{13}+\frac{N_4}{N_1}\beta_{14}t_{14}\right)\right\}+\frac{1}{2}\right]$$

$$\times\left[-\left(\frac{N_2}{N_1}\beta_{12}t_{12}+\frac{N_3}{N_1}\beta_{13}t_{13}+\frac{N_4}{N_1}\beta_{14}t_{14}\right)-\frac{1}{2}\left(\frac{N_2}{N_1}\beta_{12}t_{12}+\frac{N_3}{N_1}\beta_{13}t_{13}+\frac{N_4}{N_1}\beta_{14}t_{14}\right)^2\right]$$
$$+\left[\frac{N_2^2}{N}\left\{1-\left(\frac{N_1}{N_2}\beta_{12}t_{12}+\frac{N_3}{N_2}\beta_{23}t_{23}+\frac{N_4}{N_2}\beta_{24}t_{24}\right)\right\}+\frac{1}{2}\right]$$
$$\times\left[-\left(\frac{N_1}{N_2}\beta_{12}t_{12}+\frac{N_3}{N_2}\beta_{23}t_{23}+\frac{N_4}{N_2}\beta_{24}t_{24}\right)-\frac{1}{2}\left(\frac{N_1}{N_2}\beta_{12}t_{12}+\frac{N_3}{N_2}\beta_{23}t_{23}+\frac{N_4}{N_2}\beta_{24}t_{24}\right)^2\right]$$
$$+\left[\frac{N_3^2}{N}\left\{1-\left(\frac{N_1}{N_3}\beta_{31}t_{31}+\frac{N_2}{N_3}\beta_{23}t_{23}+\frac{N_4}{N_3}\beta_{34}t_{34}\right)\right\}+\frac{1}{2}\right]$$
$$\times\left[-\left(\frac{N_1}{N_3}\beta_{31}t_{31}+\frac{N_2}{N_3}\beta_{23}t_{23}+\frac{N_4}{N_3}\beta_{34}t_{34}\right)-\frac{1}{2}\left(\frac{N_1}{N_3}\beta_{31}t_{31}+\frac{N_2}{N_3}\beta_{23}t_{23}+\frac{N_4}{N_3}\beta_{34}t_{34}\right)^2\right]$$
$$+\left[\frac{N_4^2}{N}\left\{1-\left(\frac{N_1}{N_4}\beta_{41}t_{41}+\frac{N_2}{N_4}\beta_{42}t_{42}+\frac{N_3}{N_4}\beta_{43}t_{43}\right)\right\}+\frac{1}{2}\right]$$
$$\times\left[-\left(\frac{N_1}{N_4}\beta_{41}t_{41}+\frac{N_2}{N_4}\beta_{42}t_{42}+\frac{N_3}{N_4}\beta_{43}t_{43}\right)-\frac{1}{2}\left(\frac{N_1}{N_4}\beta_{41}t_{41}+\frac{N_2}{N_4}\beta_{42}t_{42}+\frac{N_3}{N_4}\beta_{43}t_{43}\right)^2\right]$$
$$+2\left[\frac{N_1N_2}{N}(1+\beta_{12}t_{12})+\frac{1}{2}\right]\left[\beta_{12}t_{12}-\frac{1}{2}\beta_{12}^2t_{12}^2\right]$$
$$+2\left[\frac{N_2N_3}{N}(1+\beta_{23}t_{23})+\frac{1}{2}\right]\left[\beta_{23}t_{23}-\frac{1}{2}\beta_{23}^2t_{23}^2\right]$$
$$+2\left[\frac{N_3N_1}{N}(1+\beta_{31}t_{31})+\frac{1}{2}\right]\left[\beta_{31}t_{31}-\frac{1}{2}\beta_{31}^2t_{31}^2\right]$$
$$+2\left[\frac{N_1N_4}{N}(1+\beta_{14}t_{14})+\frac{1}{2}\right]\left[\beta_{14}t_{14}-\frac{1}{2}\beta_{14}^2t_{14}^2\right]$$
$$+2\left[\frac{N_2N_4}{N}(1+\beta_{24}t_{24})+\frac{1}{2}\right]\left[\beta_{24}t_{24}-\frac{1}{2}\beta_{24}^2t_{24}^2\right]$$
$$+2\left[\frac{N_3N_4}{N}(1+\beta_{34}t_{34})+\frac{1}{2}\right]\left[\beta_{34}t_{34}-\frac{1}{2}\beta_{34}^2t_{34}^2\right]. \tag{28}$$

As $N_i \to \infty$ in (28), t_{ij} remain finite. In fact, in order to obtain the unique limiting values, we put $N_1=eh$, $N_2=mh$, $N_3=nh$, $N_4=kh$ and let h tend to infinity. When we neglect terms having higher orders of t_{ij} than the second order, we have

$$\begin{aligned}-\lim_{N_i\to\infty}\log\omega(\{X_{ij}\}) &= \log\left[c^{-1}\left\{(2\pi)^{9/2}\frac{(N_1N_2N_3N_4)^3}{N^8}\right\}\right]+\lambda_{11}t_{23}^2+\lambda_{22}t_{31}^2\\&+\lambda_{33}t_{12}^2+\lambda_{44}t_{14}^2+\lambda_{55}t_{24}^2+\lambda_{66}t_{34}^2+2\lambda_{23}t_{12}t_{13}+2\lambda_{24}t_{13}t_{14}+2\lambda_{25}t_{13}t_{24}\\&+2\lambda_{26}t_{13}t_{34}+2\lambda_{12}t_{13}t_{23}+2\lambda_{13}t_{12}t_{23}+2\lambda_{14}t_{14}t_{23}+2\lambda_{15}t_{23}t_{24}+2\lambda_{16}t_{23}t_{34}\\&+2\lambda_{34}t_{12}t_{14}+2\lambda_{35}t_{12}t_{24}+2\lambda_{36}t_{12}t_{34}+2\lambda_{45}t_{14}t_{24}+2\lambda_{46}t_{14}t_{34}+2\lambda_{56}t_{24}t_{34},\end{aligned} \tag{29}$$

where the limiting value λ_{11}, the coefficient of t_{23}^2 is given by

$$\lambda_{11}=\frac{(N_2+N_3)^2}{2N^2}\left\{1+\frac{(N_1+N_4)}{N_2N_3}N\right\} \tag{30}$$

and other λ_{ii}'s are obtained by the cyclic change of subscripts, and λ_{34} the coefficient of $t_{12}t_{14}$ is given by

$$\lambda_{34}=\frac{1}{2}\frac{N_2N_4}{N^2}\left\{1+\frac{(N_3+N_4)}{N_1N_2}N\right\}^{1/2}\left\{1+\frac{(N_2+N_3)}{N_1N_4}N\right\}^{1/2} \tag{31}$$

and other λ_{ij}'s are obtained by the cyclic change of subscripts. In addition $\lambda_{25}=\lambda_{36}=\lambda_{14}=0$, which are inserted formally. λ_{ij} can be represented by fractions such as N_i/N, however it is noted that we must treat them as constans when we derive chemical potentials and other thermodynamical quantities.

Rewriting (29) with X_{ij} we have the asymptotic expression of (23):

$$\omega(\{X_{ij}\})=c\frac{N^8}{(2\pi)^{9/2}(N_1N_2N_3N_4)^3}\exp(-\Phi) \tag{32}$$

together with

$$\begin{aligned}\Phi=&\lambda_{11}\frac{(X_{23}-\bar{X}_{23})^2}{\sigma_{23}^2}+\lambda_{22}\frac{(X_{13}-\bar{X}_{13})^2}{\sigma_{13}^2}+\lambda_{33}\frac{(X_{12}-\bar{X}_{12})^2}{\sigma_{12}^2}+\lambda_{44}\frac{(X_{14}-\bar{X}_{14})^2}{\sigma_{14}^2}\\&+\lambda_{55}\frac{(X_{24}-\bar{X}_{24})^2}{\sigma_{24}^2}+\lambda_{66}\frac{(X_{34}-\bar{X}_{34})^2}{\sigma_{34}^2}+2\lambda_{23}\frac{X_{12}-\bar{X}_{12}}{\sigma_{12}}\frac{X_{13}-\bar{X}_{13}}{\sigma_{13}}\\&+2\lambda_{24}\frac{X_{13}-\bar{X}_{13}}{\sigma_{13}}\frac{X_{14}-\bar{X}_{14}}{\sigma_{14}}+2\lambda_{25}\frac{X_{13}-\bar{X}_{13}}{\sigma_{13}}\frac{X_{24}-\bar{X}_{24}}{\sigma_{24}}\\&+2\lambda_{26}\frac{X_{13}-\bar{X}_{13}}{\sigma_{13}}\frac{X_{34}-\bar{X}_{34}}{\sigma_{34}}+2\lambda_{12}\frac{X_{13}-\bar{X}_{13}}{\sigma_{13}}\frac{X_{23}-\bar{X}_{23}}{\sigma_{23}}\\&+2\lambda_{13}\frac{X_{12}-\bar{X}_{12}}{\sigma_{12}}\frac{X_{23}-\bar{X}_{23}}{\sigma_{23}}+2\lambda_{14}\frac{X_{14}-\bar{X}_{14}}{\sigma_{14}}\frac{X_{23}-\bar{X}_{23}}{\sigma_{23}}\\&+2\lambda_{15}\frac{X_{23}-\bar{X}_{23}}{\sigma_{23}}\frac{X_{24}-\bar{X}_{24}}{\sigma_{24}}+2\lambda_{16}\frac{X_{23}-\bar{X}_{23}}{\sigma_{23}}\frac{X_{34}-\bar{X}_{34}}{\sigma_{34}}\\&+2\lambda_{34}\frac{X_{12}-\bar{X}_{12}}{\sigma_{12}}\frac{X_{14}-\bar{X}_{14}}{\sigma_{14}}+2\lambda_{35}\frac{X_{12}-\bar{X}_{12}}{\sigma_{12}}\frac{X_{24}-\bar{X}_{24}}{\sigma_{24}}\\&+2\lambda_{36}\frac{X_{12}-\bar{X}_{12}}{\sigma_{12}}\frac{X_{34}-\bar{X}_{34}}{\sigma_{34}}+2\lambda_{45}\frac{X_{14}-\bar{X}_{14}}{\sigma_{14}}\frac{X_{24}-\bar{X}_{24}}{\sigma_{24}}\\&+2\lambda_{46}\frac{X_{14}-\bar{X}_{14}}{\sigma_{14}}\frac{X_{34}-\bar{X}_{34}}{\sigma_{34}}+2\lambda_{56}\frac{X_{24}-\bar{X}_{24}}{\sigma_{24}}\frac{X_{34}-\bar{X}_{34}}{\sigma_{34}}\,.\end{aligned}\tag{33}$$

Now we can obtain the asymptotic expression of $g(\{N_i\}, \{X_{ij}\})$ (3). Recalling that $g(\{N_i\}, \{X_{ij}\})$ is different from $\omega'(\{X_{ij}\})$ (6) by a certain constant and $\omega'(\{X_{ij}\})$ is connected with $\omega(\{X_{ij}\})$ by (23), where we see that there is a constant difference betveen $\omega'(\{X_{ij}\})$ and $\omega(\{X_{ij}\})$, in addition $h(\{N_i\})$ is a constant which is to be selected to satisfy (4), we know that the essential part of $g(\{N_i\}, \{X_{ij}\})$ is $[\exp(-\Phi)]^{z/2}$ aside from various constants and therefore we have

$$g(\{N_i\}, \{X_{ij}\})=\frac{N!}{N_1!\,N_2!\,N_3!\,N_4!}c_0\exp\left(-\frac{z}{2}\Phi\right)\tag{34}$$

where c_0 is a constant determined so that the integration of $\exp\left(-\frac{z}{2}\Phi\right)$ may satisfy (4):

$$c_0^{-1}=\left(\frac{2\pi}{z}\right)^{6/2}\sigma_{12}\sigma_{23}\sigma_{31}\sigma_{14}\sigma_{24}\sigma_{34}\Omega^{-1/2}$$

together with $\Omega=|\lambda|$, defining the following matrix (see Appendix 2):

$$\lambda=\begin{pmatrix}\lambda_{11}&\lambda_{12}&\lambda_{13}&\lambda_{14}&\lambda_{15}&\lambda_{16}\\\lambda_{21}&\lambda_{22}&\lambda_{23}&\lambda_{24}&\lambda_{25}&\lambda_{26}\\\lambda_{31}&\lambda_{32}&\lambda_{33}&\lambda_{34}&\lambda_{35}&\lambda_{36}\\\lambda_{41}&\lambda_{42}&\lambda_{43}&\lambda_{44}&\lambda_{45}&\lambda_{46}\\\lambda_{51}&\lambda_{52}&\lambda_{53}&\lambda_{54}&\lambda_{55}&\lambda_{56}\\\lambda_{61}&\lambda_{62}&\lambda_{63}&\lambda_{64}&\lambda_{65}&\lambda_{66}\end{pmatrix}.\tag{35}$$

Using (34), we have the partition function having an integration form:

$$Q_c=\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty}^{\infty} g(\{N_i\}, \{X_{ij}\})\exp\left(-\frac{E+E_m}{kT}\right)\{dX_{ij}\}\,.\tag{36}$$

The integration of (36) can be obtained by elementary calculus in principle, but we can carry it out easily as follows. Rewriting (36) with t_{ij}, we can pull out

$$\exp\{-(\bar{X}_{12}w_{12}+\bar{X}_{23}w_{23}+\bar{X}_{31}w_{31}+\bar{X}_{14}w_{14}+\bar{X}_{24}w_{24}+\bar{X}_{34}w_{34})/kT-E_m/kT\}\tag{37}$$

from the sign of the integration and then remaining terms in the exponent are

$$-\frac{z}{2}[\lambda_{11}t_{23}^2+\lambda_{22}t_{13}^2+\lambda_{33}t_{12}^2+\lambda_{44}t_{14}^2+\lambda_{55}t_{24}^2+\lambda_{66}t_{34}^2+2\lambda_{23}t_{12}t_{13}+2\lambda_{24}t_{13}t_{14}$$
$$+2\lambda_{25}t_{13}t_{24}+2\lambda_{26}t_{13}t_{34}+2\lambda_{12}t_{13}t_{23}+2\lambda_{13}t_{12}t_{23}+2\lambda_{14}t_{14}t_{23}+2\lambda_{15}t_{23}t_{24}$$
$$+2\lambda_{16}t_{23}t_{34}+2\lambda_{34}t_{12}t_{14}+2\lambda_{35}t_{12}t_{24}+2\lambda_{36}t_{12}t_{34}+2\lambda_{45}t_{14}t_{24}+2\lambda_{46}t_{14}t_{34}$$
$$+2\lambda_{56}t_{24}t_{34}+2t_{12}\gamma_{12}+2t_{23}\gamma_{23}+2t_{31}\gamma_{31}+2t_{14}\gamma_{14}+2t_{24}\gamma_{24}+2t_{34}\gamma_{34}]\,, \tag{38}$$

where

$$\gamma_{12}=\frac{\sigma_{12}}{z}\frac{w_{12}}{kT}, \quad \gamma_{14}=\frac{\sigma_{14}}{z}\frac{w_{14}}{kT}, \quad \gamma_{23}=\frac{\sigma_{23}}{z}\frac{w_{23}}{kT}, \quad \gamma_{24}=\frac{\sigma_{24}}{z}\frac{w_{24}}{kT}$$
$$\gamma_{31}=\frac{\sigma_{31}}{z}\frac{w_{31}}{kT} \text{ and } \gamma_{34}=\frac{\sigma_{34}}{z}\frac{w_{34}}{kT}\,. \tag{39}$$

The integration of (36) is given by the following formula[3]:

$$C_n\int_{-\infty}^{\infty}\cdots\int\exp\Big(-\sum_{i,j}^{n}\lambda_{ij}x_ix_j\Big)\exp\Big(2\sum_i\beta_ix_i\Big)\prod_i dx_i=\exp\Big(\sum_{i,j}\alpha_{ij}\beta_i\beta_j\Big)$$

together with

$$\lambda=\{\lambda_{ij}\}, \qquad \lambda^{-1}=\{\alpha_{ij}\}$$

and

$$C_n=|\lambda|^{1/2}/(\pi^{1/2})^n\,.$$

For writing down the result of the integration correctly, it is convenient to display the inverse matrix having γ_{ij} in place of t_{ij} at the fringe of it:

$$\begin{array}{c|cccccc} & \gamma_{23} & \gamma_{13} & \gamma_{12} & \gamma_{14} & \gamma_{24} & \gamma_{34} \\ \gamma_{23} & \lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & \lambda_{15} & \lambda_{16} \\ \gamma_{13} & \lambda_{21} & \lambda_{22} & \lambda_{23} & \lambda_{24} & \lambda_{25} & \lambda_{26} \\ \gamma_{12} & \lambda_{31} & \lambda_{32} & \lambda_{33} & \lambda_{34} & \lambda_{35} & \lambda_{36} \\ \gamma_{14} & \lambda_{41} & \lambda_{42} & \lambda_{43} & \lambda_{44} & \lambda_{45} & \lambda_{46} \\ \gamma_{24} & \lambda_{51} & \lambda_{52} & \lambda_{53} & \lambda_{54} & \lambda_{55} & \lambda_{56} \\ \gamma_{34} & \lambda_{61} & \lambda_{62} & \lambda_{63} & \lambda_{64} & \lambda_{65} & \lambda_{66} \end{array}^{\,-1} \,. \tag{40}$$

Thus we have, bringing (37) together,

$$Q_c=\frac{N!}{N_1!\,N_2!\,N_3!\,N_4!}\exp\{-(\bar{X}_{12}w_{12}+\bar{X}_{23}w_{23}+\bar{X}_{31}w_{31}+\bar{X}_{14}w_{14}+\bar{X}_{24}w_{24}$$
$$+\bar{X}_{34}w_{34})/kT-E_m/kT\}\exp\Big[\frac{z}{2}\{\alpha_{11}\gamma_{23}^2+\alpha_{22}\gamma_{31}^2+\alpha_{33}\gamma_{12}^2+\alpha_{44}\gamma_{14}^2+\alpha_{55}\gamma_{24}^2$$
$$+\alpha_{66}\gamma_{34}^2+2\alpha_{21}\gamma_{23}\gamma_{13}+2\alpha_{31}\gamma_{23}\gamma_{12}+2\alpha_{41}\gamma_{23}\gamma_{14}+2\alpha_{51}\gamma_{23}\gamma_{24}+2\alpha_{61}\gamma_{23}\gamma_{34}$$
$$+2\alpha_{32}\gamma_{13}\gamma_{12}+2\alpha_{42}\gamma_{13}\gamma_{14}+2\alpha_{52}\gamma_{13}\gamma_{24}+2\alpha_{62}\gamma_{13}\gamma_{34}+2\alpha_{43}\gamma_{12}\gamma_{14}$$
$$+2\alpha_{53}\gamma_{12}\gamma_{24}+2\alpha_{63}\gamma_{12}\gamma_{34}+2\alpha_{54}\gamma_{14}\gamma_{24}+2\alpha_{64}\gamma_{14}\gamma_{34}+2\alpha_{65}\gamma_{24}\gamma_{34}\}\Big] \tag{41}$$

where α_{ij}'s are elements of the inverse matrix. For instance, introducing the fraction $\varphi_i=N_i/N$, they are given by

$$\alpha_{11}=2\frac{\left(1+\dfrac{\varphi_1+\varphi_4}{2\varphi_2\varphi_3}\right)}{\left(1+\dfrac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)}, \qquad \alpha_{12}=2\frac{\left(1-\dfrac{1}{2\varphi_3}\right)}{\left(1+\dfrac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)^{1/2}\left(1+\dfrac{\varphi_2+\varphi_4}{\varphi_1\varphi_3}\right)^{1/2}}$$

$$\alpha_{22}=2\frac{\left(1+\dfrac{\varphi_2+\varphi_4}{2\varphi_3\varphi_1}\right)}{\left(1+\dfrac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)} \text{ and } \alpha_{25}=2\frac{1}{\left(1+\dfrac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)^{1/2}\left(1+\dfrac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right)^{1/2}}\,. \tag{42}$$

From (41), by use of (20), (21) (39) and (42), we have the free energy of mixing:

$$
\begin{aligned}
F_c/NkT=&\varphi_1\log\varphi_1+\varphi_2\log\varphi_2+\varphi_3\log\varphi_3+\varphi_4\log\varphi_4+\mu H(3\varphi_1+\varphi_2-\varphi_3-3\varphi_4)/kT\\
&+(\varphi_1\varphi_2w_{12}+\varphi_2\varphi_3w_{23}+\varphi_3\varphi_1w_{31}+\varphi_1\varphi_4w_{14}+\varphi_2\varphi_4w_{24}+\varphi_3\varphi_4w_{34})/kT\\
&-\varphi_2^2\varphi_3^2\left(1+\frac{\varphi_1+\varphi_4}{2\varphi_2\varphi_3}\right)\frac{w_{23}^2}{zk^2T^2}-\varphi_3^2\varphi_1^2\left(1+\frac{\varphi_2+\varphi_4}{2\varphi_3\varphi_1}\right)\frac{w_{31}^2}{zk^2T^2}-\varphi_1^2\varphi_2^2\left(1+\frac{\varphi_3+\varphi_4}{2\varphi_1\varphi_2}\right)\frac{w_{12}^2}{zk^2T^2}\\
&-\varphi_1^2\varphi_4^2\left(1+\frac{\varphi_2+\varphi_3}{2\varphi_1\varphi_4}\right)\frac{w_{14}^2}{zk^2T^2}-\varphi_2^2\varphi_4^2\left(1+\frac{\varphi_3+\varphi_1}{2\varphi_2\varphi_4}\right)\frac{w_{24}^2}{zk^2T^2}-\varphi_3^2\varphi_4^2\left(1+\frac{\varphi_1+\varphi_2}{2\varphi_3\varphi_4}\right)\frac{w_{34}^2}{zk^2T^2}\\
&-2\varphi_1\varphi_2\varphi_3^2\left(1-\frac{1}{2\varphi_3}\right)\frac{w_{23}w_{31}}{zk^2T^2}-2\varphi_1\varphi_2^2\varphi_3\left(1-\frac{1}{2\varphi_2}\right)\frac{w_{23}w_{12}}{zk^2T^2}-2\varphi_1\varphi_2\varphi_3\varphi_4\frac{w_{23}w_{14}}{zk^2T^2}\\
&-2\varphi_2^2\varphi_3\varphi_4\left(1-\frac{1}{2\varphi_2}\right)\frac{w_{23}w_{24}}{zk^2T^2}-2\varphi_2\varphi_3^2\varphi_4\left(1-\frac{1}{2\varphi_3}\right)\frac{w_{23}w_{34}}{zk^2T^2}-2\varphi_1^2\varphi_2\varphi_3\left(1-\frac{1}{2\varphi_1}\right)\frac{w_{13}w_{12}}{zk^2T^2}\\
&-2\varphi_1^2\varphi_3\varphi_4\left(1-\frac{1}{2\varphi_1}\right)\frac{w_{13}w_{14}}{zk^2T^2}-2\varphi_1\varphi_2\varphi_3\varphi_4\frac{w_{13}w_{24}}{zk^2T^2}-2\varphi_1\varphi_3^2\varphi_4\left(1-\frac{1}{2\varphi_3}\right)\frac{w_{13}w_{34}}{zk^2T^2}\\
&-2\varphi_1^2\varphi_2\varphi_4\left(1-\frac{1}{2\varphi_1}\right)\frac{w_{12}w_{14}}{zk^2T^2}-2\varphi_1\varphi_2^2\varphi_4\left(1-\frac{1}{2\varphi_2}\right)\frac{w_{12}w_{24}}{zk^2T^2}-2\varphi_1\varphi_2\varphi_3\varphi_4\frac{w_{12}w_{34}}{zk^2T^2}\\
&-2\varphi_1\varphi_2\varphi_4^2\left(1-\frac{1}{2\varphi_4}\right)\frac{w_{14}w_{24}}{zk^2T^2}-2\varphi_1\varphi_3\varphi_4^2\left(1-\frac{1}{2\varphi_4}\right)\frac{w_{14}w_{34}}{zk^2T^2}-2\varphi_2\varphi_3\varphi_4^2\left(1-\frac{1}{2\varphi_4}\right)\frac{w_{24}w_{34}}{zk^2T^2}\ .
\end{aligned}
\tag{43}
$$

Appendix 1

When we differentiate (7) with respect to y, multiply it by (8), (9) and (10) side by side, divided by (17) side by side, and use the the conditions (11), (12), (13), we have at the right hand side

$$\frac{\sum X_{12}f(\{k_i\},\{X_{ij}\})}{\sum f(\{k_i\},\{X_{ij}\})}x^{N_1}y^{N_2-1}u^{N_3}v^{N_4}\ . \tag{A. 1}$$

This is to be equal to the coefficient of the term $x^{N_1}y^{N_2-1}u^{N_3}v^{N_4}$ in the multinomial expansion of the left side obtained at that time:

$$\frac{N_1(x+y+u+v)^{N-1}}{N!/(N_1!N_2!N_3!N_4!)}\ . \tag{A. 2}$$

Thus we have

$$\bar{X}_{12}=\frac{N_1N_2}{N}\ . \tag{A. 3}$$

Similarly others are obtained by changing subscripts cyclically.

On the other hand, taking the logarithm of (17) and differentiating it with respect to X_{ij} and k_i, making them zero, we have

$$
\left.\begin{aligned}
&X_{12}(X_{12}-k_1)=AB,\\
&X_{13}(X_{13}-k_3)=AC,\\
&X_{14}(X_{14}+k_1+k_3)=AD,\\
&X_{23}(X_{23}-k_1+k_2)=BC,\\
&X_{24}(X_{24}-k_2)=BD,\\
&X_{34}(X_{34}-k_1+k_2-k_3)=CD,
\end{aligned}\right\} \tag{A. 4. a}
$$

$$
\left.\begin{aligned}
&(X_{12}+k_1)(X_{23}-k_1+k_2)(X_{34}-k_1+k_2-k_3)=(X_{14}+k_1+k_3)BC,\\
&(X_{13}-k_1+k_2)(X_{34}-k_1+k_2-k_3)=(X_{24}-k_2)C
\end{aligned}\right\} \tag{A. 4. b}
$$

and $(X_{13}-k_3)(X_{34}-k_1+k_2-k_3)=(X_{14}+k_1+k_3)C,$

where we put as follows:

$$
\begin{aligned}
&A=(N_1-X_{12}-X_{13}-X_{14}),\\
&B=(N_2-X_{12}+k_1-X_{23}-X_{24}),\\
&C=(N_3-X_{23}+k_1-k_2-X_{13}+k_3-X_{34})
\end{aligned}
$$

and $D=(N_4-X_{34}-X_{14}-X_{24})\,.$

When we slove these simultaneous equations, we have

$$\bar{X}_{12}=\frac{N_1N_2}{N} \tag{A.5}$$

and others changed subsclipts cyclically and

$$k_i=0 \qquad i=1,2,3 \tag{A.6}$$

If we substitute (A.6) into (A.4.a), we have

$$\begin{aligned}
X_{12}^2&=(N_1-X_{12}-X_{13}-X_{14})(N_2-X_{12}-X_{23}-X_{24})\\
X_{13}^2&=(N_1-X_{12}-X_{13}-X_{14})(N_3-X_{13}-X_{23}-X_{34})\\
X_{14}^2&=(N_1-X_{12}-X_{13}-X_{14})(N_4-X_{14}-X_{24}-X_{34})\\
X_{23}^2&=(N_2-X_{12}-X_{23}-X_{24})(N_3-X_{13}-X_{23}-X_{34})\\
X_{24}^2&=(N_2-X_{12}-X_{23}-X_{24})(N_4-X_{14}-X_{24}-X_{34})
\end{aligned}$$

and

$$X_{34}^2=(N_3-X_{13}-X_{23}-X_{34})(N_4-X_{14}-X_{24}-X_{34})\,. \tag{A.6}$$

These simultaneous equations are also derived from (18b). Apparently from these we obtain

$$\bar{X}_{12}=\frac{N_1N_2}{N} \tag{A.5}$$

and so on. Thus if we take the most probable value as the mean value, we have

$$\frac{\sum X_{ij}f(\{k_i\},\{X_{ij}\})}{\sum f(\{k_i\},\{X_{ij}\})}=\frac{c\sum X_{ij}f(\{0\},\{X_{ij}\})}{c\sum f(\{0\},\{X_{ij}\})}\,. \tag{A.7}$$

Appendix 2

The determinant of matrix λ is given explicitly by

$$\begin{aligned}
|\lambda|=&\left(\frac{1}{2}\right)^6\left(1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)\left(1+\frac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)\left(1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right)\left(1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right)\left(1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right)\\
&\times\left(1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right)\begin{vmatrix}
(\varphi_2+\varphi_3)^2 & \varphi_1\varphi_2 & \varphi_1\varphi_3 & 0 & \varphi_3\varphi_4 & \varphi_2\varphi_4\\
\varphi_1\varphi_2 & (\varphi_3+\varphi_1)^2 & \varphi_2\varphi_3 & \varphi_3\varphi_4 & 0 & \varphi_1\varphi_4\\
\varphi_1\varphi_3 & \varphi_2\varphi_3 & (\varphi_1+\varphi_2)^2 & \varphi_2\varphi_4 & \varphi_1\varphi_4 & 0\\
0 & \varphi_3\varphi_4 & \varphi_2\varphi_4 & (\varphi_1+\varphi_4)^2 & \varphi_1\varphi_2 & \varphi_1\varphi_3\\
\varphi_3\varphi_4 & 0 & \varphi_1\varphi_4 & \varphi_1\varphi_2 & (\varphi_2+\varphi_4)^2 & \varphi_2\varphi_3\\
\varphi_2\varphi_4 & \varphi_1\varphi_4 & 0 & \varphi_1\varphi_3 & \varphi_2\varphi_3 & (\varphi_3+\varphi_4)^2
\end{vmatrix}\\
=&\left(\frac{1}{2}\right)^6\left(1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)\left(1+\frac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)\left(1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right)\left(1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right)\\
&\times\left(1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right)\left(1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right)2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_4^2\,.
\end{aligned}$$

Some of the minor determinants are

$$\begin{aligned}
D\binom{1}{1}=&\left(\frac{1}{2}\right)^5\left\{1+\frac{\varphi_2+\varphi_4}{\varphi_1\varphi_3}\right\}\left\{1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right\}\left\{1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right\}\\
&\times\begin{vmatrix}
(\varphi_3+\varphi_1)^2 & \varphi_2\varphi_3 & \varphi_3\varphi_4 & 0 & \varphi_1\varphi_4\\
\varphi_2\varphi_3 & (\varphi_1+\varphi_2)^2 & \varphi_2\varphi_4 & \varphi_1\varphi_4 & 0\\
\varphi_3\varphi_4 & \varphi_2\varphi_4 & (\varphi_1+\varphi_4)^2 & \varphi_1\varphi_2 & \varphi_1\varphi_3\\
0 & \varphi_1\varphi_4 & \varphi_1\varphi_2 & (\varphi_2+\varphi_4)^2 & \varphi_2\varphi_3\\
\varphi_1\varphi_4 & 0 & \varphi_1\varphi_3 & \varphi_2\varphi_3 & (\varphi_3+\varphi_4)^2
\end{vmatrix}\\
=&\left(\frac{1}{2}\right)^5\left\{1+\frac{\varphi_2+\varphi_4}{\varphi_1\varphi_3}\right\}\left\{1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right\}\left\{1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right\}\\
&\times\left\{1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right\}2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_3^2\left(1+\frac{\varphi_1+\varphi_4}{2\varphi_2\varphi_3}\right).
\end{aligned}$$

$$D\binom{1}{2}=\left(\frac{1}{2}\right)^5\left\{1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right\}^{1/2}\left\{1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right\}\left\{1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right\}$$
$$\times\left\{1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right\}\left\{1+\frac{\varphi_2+\varphi_4}{\varphi_1\varphi_3}\right\}^{1/2}(-1)2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_4^2\left(1-\frac{1}{2\varphi_3}\right)$$
$$D\binom{1}{4}=\left(\frac{1}{2}\right)^5\left\{1+\frac{\varphi_2+\varphi_4}{\varphi_1\varphi_3}\right\}\left\{1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right\}\left\{1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right\}$$
$$\times\left\{1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right\}^{1/2}\left\{1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right\}^{1/2}(-2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_4^2)$$
$$D\binom{2}{3}=\left(\frac{1}{2}\right)^5\left\{1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right\}\left\{1+\frac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right\}^{1/2}\left\{1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right\}^{1/2}\left\{1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right\}$$
$$\times\left\{1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right\}\left\{1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right\}(-1)2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_4^2\left(1-\frac{1}{2\varphi_1}\right).$$

Thus the determinant of inverse matrix λ^{-1} is given by

$$|\alpha|=2^6\left(1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)^{-1}\left(1+\frac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)^{-1}\left(1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right)^{-1}$$
$$\times\left(1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right)^{-1}\left(1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right)^{-1}\left(1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right)^{-1}$$
$$\times\begin{vmatrix}
1+\frac{\varphi_1+\varphi_4}{2\varphi_2\varphi_3} & 1-\frac{1}{2\varphi_3} & 1-\frac{1}{2\varphi_2} & 1 & 1-\frac{1}{2\varphi_2} & 1-\frac{1}{2\varphi_3}\\
1-\frac{1}{2\varphi_3} & 1+\frac{\varphi_2+\varphi_4}{2\varphi_3\varphi_1} & 1-\frac{1}{2\varphi_1} & 1-\frac{1}{2\varphi_1} & 1 & 1-\frac{1}{2\varphi_3}\\
1-\frac{1}{2\varphi_2} & 1-\frac{1}{2\varphi_1} & 1+\frac{\varphi_3+\varphi_4}{2\varphi_1\varphi_2} & 1-\frac{1}{2\varphi_1} & 1-\frac{1}{2\varphi_2} & 1\\
1 & 1-\frac{1}{2\varphi_1} & 1-\frac{1}{2\varphi_1} & 1+\frac{\varphi_2+\varphi_3}{2\varphi_1\varphi_4} & 1-\frac{1}{2\varphi_4} & 1-\frac{1}{2\varphi_4}\\
1-\frac{1}{2\varphi_2} & 1 & 1-\frac{1}{2\varphi_2} & 1-\frac{1}{2\varphi_4} & 1+\frac{\varphi_1+\varphi_3}{2\varphi_2\varphi_4} & 1-\frac{1}{2\varphi_4}\\
1-\frac{1}{2\varphi_3} & 1-\frac{1}{2\varphi_3} & 1 & 1-\frac{1}{2\varphi_4} & 1-\frac{1}{2\varphi_4} & 1+\frac{\varphi_1+\varphi_2}{2\varphi_3\varphi_4}
\end{vmatrix}$$
$$=2^6\left(1+\frac{\varphi_1+\varphi_4}{\varphi_2\varphi_3}\right)^{-1}\left(1+\frac{\varphi_2+\varphi_4}{\varphi_3\varphi_1}\right)^{-1}\left(1+\frac{\varphi_3+\varphi_4}{\varphi_1\varphi_2}\right)^{-1}\left(1+\frac{\varphi_2+\varphi_3}{\varphi_1\varphi_4}\right)^{-1}$$
$$\times\left(1+\frac{\varphi_1+\varphi_3}{\varphi_2\varphi_4}\right)^{-1}\left(1+\frac{\varphi_1+\varphi_2}{\varphi_3\varphi_4}\right)^{-1}(2^3\varphi_1^2\varphi_2^2\varphi_3^2\varphi_4^2)^{-1}.$$

References

1) Onodera, M.: J. Phys. Soc. Japan 37, 24 (1974).
2) Fowler, R. H. and Guggenheim, E. A.: Statistical Thermodynamics (GB) (Cambridge Univ. Press, 1939) Sec. 814.
3) Onodera, M.: Bull. Fac. Eng. Hokkaido Univ. 84, 109 (1977).