

THE PARTITION SUM OF SUBSTITUTIONAL BINARY ALLOYS WITHIN THE COLLECTIVE VARIABLES METHOD. ρ^4 APPROXIMATION

YU. KHOKHLOV, Z.O. GURSKII

*Institute for Condensed Matter Physics,
the Ukrainian National Academy of Sciences,
1 Svientsitsky St., UA-290011 Lviv, Ukraine*

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The phase transition theory developed by I. Yukhnovskii within the collective variables method is applied to the binary alloys. The features of the binary alloy problem in comparison with the Ising model are discussed and analyzed. The Jacobian of the transition from the site variables of the occupation number to the collective variables space is calculated. The explicit expression for the partition sum of the substitutional binary alloy is obtained.

1. Introduction

Calculation of the alloy free energy $F(T, c)$ belongs to the important problems of the modern condensed matter physics. Knowledge of $F(T, c)$ as a function of temperature T and alloy concentration c allows one to predict an alloy behaviour under changing external parameters and construct the phase diagram (diagram of state) [1].

Two ways to determine $F(T, c)$ exist in the microscopic theory.

1. The "pure structural" way

$$F(T, c) = E - TS \quad (1.1)$$

means that the alloy internal energy E and the entropy S are calculated separately and usually within different methods and approximations [2].

2. The *ab initio* calculation proceeds from the alloy partition sum Z

$$F = -k_B T \ln Z, \quad (1.2)$$

where k_B is the Boltzmann constant. Details about the approach 2 see in [3]. Another approach based on computer simulation methods becomes commonly used in the present alloy theory [4].

Analytical theory of the alloy thermodynamic properties proceeds from the various modifications of the mean field theory [1,2,5]. The static concentration waves method [5] is one of the most commonly used among such modifications.

An adequate description of the alloy thermodynamic properties near the phase transition temperature is necessary to construct the real phase

diagram. The mean field approximation is not sufficient for this purpose [3]. The last statement can be easily illustrated by analysis of the formula for the order-disorder phase transition temperature, obtained within the random phase approximation [3,5]

$$T_0 = -\frac{1}{k_B} V_2(\mathbf{k}^*) c_A c_B. \quad (1.3)$$

Here $V_2(\mathbf{k}^*)$ is a value of the ordering potential Fourier transform at the points \mathbf{k}^* of the absolute minimum, $c_i (i = A, B)$ is a concentration of i -kind atoms. The explicit expression for $V_2(\mathbf{k})$ is given in [3].

The order-disorder phase diagram should have extremum and be symmetric with reference to the point $c_A = c_B = 0.5$ accordingly to the Eq.(1.3), but such a situation does not often occur in real alloys [6]. Besides, the Eq.(1.3) does not describe adequately the phase diagram of dilute alloys: $c_B \ll 1, c_A \rightarrow 1$.

The order-disorder phase transition temperature obtained from the Eq.(1.3) in the case of polyvalent metal alloys exceeds essentially the experimental data [7]. Rather common opinion exists that a poor agreement between theoretically predicted value of T_0 ($T_0^{(theor)}$) and the experimental one ($T_0^{(exp)}$) is mainly caused by accuracy of determination of $V_2(\mathbf{k}^*)$ in the frames of pseudopotential method. But various modifications of $V_2(\mathbf{k}^*)$ calculation procedure did not improve essentially agreement between $T_0^{(theor)}$ and $T_0^{(exp)}$ [7].

In our opinion solution of this problem should be under way on the following items.

1. Application of the phase transition theory which is beyond the mean field approximation.
2. Account of the atomic thermal vibrations and local static displacements that renormalizing the ordering potential $V_2(\mathbf{k}^*)$ [8,9].

The present paper is dedicated to the development of the item 1. It is organized in the following way. The main ideas of the collective variables (CV) method [10], used for this purpose, are given in the section 2. The alloy partition sum calculation within the so-called " ρ^4 approximation" of the CV method is presented in the section 3.

2. The alloy partition sum. Problem statement and Jacobian of the transition to collective variables.

Let us consider a substitutional binary alloy. The atom sites are given by the vectors \mathbf{R} . There are N_i atoms of the i -kind ($i = A, B$) in the alloy with condition $N_A + N_B = N$. The distribution of two kinds of atoms over the lattice sites is given by the set of occupation numbers $\sigma_{\mathbf{R}}$

$$\sigma_{\mathbf{R}} = \begin{cases} +1 & \text{if the site } \mathbf{R} \text{ is occupied by an atom of kind } A \\ -1 & \text{otherwise} \end{cases}$$

According to [3] the partition sum of such an alloy in the interatomic pair potential approximation may be written as follows

$$Z = \exp(-N\beta V_0) Tr_{\{\sigma_{\mathbf{R}}\}} \exp \left\{ -\beta \left[\sum_{\mathbf{R}} V_1(\mathbf{R}) \sigma_{\mathbf{R}} \right. \right.$$

$$+ \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} V_2(\mathbf{R}, \mathbf{R}') \sigma_{\mathbf{R}} \sigma_{\mathbf{R}'} \left. \right] - \beta \sum_{i=A,B} \mu_i N_i \left. \right\}. \quad (2.1)$$

Here V_0 is the configuration independent part of the alloy energy, $V_1(\mathbf{R})$ characterizes the distinction in the atomic properties of the two kinds of atoms, $V_2(\mathbf{R}, \mathbf{R}')$ is the ordering potential (for the explicit expressions for V_0 , V_1 and V_2 see [3,11]), $\beta = 1/(k_B T)$ is the inverse temperature, μ_i the chemical potential of a metal of kind i . Symbol $Tr_{\{\sigma_{\mathbf{R}}\}}$ denotes that the trace in (2.1) is taken over the eigenvalues of all $\sigma_{\mathbf{R}}$.

Passing to the Fourier transforms $\hat{\rho}_{\mathbf{k}}$ of the occupation numbers $\sigma_{\mathbf{R}}$ one gets for (2.1):

$$Z = \exp(-N\beta V_0) Tr_{\{\sigma_{\mathbf{R}}\}} \times \exp \left\{ -\beta \left[\sqrt{N} V_1 \hat{\rho}_0 + \frac{1}{2} \sum_{\mathbf{k} \in BZ} V_2(\mathbf{k}) \hat{\rho}_{\mathbf{k}} \hat{\rho}_{-\mathbf{k}} \right] - \beta \sum_{i=A,B} \mu_i N_i \right\}, \quad (2.2)$$

$$\hat{\rho}_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sigma_{\mathbf{R}} \exp(-i\mathbf{k}\mathbf{R}). \quad (2.3)$$

Vector \mathbf{k} in (2.2) lies inside the first Brillouin zone (BZ). We shall use the CV method [10] for the calculation of Z . According to the CV method [3,11],

$$Z = \exp(-N\beta V_0) \int \dots \int \exp \left\{ -\beta \left[\sqrt{N} V_1 \rho_0 + \frac{1}{2} \sum_{\mathbf{k} \in BZ} V_2(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right] \right\} J(\rho) \prod_{\mathbf{k} \in BZ} d\rho_{\mathbf{k}}, \quad (2.4)$$

where

$$J(\rho) = Tr_{\{\sigma_{\mathbf{R}}\}} \prod_{\mathbf{k} \in BZ} \delta \left(\rho_{\mathbf{k}} - \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sigma_{\mathbf{R}} \exp(-i\mathbf{k}\mathbf{R}) \right) \times \exp \left[-\beta \left(\mu_A \sum_{\mathbf{R}} \frac{1 + \sigma_{\mathbf{R}}}{2} + \mu_B \sum_{\mathbf{R}} \frac{1 - \sigma_{\mathbf{R}}}{2} \right) \right] \quad (2.5)$$

is the Jacobian of transition from the set of variables $\sigma_{\mathbf{R}}$ to the CV $\rho_{\mathbf{k}}$ space (see for details refs [3,10,11]). The terms containing chemical potentials in $J(\rho)$ (2.5) take into account that there are

$$N_A = \sum_{\mathbf{R}} \frac{1 + \sigma_{\mathbf{R}}}{2}, \quad N_B = \sum_{\mathbf{R}} \frac{1 - \sigma_{\mathbf{R}}}{2}$$

atoms of two kinds in the binary alloy. Presence of the chemical potentials in the Eq. (2.5) permits one to perform the trace operation for certain configuration at each site independently [3].

It is seen from the Eq. (2.5) that only the values of CV $\rho_{\mathbf{k}}$ equal to the occupation number $\sigma_{\mathbf{R}}$ Fourier components $\hat{\rho}_{\mathbf{k}}$ (2.3) will contribute to the transition Jacobian $J(\rho)$.

Using the integral representation for the δ -functions $\delta(\rho_{\mathbf{k}} - \hat{\rho}_{\mathbf{k}})$, one can rewrite the transition Jacobian $J(\rho)$ in cummulant form [3,11]

$$J(\rho) = \int \dots \int \exp \left(2\pi i \sum_{\mathbf{k} \in BZ} \omega_{\mathbf{k}} \rho_{\mathbf{k}} \right) \exp \left[\sum_{n=0}^{\infty} D_n(\omega) \right] \prod_{\mathbf{k} \in BZ} d\omega_{\mathbf{k}}, \quad (2.6)$$

where

$$D_n(\omega) = \left(\frac{2\pi i}{\sqrt{N}} \right)^n \frac{1}{n!} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_n \in BZ} M_n(\mathbf{k}_1 \dots \mathbf{k}_n) \omega_{\mathbf{k}_1} \dots \omega_{\mathbf{k}_n}, \quad (2.7)$$

$$M_n(\mathbf{k}_1 \dots \mathbf{k}_n) = M_n \sum_{\mathbf{R}} \exp [i(\mathbf{k}_1 + \dots + \mathbf{k}_n) \mathbf{R}], \quad (2.8)$$

$$M_n = \frac{\partial^n}{\partial q^n} \ln [\exp(\beta\mu_B - q) + \exp(\beta\mu_A + q)] |_{q=0}. \quad (2.9)$$

The vector \mathbf{k} in (2.5) - (2.7) takes on all values in the first BZ . The cummulants M_n (2.9) are complex functions of the alloy component chemical potentials and temperature [3,11]. Let us put down the first cummulants which will be required in the following

$$M_0 = \ln \sum_{i=A,B} \exp(\beta\mu_i) = \ln D_0, \quad (2.10a)$$

$$M_1 = \frac{\exp(\beta\mu_A) - \exp(\beta\mu_B)}{D_0}, \quad (2.10b)$$

$$M_2 = \frac{4 \exp(\beta\mu_A) \exp(\beta\mu_B)}{D_0^2}, \quad (2.10c)$$

$$M_3 = -2M_1M_2, \quad M_4 = 2M_2(2M_1^2 - M_2). \quad (2.10d)$$

To separate the integration variables $\omega_{\mathbf{k}}$ in the Eq. (2.6) for the Jacobian let us introduce new variables $\omega_{\mathbf{R}}$ and $\rho_{\mathbf{R}}$ connected with $\omega_{\mathbf{k}}$ and $\rho_{\mathbf{k}}$ by the relations

$$\omega_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in BZ} \omega_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}), \quad (2.11a)$$

$$\rho_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in BZ} \rho_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}). \quad (2.11b)$$

Then (see [10] for details):

$$J(\rho) = \exp(NM_0) \prod_{\mathbf{R}} J_{\mathbf{R}}(\rho), \quad (2.12)$$

where

$$J_{\mathbf{R}}(\rho) = \int_{-\infty}^{\infty} d\omega_{\mathbf{R}} \exp \left(2\pi i \omega_{\mathbf{R}} \rho_{\mathbf{R}} + 2\pi i M_1 \omega_{\mathbf{R}} + \frac{(2\pi i)^2}{2!} M_2 \omega_{\mathbf{R}}^2 \right)$$

$$+ \frac{(2\pi i)^3}{3!} M_3 \omega_{\mathbf{R}}^3 + \frac{(2\pi i)^4}{4!} M_4 \omega_{\mathbf{R}}^4 + \dots \Big). \quad (2.13)$$

The function $J(\rho)$ (2.12) can be represented as exponential infinite series [3,11]

$$\begin{aligned} J(\rho) = \exp(NM_0)Q^N \prod_{\mathbf{R}} \exp \left(-a_1 \rho_{\mathbf{R}} - \frac{a_2}{2!} \rho_{\mathbf{R}}^2 - \frac{a_3}{3!} \rho_{\mathbf{R}}^3 \right. \\ \left. - \frac{a_4}{4!} \rho_{\mathbf{R}}^4 - \dots \right) \equiv \exp(NM_0)Q^N \exp \left[-a_1 \sqrt{N} \rho_0 - \frac{a_2}{2!} \sum_{\mathbf{k} \in BZ} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right. \\ \left. - \frac{a_3}{3! \sqrt{N}} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \right. \\ \left. - \frac{a_4}{4! N} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) - \dots \right] \quad (2.14) \end{aligned}$$

with $\delta(\mathbf{k}_1 + \dots + \mathbf{k}_i)$ the Kronecker symbols. The following notations are accepted in (2.14):

$$\begin{aligned} Q = \int_{-\infty}^{\infty} \exp \left[2\pi i M_1 \omega_{\mathbf{R}} + \frac{(2\pi i)^2}{2!} M_2 \omega_{\mathbf{R}}^2 \right. \\ \left. + \frac{(2\pi i)^3}{3!} M_3 \omega_{\mathbf{R}}^3 + \dots \right] d\omega_{\mathbf{R}}, \quad (2.15) \end{aligned}$$

$$a_1 = -\frac{\partial \ln Q}{\partial M_1}, \quad a_2 = a_1^2 - 2! \frac{\partial \ln Q}{\partial M_2}, \quad (2.16)$$

$$a_3 = 3a_1 a_2 - a_1^3 - 3! \frac{\partial \ln Q}{\partial M_3}, \quad (2.17)$$

$$a_4 = a_1^4 - 6a_1^2 a_2 + 4a_1 a_3 + 3a_2^2 - 4! \frac{\partial \ln Q}{\partial M_4}. \quad (2.18)$$

Let us write down the useful relation

$$n! \frac{\partial \ln Q}{\partial M_n} = \frac{1}{Q} \frac{\partial^n Q}{\partial M_1^n}. \quad (2.19)$$

The quantities $a_i (i = 1, 2, \dots)$ are the coefficients of the transition Jacobian. As follows from (2.15) - (2.19) a_i are complex functions of the chemical potentials and temperature.

It is seen from Eqs. (2.4) and (2.14), (2.15) that neither the partition sum nor the transition Jacobian can be integrated exactly. Then the problem to restrict oneself with the "proper measure density" (proper coefficient a_n in (2.14)) arises in the CV method [10]. For the alloy case it means to choose such a measure density in Eqs. (2.14) and (2.15) which could permit to describe the alloy thermodynamic properties adequately in a wide temperature region.

It has been shown in [3,11] that the Gaussian measure density is right at high temperatures. Putting according to this approximation $M_3 = M_4 = \dots = 0$ in (2.15) one may obtain that [3,11]

$$Q^G = \frac{1}{\sqrt{2\pi M_2}} \exp\left(\frac{-M_1^2}{2M_2}\right), a_1^G = \frac{M_1}{M_2}, a_2^G = \frac{1}{M_2}, a_3^G = a_4^G = \dots = 0 \quad (2.20)$$

and

$$Z^G = (Q^G)^N \exp(NM_0) \exp(-N\beta V_0) \int \dots \int \exp\left[-(a_1^G + \beta V_1)\sqrt{N}\rho_0 - \frac{1}{2} \sum_{\mathbf{k} \in BZ} (a_2^G + \beta V_2(\mathbf{k})) \rho_{\mathbf{k}} \rho_{-\mathbf{k}}\right] \prod_{\mathbf{k} \in BZ} d\rho_{\mathbf{k}}. \quad (2.21)$$

It is seen from (2.21) that the Fourier components $\rho_{\mathbf{k}}$ (2.3) are assumed to be independent in the Gaussian approximation. Thus this approach is equivalent to the random phases approximation [10].

Integration over $\rho_{\mathbf{k}}$ in (2.21) has a sense if

$$d_2^G = a_2^G + \beta V_2(\mathbf{k}) > 0 \quad (2.22)$$

for all vectors \mathbf{k} in the first BZ. For polyvalent metal alloys the inequality (2.22) does not take place in some parts of BZ even at temperatures above liquidus. It means that the Gaussian measure density fails and one must take into account the coefficients a_3 and a_4 in the transition Jacobian (2.14) to determine the behaviour of the alloy thermodynamic properties near T_0 adequately [3,11]. Then one obtains the correct values for critical indexes and a finite function for the free energy at $T = T_0$ [3]. But the theoretical results, presented in [3] are too complicated for numerical realization. Therefore a different approach within the same measure density of ρ^4 but simpler for calculations is developed in the present paper.

Let us put in Eq. (2.15) $M_5 = M_6 = \dots = 0$ within the ρ^4 measure density. Then the problem of calculation of the following expression arises:

$$Q^{(4)} = \int_{-\infty}^{\infty} \exp\left[\sum_{n=1}^4 \frac{(2\pi i)^n}{n!} M_n \omega_{\mathbf{R}}^n\right] d\omega_{\mathbf{R}}. \quad (2.23)$$

Let us introduce a new variable $\tilde{\omega}$ to remove the cubic term ($\sim M_3 \omega_{\mathbf{R}}^3$) of the sum in (2.23). The $Q^{(4)}$ becomes of the form

$$Q^{(4)} = Q_0^{(4)} \int_{-\infty}^{\infty} \exp\left[2\pi i \tilde{M}_1 \tilde{\omega} + \frac{(2\pi i)^2}{2!} \tilde{M}_2 \tilde{\omega}^2 - \frac{(2\pi i)^4}{4!} \tilde{M}_4 \tilde{\omega}^4\right] d\tilde{\omega}, \quad (2.24)$$

where

$$Q_0^{(4)} = \exp\left[\frac{M_1 M_3}{\tilde{M}_4} + \frac{1}{2} \frac{M_2 M_3^2}{\tilde{M}_4^2} + \frac{1}{8} \frac{M_3^4}{\tilde{M}_4^3}\right], \quad (2.25)$$

$$\tilde{M}_1 = M_1 + \frac{M_2 M_3}{\tilde{M}_4} + \frac{1}{3} \frac{M_3^3}{\tilde{M}_4^2}, \quad (2.26)$$

$$\tilde{M}_2 = M_2 + \frac{1}{2} \frac{M_3^2}{M_4}, \quad (2.27)$$

$$\tilde{M}_4 = |M_4|. \quad (2.28)$$

The integrals (2.23) and (2.24) exist if

$$M_4 < 0. \quad (2.29)$$

Condition (2.29) determines the relationship between chemical potentials of alloy components within the CV method approximation of ρ^4 , see (2.10).

Expanding $\exp[2\pi i \tilde{M}_1 \tilde{\omega}]$ into a series in Eq.(2.24) and taking into account that

$$\int_{-\infty}^{\infty} \tilde{\omega}^{2n+1} \exp[-\alpha \tilde{\omega}^2 - \gamma \tilde{\omega}^4] d\tilde{\omega} \equiv 0 \quad (2.30)$$

one can get the following result for $Q^{(4)}$

$$Q^{(4)} = Q_0^{(4)} \frac{1}{2\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\tilde{M}_1^{2n}}{(2n)!} \Gamma\left(n + \frac{1}{2}\right) \left[\frac{6}{\tilde{M}_4}\right]^{\left(\frac{n}{2} + \frac{1}{4}\right)} \times \Psi\left[\frac{n}{2} + \frac{1}{4}, \frac{1}{2}, \frac{3}{2} \frac{\tilde{M}_2^2}{\tilde{M}_4}\right]. \quad (2.31)$$

Here $\Gamma(m)$ is the Euler gamma function and $\Psi(a, b, z)$ is the confluent hypergeometric function. The properties of these functions are given in detail in [12]. Function $\Psi(a, b, z)$ has the form [12]

$$\Psi(a, b, z) = \frac{\pi}{\sin \pi b} \left\{ \frac{{}_1F_1(a, b, z)}{\Gamma(1+a-b)\Gamma(b)} - z^{1-b} \frac{{}_1F_1(1+a-b, 2-b, z)}{\Gamma(a)\Gamma(2-b)} \right\} \quad (2.32)$$

with the Kummer function ${}_1F_1(a, b, z)$ [12]

$${}_1F_1(a, b, z) = \sum_{m=0}^{\infty} \frac{(a)_m z^m}{(b)_m m!}, \quad (b)_m = b(b+1)(b+2)\dots(b+m-1). \quad (2.33)$$

To find the coefficients of the transition Jacobian is necessary to know derivatives $\partial^n Q^{(4)} / \partial M_1^n$, see (2.15)-(2.19).

Taking into account that just only $Q^{(4)}$ (2.25) and \tilde{M}_1 (2.26) depend on M_1 one gets the following result

$$\frac{\partial^n Q^{(4)}}{\partial M_1^n} = \sum_{i=0}^n C_i^n \left(\frac{M_3}{M_4}\right)^{n-i} W(i) \quad (2.34)$$

where C_i^n being binomial coefficients and

$$W(2j) = Q^{(4)} \frac{1}{2\pi} \sum_{m=0}^{\infty} (-1)^{m+j} \frac{\tilde{M}_1^{2m}}{(2m)!} \Gamma\left(m+j+\frac{1}{2}\right) \times \left[\sqrt{\frac{6}{\tilde{M}_4}} \right]^{m+j+\frac{1}{2}} \Psi \left[\frac{1}{2} \left(m+j+\frac{1}{2} \right), \frac{1}{2}, \frac{3}{2} \frac{\tilde{M}_2^2}{\tilde{M}_4} \right], \quad (2.35)$$

$$W(2j+1) = Q^{(4)} \frac{1}{2\pi} \sum_{m=1}^{\infty} (-1)^{m+j} \frac{\tilde{M}_1^{2m-1}}{(2m-1)!} \Gamma\left(m+j+\frac{1}{2}\right) \times \left[\sqrt{\frac{6}{\tilde{M}_4}} \right]^{m+j+\frac{1}{2}} \Psi \left[\frac{1}{2} \left(m+j+\frac{1}{2} \right), \frac{1}{2}, \frac{3}{2} \frac{\tilde{M}_2^2}{\tilde{M}_4} \right]. \quad (2.36)$$

Here j in Eqs. (2.35), (2.36) is integer and $W(0) = Q^{(4)}$. In view of Eqs. (2.15)-(2.19) and (2.34) the coefficients of the transition Jacobian take the form:

$$a_1 = -\frac{1}{Q^{(4)}} \sum_{i=0}^1 C_i^1 \left(\frac{M_3}{\tilde{M}_4} \right)^{1-i} W(i), \quad (2.37)$$

$$a_2 = a_1^2 - \frac{1}{Q^{(4)}} \sum_{i=0}^2 C_i^2 \left(\frac{M_3}{\tilde{M}_4} \right)^{2-i} W(i), \quad (2.38)$$

$$a_3 = 3a_1 a_2 - a_1^3 - \frac{1}{Q^{(4)}} \sum_{i=0}^3 C_i^3 \left(\frac{M_3}{\tilde{M}_4} \right)^{3-i} W(i), \quad (2.39)$$

$$a_4 = a_1^4 - 6a_1^2 a_2 + 4a_1 a_3 + 3a_2^2 - \frac{1}{Q^{(4)}} \sum_{i=0}^4 C_i^4 \left(\frac{M_3}{\tilde{M}_4} \right)^{4-i} W(i). \quad (2.40)$$

If $\exp(\beta\mu_A) = \exp(\beta\mu_B)$, then

$$M_1 = M_3 = 0, \quad M_2 = 1, \quad \tilde{M}_4 = |M_4| = 2$$

(see (2.10)) and the results for the Ising model [10] follow from Eqs. (2.31) and (2.37)-(2.40)

$$Q_I^{(4)} = \frac{1}{2\pi} \Gamma\left(\frac{1}{2}\right) \sqrt[4]{3} \Psi \left[\frac{1}{4}, \frac{1}{2}, \frac{3}{4} \right] = \frac{1}{2\pi} \sqrt[4]{12} \left(\frac{3}{8}\right)^{1/4} \exp(3/8) K_{\frac{1}{4}} \left(\frac{3}{8}\right), \quad (2.41)$$

$$a_1 = a_3 = 0,$$

$$a_2 = \frac{1}{2\pi} \Gamma\left(\frac{3}{2}\right) \sqrt[4]{27} \Psi \left[\frac{3}{4}, \frac{1}{2}, \frac{3}{4} \right] = \frac{1}{4\sqrt{\pi}} 6^{3/4} \exp(3/8) U \left(1, \sqrt{\frac{3}{2}} \right), \quad (2.42)$$

$$a_4 = 3a_2^2 - \frac{1}{2\pi} \Gamma\left(\frac{5}{2}\right) 3\sqrt[4]{3} \Psi \left[\frac{5}{4}, \frac{1}{2}, \frac{3}{4} \right] = \frac{3}{8\sqrt{\pi}} 6^{5/4} \exp(3/8) \times \left\{ \frac{1}{\sqrt{\pi} 2} \sqrt[4]{6} \exp(3/8) U^2 \left(1, \sqrt{\frac{3}{2}} \right) - U \left(2, \sqrt{\frac{3}{2}} \right) \right\}. \quad (2.43)$$

The following notations are accepted in (2.41)-(2.43): $K_\nu(z)$ is the modified Bessel function and $U(a, x)$ is the function of parabolic cylinder. The following relations have been used to obtain (2.41)-(2.43):

$$\begin{aligned} \Psi \left[\nu + \frac{1}{2}, 2\nu + 1, 2z \right] &= \frac{1}{\sqrt{\pi}} \exp(z) \frac{1}{(2z)^\nu} K_\nu(z), \\ K_\nu(z) &= K_{-\nu}(z), \\ U(a, x) &= 2^{-1/4-a/2} \exp\left(-\frac{x^2}{4}\right) \Psi \left[\frac{a}{2} + \frac{1}{4}, \frac{1}{2}, \frac{x^2}{2} \right], \\ \Psi \left[\frac{a}{2} + \frac{1}{4}, \frac{1}{2}, \frac{x^2}{2} \right] &= \frac{\sqrt{\pi}}{\sin \pi b} \left\{ \frac{{}_1F_1(a/2 + 1/4, 1/2, x^2/2)}{\Gamma(a/2 + 3/4)} \right. \\ &\quad \left. - \sqrt{2} x \frac{{}_1F_1(a/2 + 3/4, 3/2, x^2/2)}{\Gamma(a/2 + 1/4)} \right\}. \end{aligned}$$

The results (2.41)-(2.43) indicate that the more general than in [3,10] approach to transition Jacobian calculation, developed in the present paper, is correct.

3. Calculation of the alloy partition sum by the CV method within ρ^4 approximation.

According to ρ^4 approximation one should put the coefficients $a_5 = a_6 = \dots = 0$ in the Eq.(2.14) defining the Jacobian of the transition to the CV. The partition sum has the form, see Eqs. (2.4) and (2.14)

$$\begin{aligned} Z^{(4)} &= \exp(NM_0) \exp(-N\beta V_0) [Q^{(4)}]^N \int \dots \int \exp\{-(a_1 + \beta V_1) \sqrt{N} \rho_0 \\ &\quad - \frac{1}{2} \sum_{\mathbf{k} \in BZ} (a_2 + \beta V_2(\mathbf{k})) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - \frac{a_3}{3! \sqrt{N}} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \\ &\quad - \frac{a_4}{4! N} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4)\} \prod_{\mathbf{k} \in BZ} d\rho_{\mathbf{k}}. \end{aligned} \quad (3.1)$$

The variable ρ_0 is related to the macroscopic quantity. Really [3]:

$$\langle \rho_0 \rangle = \sqrt{N} (c_A - c_B), \quad (3.2)$$

where $\langle \rho_0 \rangle$ is the Fourier component of the one-particle distribution function $\langle \sigma_{\mathbf{R}} \rangle$ at $\mathbf{k} = 0$. Let us introduce a new variable ρ'_0 to separate the macroscopic part

$$\rho_0 = \langle \rho_0 \rangle + \rho'_0. \quad (3.3)$$

Substituting (3.4) into (3.1) one obtains for the partition sum:

$$Z^{(4)} = \bar{Z} \int \dots \int \exp \left\{ -\sqrt{N} h \rho'_0 - \frac{1}{2} \sum_{\mathbf{k} \in BZ} d(\mathbf{k}) \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right.$$

$$\left. \begin{aligned} & -\frac{\tilde{a}_3}{3!\sqrt{N}} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \\ & -\frac{\tilde{a}_4}{4!N} \sum_{\mathbf{k}_i \in BZ} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \end{aligned} \right\} \prod_{\mathbf{k} \in BZ} d\rho_{\mathbf{k}}, \quad (3.4)$$

where

$$\begin{aligned} \bar{Z} = \exp(NM_0) \exp(-N\beta V_0) & \left[Q^{(4)} \right]^N \exp\{-N[(a_1 + \beta V_1) c_{12} \\ & + \frac{1}{2!}(a_2 + \beta V_2(0))c_{12}^2 + \frac{1}{3!}a_3 c_{12}^3 + \frac{1}{4!}a_4 c_{12}^4]\}, \\ h = \tilde{a}_1 + \beta V_1, \quad d(\mathbf{k}) = \tilde{a}_2 + \beta V_2(\mathbf{k}), \quad c_{12} = c_A - c_B, \end{aligned} \quad (3.5)$$

$$\begin{aligned} \tilde{a}_1 &= a_1 + (a_2 + \beta V_2(0)) c_{12} + \frac{1}{2!} a_3 c_{12}^2 + \frac{a_4}{3!} a_4 c_{12}^3, \\ \tilde{a}_2 &= a_2 + a_3 c_{12} + \frac{1}{2} a_4 c_{12}^2, \\ \tilde{a}_3 &= a_3 + a_4 c_{12}, \quad \tilde{a}_4 = a_4. \end{aligned} \quad (3.6)$$

\bar{Z} in (3.5) is a partition sum of a "mean alloy". It can be treated as the partition function of a reference system. The random ideal alloy is such a system. The coefficients a_2 and a_4 of the transition Jacobian are positive [3]. One can choose alloy components A and B in such a way that $c_{12} = c_A - c_B > 0$, providing the positive values for \tilde{a}_2 .

Suppose that the absolute minimum of potential $V_2(\mathbf{k})$ is at points \mathbf{k}^* which form the star $\{\mathbf{k}^*\}$. Consider such a temperature that the mean value of function $d(\mathbf{k})$ over the whole BZ with the vectors of the star $\{\mathbf{k}^*\}$ excluded, is equal to a positive constant that is

$$\overline{d(\mathbf{k})} = \tilde{a}_2 + \beta \overline{V_2(\mathbf{k})} = const > 0. \quad (3.7)$$

Let us replace function $d(\mathbf{k})$ by its mean value $\overline{d(\mathbf{k})}$ (3.7) in this part of the BZ and integrate over variables $\rho_{\mathbf{k}}$ ($\mathbf{k} \notin \{\mathbf{k}^*\}$) by the method, developed in [10]. Substitution of the mean value $\overline{V_2(\mathbf{k})}$ instead of the real potential $V_2(\mathbf{k})$ is an approximation the applicability of which is discussed in [10]. Nevertheless it will allow one to separate the integration variables in Eq.(3.4).

Introducing a new notation for the variables $\rho_{\mathbf{k}}$ over which the integration is performed

$$\rho_{\mathbf{k}} \equiv \eta_{\mathbf{k}} \quad \text{for} \quad \mathbf{k} \notin \{\mathbf{k}^*\}.$$

One can reduce partition function to the form [3,10]

$$\begin{aligned} Z = \bar{Z} \int \dots \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}=\mathbf{k}^*} [d(\mathbf{k}) - \overline{d(\mathbf{k})}] \rho_{\mathbf{k}} \rho_{-\mathbf{k}} - 2\pi i \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \rho_{\mathbf{k}} \right\} \\ \times J(\nu) \prod_{\mathbf{k}=\mathbf{k}^*} d\nu_{\mathbf{k}} \prod_{\mathbf{k}=\mathbf{k}^*} d\rho_{\mathbf{k}}, \end{aligned} \quad (3.8)$$

with

$$\begin{aligned}
 J(\nu) = \int \dots \int \exp \left\{ 2\pi i \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \eta_{\mathbf{k}} - h\sqrt{N} \eta_0 - \frac{1}{2} \overline{d(\mathbf{k})} \sum_{\mathbf{k} \in BZ} \eta_{\mathbf{k}} \eta_{-\mathbf{k}} \right. \\
 \left. - \frac{\tilde{a}_3}{3! \sqrt{N}} \sum_{\mathbf{k}_i \in BZ} \eta_{\mathbf{k}_1} \dots \eta_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \right. \\
 \left. - \frac{\tilde{a}_4}{4! N} \sum_{\mathbf{k}_i \in BZ} \eta_{\mathbf{k}_1} \dots \eta_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \right\} \prod_{\mathbf{k} \in BZ} d\eta_{\mathbf{k}}. \quad (3.9)
 \end{aligned}$$

Vector \mathbf{k} in Eq.(3.9) lies inside the first BZ and we require that $\eta_{\mathbf{k}}$ coincide with the $\rho_{\mathbf{k}}$ variables at $\mathbf{k} = \mathbf{k}^*$. The integral representation for the product of the Dirac functions $\prod_{\mathbf{k}=\mathbf{k}^*} \delta(\rho_{\mathbf{k}} - \eta_{\mathbf{k}})$ has been used to write down this requirement in (3.8) and (3.9) [3,10].

Comparison of the expressions for $J(\nu)$ (3.9) with the Eqs.(2.6) and (2.7) indicates that the problems concerning calculations of $J(\nu)$ and $J(\rho)$ are similar. Introducing a new variable

$$\eta_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in BZ} \eta_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}) \quad (3.10)$$

and a new notation

$$\nu_{\mathbf{R}} \equiv \frac{1}{\sqrt{N}} \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}) \quad (3.11)$$

one can represent $J(\nu)$ as follows

$$\begin{aligned}
 J(\nu) = \int \dots \int \exp \left[2\pi i \sum_{\mathbf{R}} \nu_{\mathbf{R}} \eta_{\mathbf{R}} - h \sum_{\mathbf{R}} \eta_{\mathbf{R}} - \frac{1}{2!} \overline{d(\mathbf{k})} \sum_{\mathbf{R}} \eta_{\mathbf{R}}^2 \right. \\
 \left. - \frac{\tilde{a}_3}{3!} \sum_{\mathbf{R}} \eta_{\mathbf{R}}^3 - \frac{\tilde{a}_4}{4!} \sum_{\mathbf{R}} \eta_{\mathbf{R}}^4 \right] \prod_{\mathbf{R}} d\eta_{\mathbf{R}} = \prod_{\mathbf{R}} J_{\mathbf{R}}(\nu), \quad (3.12a)
 \end{aligned}$$

where

$$J_{\mathbf{R}}(\nu) = Q_1^{(4)} \exp \left[- \sum_{n=2}^{\infty} \frac{(2\pi i)^n}{n!} T_n \nu_{\mathbf{R}}^n \right]. \quad (3.12b)$$

The expressions for $Q_1^{(4)}$ and coefficients T_n can be obtained easily from Eqs.(2.31) and (2.37)-(2.40) by means of the following substitutions

$$-2\pi i \tilde{M}_1 \rightarrow h, \quad (2\pi)^2 \tilde{M}_2 \rightarrow \overline{d(\mathbf{k})}, \quad i(2\pi)^3 \tilde{M}_3 \rightarrow \tilde{a}_3, \quad (2\pi)^4 \tilde{M}_4 \rightarrow \tilde{a}_4 \quad (3.13)$$

and

$$\frac{1}{Q_1^{(4)}} \frac{\partial^n Q_1^{(4)}}{\partial M_1^n} \rightarrow \frac{(-1)^n}{Q_1^{(4)}} \frac{\partial^n Q_1^{(4)}}{\partial h^n}. \quad (3.14)$$

The partition sum after integration over $\eta_{\mathbf{k}}$ takes the form:

$$\begin{aligned}
 Z = \bar{Z} [Q_1^{(4)}]^N \int \dots \int \exp \left\{ -2\pi i \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \rho_{\mathbf{k}} - \frac{1}{2} \sum_{\mathbf{k}=\mathbf{k}^*} [d(\mathbf{k}) - \overline{d(\mathbf{k})}] \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right. \\
 \left. - \frac{(2\pi i)^2}{2!} T_2 \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \nu_{-\mathbf{k}} - \frac{(2\pi i)^3}{3! \sqrt{N}} T_3 \sum_{\mathbf{k}_i=\mathbf{k}^*} \nu_{\mathbf{k}_1} \dots \nu_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \right. \\
 \left. - \frac{(2\pi i)^4}{4! N} T_4 \sum_{\mathbf{k}_i=\mathbf{k}^*} \nu_{\mathbf{k}_1} \dots \nu_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \right\} \prod_{\mathbf{k}=\mathbf{k}^*} d\nu_{\mathbf{k}} \prod_{\mathbf{k}=\mathbf{k}^*} d\rho_{\mathbf{k}}. \quad (3.15)
 \end{aligned}$$

The coefficient T_1 is absent in (3.12) and (3.15) because of the requirement (see (3.3))

$$\langle \rho'_0 \rangle \equiv \langle \eta_0 \rangle = 0 \quad (3.16)$$

which can be written as follows

$$\langle \rho'_0 \rangle = -\frac{\partial \ln Z}{\partial \sqrt{N} h} = -\frac{1}{Q_1^{(4)}} \frac{\partial Q_1^{(4)}}{\partial h} = T_1 = 0. \quad (3.17)$$

Equation (3.17) is used for determination of the chemical potentials of alloy component.

Integration over $\nu_{\mathbf{k}}$ variables in Eq.(3.15) has some features demanding some additional explanations. In order to factorize the integrals in (3.15) let us introduce an auxiliary lattice, containing N^* sites. One can take a superlattice, realized in ordered alloy below the temperature of the order-disorder phase transition as such an auxiliary lattice.

The Dirac functions $\delta(\mathbf{k}_1 + \dots + \mathbf{k}_i)$ are defined on a new lattice as follows

$$\delta(\mathbf{k}_1^* + \dots + \mathbf{k}_i^*) = \frac{1}{N^*} \sum_{\mathbf{R}^*} \exp [i(\mathbf{k}_1^* + \dots + \mathbf{k}_i^*) \mathbf{R}^*], \quad (3.18)$$

where \mathbf{R}^* are the superlattice sites.

Introducing new variables

$$\nu_{\mathbf{R}^*} = \frac{1}{\sqrt{N^*}} \sum_{\mathbf{k}=\mathbf{k}^*} \nu_{\mathbf{k}} \exp (-i\mathbf{k}\mathbf{R}^*), \quad (3.19a)$$

$$\rho_{\mathbf{R}^*} = \frac{1}{\sqrt{N^*}} \sum_{\mathbf{k}=\mathbf{k}^*} \rho_{\mathbf{k}} \exp (i\mathbf{k}\mathbf{R}^*) \quad (3.19b)$$

and taking into account definition (3.18) one obtains for the partition sum (3.15):

$$\begin{aligned}
 Z = \bar{Z} [Q_1^{(4)}]^N \int \dots \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}=\mathbf{k}^*} [d(\mathbf{k}) - \overline{d(\mathbf{k})}] \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right\} \\
 \times J_1(\rho) \prod_{\mathbf{k}=\mathbf{k}^*} d\rho_{\mathbf{k}}. \quad (3.20)
 \end{aligned}$$

Here

$$\begin{aligned}
 J_1(\rho) &= \int \dots \int \exp \left[-2\pi i \sum_{\mathbf{R}^*} \nu_{\mathbf{R}^*} \rho_{\mathbf{R}^*} - \frac{(2\pi i)^2}{2!} \tilde{T}_2 \sum_{\mathbf{R}^*} \nu_{\mathbf{R}^*}^2 \right. \\
 &\quad \left. - \frac{(2\pi i)^3}{3!} \tilde{T}_3 \sum_{\mathbf{R}^*} \nu_{\mathbf{R}^*}^3 - \frac{(2\pi i)^4}{4!} \tilde{T}_4 \sum_{\mathbf{R}^*} \nu_{\mathbf{R}^*}^4 \right] \prod_{\mathbf{R}^*} d\nu_{\mathbf{R}^*} \\
 &= [Q_2^{(4)}]^{N^*} \prod_{\mathbf{R}^*} \exp \left[- \sum_{n=2}^{\infty} \frac{P_n}{n!} \rho_{\mathbf{R}^*}^n \right] \quad (3.21)
 \end{aligned}$$

with (compare with (2.31))

$$\begin{aligned}
 Q_2^{(4)} &= \frac{1}{2\pi} \sum_{m=0}^{\infty} (-1)^m \frac{1}{(2m)!} \left(\frac{\tilde{T}_3}{6} \right)^{2m} \Gamma \left(3m + \frac{1}{2} \right) \left(\frac{6}{\tilde{T}_4} \right)^{\frac{3m}{2} + \frac{1}{4}} \\
 &\quad \times \Psi \left(\frac{3m}{2} + \frac{1}{4}, \frac{1}{2}, \frac{3}{2} \frac{T_2^2}{\tilde{T}_4} \right) \quad (3.22)
 \end{aligned}$$

and

$$\tilde{T}_2 = T_2, \quad \tilde{T}_3 = \sqrt{\frac{N^*}{N}} T_3, \quad \tilde{T}_4 = \frac{N^*}{N} T_4. \quad (3.23)$$

The coefficients P_n in (3.21) are defined by equations like (2.37)-(2.40) with the following substitutions

$$a_i \rightarrow (-1)^i P_i, \quad Q^{(4)} \rightarrow Q_2^{(4)}, \quad \tilde{M}_i \rightarrow \tilde{T}_i. \quad (3.24)$$

One should restrict oneself by the coefficient P_4 in (3.21) within the ρ^4 approximation.

The result of integration over $\nu_{\mathbf{k}}$ variables is the following:

$$\begin{aligned}
 Z &= \bar{Z} [Q_1^{(4)}]^N [Q_2^{(4)}]^{N^*} \int \dots \int \exp \left\{ -\frac{1}{2} \sum_{\mathbf{k}=\mathbf{k}^*} [\tilde{P}_2 + \beta V_2(\mathbf{k})] \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right. \\
 &\quad \left. - \frac{P_3}{3! \sqrt{N^*}} \sum_{\mathbf{k}_i=\mathbf{k}^*} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_3} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) \right. \\
 &\quad \left. - \frac{P_4}{4! N^*} \sum_{\mathbf{k}_i=\mathbf{k}^*} \rho_{\mathbf{k}_1} \dots \rho_{\mathbf{k}_4} \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \right\} \prod_{\mathbf{k}=\mathbf{k}^*} d\rho_{\mathbf{k}}, \quad (3.25)
 \end{aligned}$$

where

$$\tilde{P}_2 = P_2 - \beta \overline{V_2(\mathbf{k})}. \quad (3.26)$$

The result obtained is of a great importance. The extremum of the integrand in (3.25)

$$E^{(4)} = \frac{1}{2} \sum_{\mathbf{k}=\mathbf{k}^*} (\tilde{P}_2 + \beta V_2(\mathbf{k})) \rho_{\mathbf{k}}^0 \rho_{-\mathbf{k}}^0 + \frac{P_3}{3! \sqrt{N^*}} \sum_{\mathbf{k}_i=\mathbf{k}^*} \rho_{\mathbf{k}_1}^0 \dots \rho_{\mathbf{k}_3}^0$$

$$\times \delta(\mathbf{k}_1 + \dots + \mathbf{k}_3) + \frac{P_4}{4!N^*} \sum_{\mathbf{k}_i=\mathbf{k}^*} \rho_{\mathbf{k}_1}^0 \dots \rho_{\mathbf{k}_4}^0 \delta(\mathbf{k}_1 + \dots + \mathbf{k}_4) \quad (3.27)$$

represents the Landau free energy in terms of series in order parameter. The explicit expressions for the expansion coefficients (\tilde{P}_2, P_3, P_4) are obtained.

The system of equations

$$\frac{\partial E^{(4)}}{\partial \rho_{\mathbf{k}^*}^0} = 0$$

determine the coordinates of the $E^{(4)}$ function extremum [3,10]. The $\rho_{\mathbf{k}}^0$ values have the clear physical sense. They are equal to the Fourier components of the long-range order parameter [3].

The presence of the cubic term in $\rho_{\mathbf{k}}$ in (3.25), (3.27) is necessary but not sufficient condition for realization of the first order phase transition.

Let us perform the final step of the partition sum calculation. We are interested in the second order phase transitions in binary alloys. Thus, the cubic term is absent in the integrand of (3.25) and the temperature of the phase transition is defined by

$$\tilde{P}_2 + \beta_c V_2(\mathbf{k}^*) = 0. \quad (3.28)$$

The coefficient \tilde{P}_2 is a complex function of temperature and a complex equation with respect to β_c results.

Let us write down the final formula for Z , omitting details of calculations

$$Z = \bar{Z} [Q_1^{(4)}]^N [Q_2^{(4)}]^{N^*} [Q_3^{(4)}]^{N^*}, \quad (3.29)$$

where (see (2.41))

$$Q_3^{(4)} = \frac{1}{2\pi} \Gamma\left(\frac{1}{2}\right) \left(\frac{6}{P_4}\right)^{\frac{1}{4}} \Psi\left(\frac{1}{4}, \frac{1}{2}, \frac{3\tilde{P}_2^2}{2P_4}\right). \quad (3.30)$$

The free energy per one atom

$$F = -\frac{1}{N} k_B T \ln Z$$

is a function of temperature and chemical potentials of the alloy components. The equations

$$c_i = -\frac{\partial F}{\partial \mu_i} \quad i = A, B \quad (3.31)$$

allows one to perform the Legendre transformation

$$F(T, c_A, c_B) = F(T, \mu_A, \mu_B) - \sum_{i=A,B} \mu_i c_i \quad (3.32)$$

and get the expression for the free energy as a function of T and $c_i (i = A, B)$.

4. Conclusions

The approach initiated by professor I. Yukhnovskii for solving the three-dimensional Ising model [10] is developed in the given paper. We tried to show the efficiency of the Yukhnovskii method, applying it to the problem of binary alloy thermodynamic property investigations.

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РОЗРАХУНОК СТАТИСТИЧНОЇ СУМИ БІНАРНИХ СПЛАВІВ ЗАМІЩЕННЯ МЕТОДОМ КОЛЕКТИВНИХ ЗМІННИХ. НАБЛИЖЕННЯ ρ^4

Ю. Хохлов, З.О. Гурський

Теорія фазових переходів, розвинута І.Р.Юхновським в рамках методу колективних змінних, застосовується для випадку бінарних сплавів заміщення. Розглядаються і аналізуються особливості розрахунку статистичної суми бінарного сплаву в порівнянні з моделлю Ізінга. В явному вигляді розраховується якобіан переходу до колективних змінних з включенням у нього хімічних потенціалів компонент сплаву. Запропоновано метод розрахунку статистичної суми в межах наближення ρ^4 .