

# Statistical Mechanics of Quantum Mixtures III

—Surface Tension of the liquid  $^3\text{He}$ - $^4\text{He}$  system—

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We develop a theory of the surface tension for the liquid  $^3\text{He}$ - $^4\text{He}$  system basing on the cluster expansion scheme modified for the quantum system which the present author has proposed previously with K. Shimojima. We derive a general formula of the surface tension for the quantum mixtures and apply it to the dilute solution of  $^4\text{He}$  in liquid  $^3\text{He}$ .

## 1. Introduction

The theoretical calculation of the surface tension at the liquid surface from the first principles is quite a subtle problem. Although the general formulation has been given many years ago by several authors, specific applications are very few, especially for the quantum liquids.

In the present paper, we propose a method of calculation of the surface tension based on the cluster expansion scheme for the quantum system which has been given in the previous papers<sup>3)1)2)</sup>.

In our formalism, the effect of the existence of the surface is taken into consideration through the calculation of the modified cluster integral which appear in the theory. In the next section, a general formula for the surface tension of the liquid  $^3\text{He}$ - $^4\text{He}$  system is given. In the section 3, the detailed calculation for the dilute solution of  $^4\text{He}$  in the liquid  $^3\text{He}$  is described. In the appendix, the details of the statistical mechanical derivation of the Helmholtz free energy of the quantum mixture system are given together with the errata for the previous paper<sup>2)</sup>.

## 2. Surface tension

The surface tension  $\gamma$  of the liquid  $^3\text{He}$ - $^4\text{He}$  mixture system may be given by the following formula based on the thermodynamic theory.

$$\gamma A = F_{N_3 N_4}^\sigma(T, V, A) - F_{N_3 N_4}^l(T, V) \quad (2.1)$$

Here  $F_{N_3 N_4}(T, V)$  is the Helmholtz free energy of the liquid system composed of  $N_3$   $^3\text{He}$  atoms and  $N_4$   $^4\text{He}$  atoms in the volume  $V$  at the temperature  $T$  and has free surface of the area  $A$ . Hereafter we denote by the superscript  $\sigma$  the quantities concerning the system for which the effects of the existence of the surface are taken into consideration.  $F_{N_3 N_4}^l(T, V)$  is the Helmholtz free energy of the same liquid system when the effect of the surface is neglected. The superscript  $l$  is used to denote this instance.

Now we adopt the cluster expansion scheme modified for the quantum system<sup>1)3)</sup> and obtain

$$\begin{aligned} F_{N_3 N_4} &= F_{N_3} + F_{N_4} + \hat{F}_{N_3 N_4} \quad (2.2) \\ F_{N_3} &= F_{N_3}^0 - kTN_3 \sum_{k=1}^{\infty} \frac{1}{k+1} \beta_{k,0}^{(3)} \rho_3^k \\ F_{N_4} &= F_{N_4}^0 - kTN_4 \sum_{q=1}^{\infty} \frac{1}{q+1} \beta_{0,q}^{(4)} \rho_4^q \end{aligned} \quad (2.3)$$

$$\hat{F}_{N_3 N_4} = - \frac{kT}{2} N_3 \sum_{k=0}^{\infty} \sum_{q=1}^{\infty} \frac{1}{k+1} \beta_{k,q}^{(3)} \rho_3^k \rho_4^q$$

$$-\frac{kT}{2}N_4\sum_{k=1}\sum_{q=0}\frac{1}{q+1}\beta_{k,q}^{(4)}\rho_3^k\rho_4^q \quad (2.4)$$

where  $\rho_3=N_3/V$ ,  $\rho_4=N_4/V$ .

$F_{N_3}$  ( $F_{N_4}$ ) is the Helmholtz free energy of the pure  $^3\text{He}$  ( $^4\text{He}$ ) system and  $F_{N_3}^0$  is that of the corresponding ideal system. The derivation of these formulae and the definitions of the cluster integrals which appear in them are given in the appendix. Originally the scheme of the cluster expansion is constructed for the low density gas, but we can utilize it as the starting expansion for the various techniques for the case of the liquid.

Substituting these formulae for  $F_{N_3N_4}$  in (2.1), we have

$$\gamma A = \gamma_3 A + \gamma_4 A + \Delta\gamma A \quad (2.5)$$

$$\gamma_3 A = F_{N_3}^{0\sigma} - F_{N_3}^{0l} - kT \sum_{k=1} \frac{1}{k+1} \Delta\beta_{k,0}^{(3)} \rho_3^k \quad (2.6)$$

$$\gamma_4 A = F_{N_4}^{0\sigma} - F_{N_4}^{0l} - kT \sum_{q=1} \frac{1}{q+1} \Delta\beta_{0,q}^{(4)} \rho_4^q \quad (2.7)$$

$$\begin{aligned} \Delta\gamma A = & -\frac{kTN_3}{2} \sum_{k=1} \sum_{q=1} \frac{1}{k+1} \Delta\beta_{k,q}^{(3)} \rho_3^k \rho_4^q \\ & -\frac{kTN_4}{2} \sum_{k=1} \sum_{q=0} \frac{1}{q+1} \Delta\beta_{k,q}^{(4)} \rho_3^k \rho_4^q \end{aligned} \quad (2.8)$$

where abbreviations

$$\begin{aligned} \Delta\beta_{k,0}^{(3)} &= \beta_{k,0}^{(3)\sigma} - \beta_{k,0}^{(3)l}, \\ \Delta\beta_{k,q}^{(3)} &= \beta_{k,q}^{(3)\sigma} - \beta_{k,q}^{(3)l}, \text{ etc.} \end{aligned} \quad (2.9)$$

are used.

In our formalism, the effects of the existence of the surface are taken into consideration through the evaluation of the integrals  $\beta_{k,q}^{(3)\sigma}$  or  $\beta_{k,q}^{(4)\sigma}$ . The details of such calculations will be given in the next section. Here  $\gamma_3$  and  $\gamma_4$  are the surface tension of the pure liquid  $^3\text{He}$  and  $^4\text{He}$  respectively and  $\Delta\gamma$  gives the effect of mixing. The calculation of these  $\gamma_3$  or  $\gamma_4$  is itself very interesting and difficult problem. In this paper, however, we do not go into those problem. We want to show how the

effect of mixing can be described by our formulation. Basing on the general formula (2.5), we can consider various cases of  $^3\text{He}$ - $^4\text{He}$  liquid mixtures. As an example we take up the dilute solution of  $^4\text{He}$  in the liquid  $^3\text{He}$ . We have chosen this case because we can expect that the process of calculation is fairly simple. The case of the dilute solution of  $^3\text{He}$  in the superfluid  $^4\text{He}$  will be more interesting and will require more complicated reasoning as may be guessed from the experimental facts. The consideration of this case will be given in the next paper.

### 3. Surface tension of the dilute solution of $^4\text{He}$ in the liquid $^3\text{He}$ .

In this case, we can assume that the number of  $^4\text{He}$  atoms is very small compared to that of  $^3\text{He}$ , i. e.  $N_4 \ll N_3$  or  $\rho_4 \ll \rho_3$ .

Then we obtain

$$\begin{aligned} \Delta\gamma A = & -\frac{kTN_3}{2} \left( \sum_{k=0} \frac{1}{k+1} \Delta\beta_{k,1}^{(3)} \rho_3^k \right) \rho_4 \\ & -\frac{kTN_4}{2} \sum_{k=1} \Delta\beta_{k,0}^{(4)} \rho_3^k \\ & -\frac{kTN_3}{2} \left( \sum_{k=0} \frac{1}{k+1} \Delta\beta_{k,2}^{(3)} \rho_3^k \right) \rho_4^2 \\ & -\frac{kTN_4}{2} \left( \sum_{k=1} \Delta\beta_{k,1}^{(4)} \rho_3^k \right) \rho_4 + O(\rho_4^3) \end{aligned} \quad (3.1)$$

The first row terms in (3.1) comes from the interaction on one  $^4\text{He}$  atom with its surrounding  $^3\text{He}$  atom, and the second row terms gives the effects of the interaction of one pair of  $^4\text{He}$  atoms with their surrounding  $^3\text{He}$  atoms, and so forth. Here we restrict our consideration to the first order in  $\rho_4$ . Hence we have

$$\begin{aligned} \Delta\gamma A = & -\frac{kTN_3}{2} \rho_4 \sum_{k=0} \frac{1}{k+1} \Delta\beta_{k,1}^{(3)} \rho_3^k \\ & -\frac{kTN_4}{2} \sum_{k=1} \Delta\beta_{k,0}^{(4)} \rho_3^k \end{aligned} \quad (3.2)$$

The straightforward calculation of the summation in (3.2) will be almost impossible be-

cause of the liquid density of  ${}^3\text{He}$ . Here, as a tentative step, we try a very crude approximation. We retain only the first terms in the summation, but, instead, we introduce an effective interaction between  ${}^3\text{He}$  atom and  ${}^4\text{He}$  atom in the evaluation of the cluster integrals.

Now we have

$$\begin{aligned} \Delta\gamma A &= -kTV\rho_3\rho_4\Delta\beta_{0,1}^{(3)} \\ &(\beta_{1,0}^{(4)} = \beta_{0,1}^{(3)} \text{ is used}) \quad (3.3) \end{aligned}$$

From the definitions given in the appendix and in the paper [2],

$$\begin{aligned} \beta_{0,1}^{(3)} &= \tilde{b}_{1,1} = \beta_{1,0}^{(4)} \\ &= \frac{1}{V} \int d\mathbf{r}^{(3)} d\mathbf{r}^{(4)} \delta(\mathbf{r}^{(3)} - \mathbf{r}^{(4)}) \\ &\quad \int d\mathbf{r}^{(3)} d\mathbf{r}^{(4)} \delta(\mathbf{r}^{(3)} - \mathbf{r}^{(4)}) \\ &\quad (\mathbf{r}^{(3)} \mathbf{r}^{(4)} | \tilde{U}_{1,1} | \mathbf{r}^{(3)} \mathbf{r}^{(4)}) \quad (3.4) \end{aligned}$$

$$\tilde{U}_{1,1} = w_{1,1} \cdot \sigma_1^{(3)} / \rho_3 \cdot \sigma_1^{(4)} / \rho_4 \quad (3.5)$$

$$w_{1,1} = U_{1,1} = W_{1,1} - 1,$$

$$W_{1,1} = \exp(-\beta(H_1^{(3)} + H_1^{(4)} + \phi(\mathbf{r}^{(3)}, \mathbf{r}^{(4)}))) \quad (3.6)$$

$$\begin{aligned} \sigma_1(\mathbf{r}, \mathbf{r}') &= \frac{1}{V} \sum_{k,\lambda} f_k e^{ik(\mathbf{r}-\mathbf{r}')} \theta_\lambda(\xi) \theta_\lambda^*(\xi') \\ &\quad (3.7) \end{aligned}$$

where  $\phi$  is the effective interaction potential between  ${}^3\text{He}$  atom at  $\mathbf{r}^{(3)}$  and  ${}^4\text{He}$  atom at  $\mathbf{r}^{(4)}$ , and  $f_k$  is the distribution function of the quantum statistics. All the quantum effects are taken into account in our formulation in principle. Here, however, we make classical approximation, and use the form

$$V\tilde{b}_{1,1} = \int d\mathbf{r}^{(3)} d\mathbf{r}^{(4)} (e^{-\beta\phi(\mathbf{r}^{(3)}, \mathbf{r}^{(4)})} - 1) \quad (3.8)$$

Further we assume the hard-sphere interaction combined with square-well potential, that is,

$$\phi(r) = \begin{cases} +\infty & r \leq a_3 + a_4 \\ -\phi & a_3 + a_4 < r < l, \\ 0 & l < r \end{cases} \quad (3.9)$$

$$r = |\mathbf{r}^{(3)} - \mathbf{r}^{(4)}|$$

$a_3$  ( $a_4$ ) is the hard-sphere radius of  ${}^3\text{He}$  ( ${}^4\text{He}$ ) atom.  $l$  is the width of the square-well and  $\phi$  is its depth.

Here we introduce the surface region of the thickness  $\delta$  at the solvent (liquid  ${}^3\text{He}$ ) surface and in this region the depth parameter is assumed to have different value  $\phi^*$ .

With these approximations, we obtain

$$\begin{aligned} &V(\tilde{b}_{1,1}^s - \tilde{b}_{1,1}^l) \\ &= A\delta \left( \frac{4\pi}{3} (l^3 - (a_3 + a_4)^3) \right) (e^{\beta\phi^*} - e^{\beta\phi}) \quad (3.10) \end{aligned}$$

and then, we have

$$\begin{aligned} \Delta\gamma &= \delta kT\rho_3\rho_4 (e^{\beta\phi} - e^{\beta\phi^*}) v^*, \\ v^* &= \frac{4\pi}{3} (l^3 - (a_3 + a_4)^3) \quad (3.11) \end{aligned}$$

Hence we obtain

$$\begin{aligned} \gamma &= \gamma_3 + \gamma_4 + \Delta\gamma, \\ \Delta\gamma &= kT \frac{N\delta}{V} \frac{Nv^*}{V} (e^{\beta\phi} - e^{\beta\phi^*}) c_4 \\ &(N = N_3 + N_4, \quad c_4 = N_4/N) \quad (3.12) \end{aligned}$$

Here  $c_4$  is the concentration of  ${}^4\text{He}$ . At low concentrations  $\gamma_4$  can be neglected. So we have finally,

$$\begin{aligned} \gamma &= \gamma_3 + \Gamma_1 c_4, \\ \Gamma_1 &= kT (e^{\beta\phi} - e^{\beta\phi^*}) \frac{N\delta}{V} \frac{Nv^*}{V} \quad (3.13) \end{aligned}$$

This may be compared with the experimental

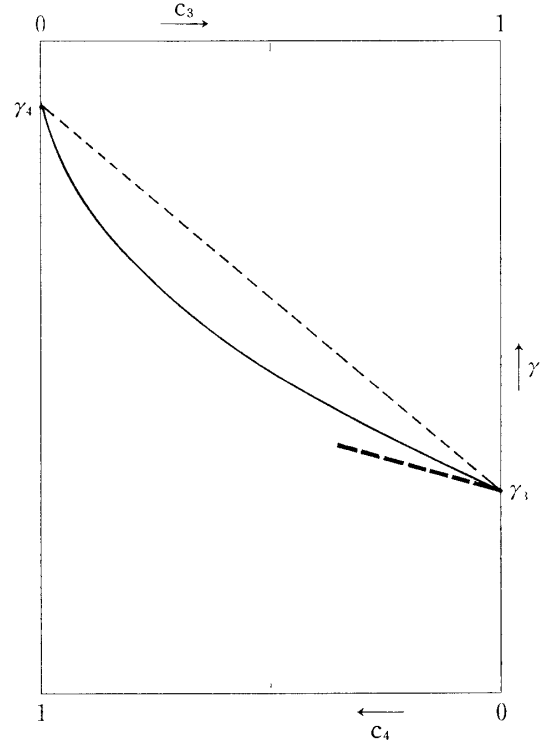


Fig. 1

results, e. g. Esel'son et al<sup>5)</sup>. But we think, our approximations are too crude to attempt such numerical comparison. Fig.1 shows schematic  $\gamma$ - $c_4$  curve (solid line) and our  $\Gamma_1$  is the gradient of this curve at  $c_4=0$ . As mentioned above, our approximations are very crude, but we can show that our  $\Gamma_1$  gives correct order of magnitude and sign under reasonable assumptions for  $\delta$ ,  $\phi$ ,  $\phi^*$ , and  $l$ . We are planning to refine our treatment in the near future.

#### Appendix. Derivation of the formula for $F_{N_3N_4}(T, V)$

We start with the following Hamiltonian as in the paper [2].

$$\begin{aligned} \mathcal{H}_{N_3N_4} &= \mathcal{H}_{N_3} + \mathcal{H}_{N_4} + \Phi_{N_3N_4}, \\ \mathcal{H}_{N_X} &= \mathcal{H}_{N_X}^0 + \Phi_{N_XN_X}, \\ \mathcal{H}_{N_X}^0 &= -\frac{\hbar^2}{2m_X} \sum_{i=1}^{N_X} \Delta_{X_i}^2, \\ \Phi_{N_XN_Y} &= \sum_{i < j} \phi_{XY}(i, j), \quad (X, Y=3, 4) \quad (\text{A.1}) \end{aligned}$$

We use similar definitions and notations as in the paper [2], but replacements such as  $N_A \rightarrow N_3$ ,  $N_B \rightarrow N_4$ , etc. are made in them. Decomposition of the partition function of our system completely similar to that given in [2]. However, there are some errors in the description in [2]. Hence we give here necessary corrections. Instead of [2]-(2.5) (This means the eq. (2.5) in the paper [2].), we should give

$$\begin{aligned} W_{N_3N_4} &= \sum_{\{m_{l,p}\}} S_3 S_4 \prod_l \prod_p \underbrace{U_{l,p} \cdots U_{l,p}}_{m_{l,p} \text{ factors}} \\ & \left( \sum_l \sum_p l m_{l,p} = N_3, \sum_l \sum_p p m_{l,p} = N_4 \right) \\ W_{0,0} &= 1 = U_{0,0} \\ W_{1,0} &= W_{0,1} = 1 = U_{1,0} = U_{0,1} \quad (\text{A.2}) \end{aligned}$$

Here  $\sum_{\{m_{l,p}\}}$  means to sum over all possible values of  $m_{l,p}$  under the conditions given in the bracket.

[2]-(2.6) should be given as

$$w_{m,n} = \sum_{\{m_{l,p}\}} S_3 S_4 \prod_l \prod_p \underbrace{U_{l,p} \cdots U_{l,p}}_{m_{l,p} \text{ factors}}$$

$$\begin{aligned} & \left( \sum_l \sum_p l m_{l,p} = m, \sum_l \sum_p p m_{l,p} = n \right) \\ & l + p \geq 2, \quad m + n \geq 2 \end{aligned}$$

$$w_{0,0} = 1, \quad w_{1,0} = w_{0,1} = 0 \quad (\text{A.3})$$

Then, [2]-(2.14) should be given as

$$\begin{aligned} \tilde{w}_{m,n} &= \sum_{\{m_{l,p}\}} S_3 S_4 \prod_l \prod_p \underbrace{\tilde{U}_{l,p} \cdots \tilde{U}_{l,p}}_{m_{l,p} \text{ factors}} \\ & \left( \sum_l \sum_p l m_{l,p} = m, \sum_l \sum_p p m_{l,p} = n, \right. \\ & \left. l + p \geq 2, \quad m + n \geq 2 \right) \quad (\text{A.4}) \end{aligned}$$

and [2]-(2.15) as

$$\begin{aligned} \tilde{W}_{N_3N_4} &= \sum_{\{m_{l,p}\}} S_3 S_4 \prod_l \prod_p \underbrace{\tilde{U}_{l,p} \cdots \tilde{U}_{l,p}}_{m_{l,p} \text{ factors}} \\ & \left( \sum_l \sum_p l m_{l,p} = N_3, \sum_l \sum_p p m_{l,p} = N_4 \right) \quad (\text{A.5}) \end{aligned}$$

Hence the decomposition goes as follows.

$$\begin{aligned} Z_{N_3N_4} &= Z_{N_3N_4}^{(0)} \cdot Y_{N_3N_4} \\ Y_{N_3N_4} &= \frac{1}{V^{N_3+N_4}} \int \left( \prod_1^{N_3} \right) \int \left( \prod_1^{N_4} \right) \tilde{W}_{N_3N_4} \\ &= \frac{N_3! N_4!}{V^{N_3+N_4}} \sum_{\{m_{l,p}\}} \frac{(V \tilde{b}_{l,p})^{m_{l,p}}}{m_{l,p}!} \\ & \left( \sum_l \sum_p l m_{l,p} = N_3, \sum_l \sum_p p m_{l,p} = N_4 \right) \quad (\text{A.6}) \end{aligned}$$

$$V! l! p! \tilde{b}_{l,p} = \int \left( \prod_1^l \right) \int \left( \prod_1^p \right) \tilde{U}_{l,p} \quad (\text{A.7})$$

This is our modified cluster integral. Using the standard technique, we have

$$\begin{aligned} Y_{N_3N_4} &= \frac{N_3! N_4!}{V^{N_3+N_4}} \frac{1}{(2\pi i)^2} \oint \oint \exp \left( \sum_l \sum_p V \tilde{b}_{l,p} x^l y^p \right) dx dy \\ &= \frac{N_3! N_4!}{V^{N_3+N_4}} \exp \left( V \sum_l \sum_p \tilde{b}_{l,p} x_0^l y_0^p - N_3 \log x_0 \right. \\ & \quad \left. - N_4 \log y_0 \right) \quad (\text{A.8}) \end{aligned}$$

where  $x_0, y_0$  are determined from

$$\begin{aligned} \sum_l \sum_p l \tilde{b}_{l,p} x_0^l y_0^p &= N_3/V = \rho_3 \\ \sum_l \sum_p p \tilde{b}_{l,p} x_0^l y_0^p &= N_4/V = \rho_4 \quad (\text{A.9}) \end{aligned}$$

and then

$$\begin{aligned} Y_{N_3N_4} &= \exp \left( V \sum_l \sum_p \tilde{b}_{l,p} x_0^l y_0^p - N_3 \log x_0 / \rho_3 \right. \\ & \quad \left. - N_3 - N_4 \log y_0 / \rho_4 - N_4 \right) \quad (\text{A.10}) \end{aligned}$$

Here we have used  $\log N! = N \log N - N$ .  $x_0$  and  $y_0$  correspond to the chemical potentials as may be seen from [2]-(4.1) and [2]-(4.2).

Inversion of these formula with the definition of  $\beta_{k,q}^{(3)}$ ,  $\beta_{k,q}^{(4)}$  goes completely same way as in the paper [2]

The term

$$S(x_0, y_0) = \sum_l \sum_p \tilde{b}_{l,p} x_0^l y_0^p \quad (\text{A. 11})$$

can be transformed into the series in  $\rho_3$  and  $\rho_4$  with the use of the relations  $x_0 \partial S / \partial x_0 = \rho_3$  and  $y_0 \partial S / \partial y_0 = \rho_4$ .

Using the standard technique we have

$$\begin{aligned} S &= \rho_3 - \sum_{k=1} \frac{k}{k+1} \beta_{k,0}^{(3)} \rho_3^{k+1} \\ &+ \rho_4 - \sum_{q=1} \frac{q}{q+1} \beta_{0,q}^{(4)} \rho_4^{q+1} \\ &- \sum_{k=0} \sum_{q=1} \beta_{k,q}^{(3)} \rho_3^{k+1} \rho_4^q \\ &- \sum_{k=1} \sum_{q=1} \frac{q}{q+1} \beta_{k,q}^{(4)} \rho_3^k \rho_4^{q+1} \\ &= \quad // \\ &+ \quad // \\ &- \sum_{k=1} \sum_{q=0} \beta_{k,q}^{(4)} \rho_3^k \rho_4^{q+1} \\ &- \sum \sum \frac{k}{k+1} \beta_{k,q}^{(3)} \rho_3^{k+1} \rho_4^q \quad (\text{A. 12}) \end{aligned}$$

The equivalence of the above two expressions is guaranteed by the relations between  $\beta_{k,q}^{(3)}$  and  $\beta_{k,q}^{(4)}$  which can be obtained successively. Hence we can use the symmetrized expression for  $S$  in  $\rho_3$  and  $\rho_4$ . Substituting these forms

into (A.10) we obtain finally

$$\begin{aligned} Z_{N_3 N_4} &= Z_{N_3 N_4}^{(0)} Y_{N_3 N_4} \\ Y_{N_3 N_4} &= \exp(I_{N_3 N_4}) \quad (\text{A. 13}) \\ I_{N_3 N_4} &= N_3 \sum_{k=1} \frac{1}{k+1} \beta_{k,0}^{(3)} \rho_3^k \\ &+ N_4 \sum_{q=1} \frac{1}{q+1} \beta_{0,q}^{(4)} \rho_4^q \\ &+ \frac{1}{2} N^3 \sum_{k=0} \sum_{q=1} \frac{1}{k+1} \beta_{k,q}^{(3)} \rho_3^k \rho_4^q \\ &+ \frac{1}{2} N_4 \sum_{k=1} \sum_{q=1} \frac{1}{q+1} \beta_{k,q}^{(4)} \rho_3^k \rho_4^q \end{aligned}$$

Then the Helmholtz free energy  $F_{N_3 N_4}$  is given by

$$\begin{aligned} F_{N_3 N_4} &= -kT \log Z_{N_3 N_4} = F_{N_3}^0 + F_{N_4}^0 - kT I_{N_3 N_4} \\ &- kT \log Z_{N_3 N_4}^{(0)} = F_{N_3}^0 + F_{N_4}^0 \quad (\text{A. 14}) \end{aligned}$$

Here  $F_{N_3}^0$ ,  $F_{N_4}^0$  are of the pure systems. Thus we have reached (2.2).

### References

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