Theory of Inhomogeneous Short Range Order and Calphad Modeling.

Part 7. Surrounded Atom Model Reconstructed

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Abstract

Formalism of Theory of Inhomogeneous Short Range Order is applied to the case of "surrounded atoms". It is shown that the derived equations have significantly higher precision in describing the Short Range Order effects than the commonly used Surrounded Atoms Model.

We argue also that the form of dependence of interatomic interaction on the composition, postulated by the Surrounded Atom Model, is artificial and limits the area of applicability of the model.

Keywords: Phase Diagram calculation; Computational Thermodynamics; Thermodynamic Modeling; Multicomponent systems; Surrounded Atoms Model

1. Introduction

The Surrounded Atom Model (SAM) was introduced in [1, 2] as a direct generalization of Quasichemical Theory (QT) [3–5].

The motivation for such generalization was the well-known deficiency of QT [6] which is not capable to describe systems with any asymmetry on the curve representing the dependence of thermodynamic values on the composition.

The generalization was achieved by replacing the dimers, used as the basis of QT, by groups of $z + 1$ atoms, where every group consists of one "central" atom and all z its nearest neighbors. This approach opens the possibility to introduce the direct dependence of atom interactions on the local composition and explain in this way the asymmetry, if any.

Though SAM cannot be considered as popular as QT, it is still in use [7–10] because of its intuitive appeal.

The formalism of theory was constructed to mimic the arguments used in [3] to derive the classical QT equations, but a sad mistake in calculating the combinatorial factor – the basic element of theory – significantly impaired the quality of the resulting model.

Other sad error is related to enforcing an artificial one-parametric *parabolic* dependence of energy of "surrounded atoms" on composition. This automatically excludes the possibility to describe systems similar to Ising model [11] which would exhibit *linear* dependence of the energy of "surrounded atoms" on the composition.

As a result, it has become impossible to apply SAM to the Ising model and this fact may explain why the pronounced error in the combinatorial factor remains hidden from the most users.

To make the problem evident we will in this article consider the same group of atoms that is used by SAM, but do it inside the framework of Theory of Inhomogeneous Short Range Order (TISR) [12].

TISR is especially appropriate for this task, thanks to the special attention that this theory provides to the quality of the combinatorial factor.

Based on this, we will compare the results of TISR and SAM applications to identify the place where SAM could be improved.

To evaluate the quality of two theories we will replace the postulated by SAM parabolic dependence of "surrounded atom" energy on composition with linear dependence, that is specific for the Ising model.

Combinatorial factor is by its nature a pure geometrical attribute that depends exclusively on the geometry and dimensionality of the lattice and cannot therefore be changed by interatomic interaction (if, of course, this interaction isn't strong enough to change the lattice itself!).

Thus, using the assumptions of the Ising model, we can focus our attention on the combinatorial factor, leaving out the insignificant in this case details of the interatomic interaction postulated by SAM.

High attention in SAM is devoted [1, 2] to possibility to treat "surrounded atoms" as "Einstein oscillators" where frequency of oscillations is defined by the "surrounded atoms" composition. Such assumption is equivalent to introduction a formal dependence of energy of "surrounded atoms" on the temperature and in this sense brings nothing new to the model.

2. Surrounded Atoms by TISR

To describe the "surrounded atoms" in the framework of TISR, we selecting as a cell the same configuration as SAM does: atom surrounded by z nearest neighbors. Only z links between central atom and the shell are included in the cell; links between the surrounding atoms are excluded.

Such choice of cells means that not all knots inside a cell are equivalent and therefore has to be treated inside TISR using the "two-sub-cells" version, as described in [13], section 3.

This version is based on the following expression for the free energy:

$$\begin{aligned}
F(N_1, N_2, \lambda_1, \lambda_2, \lambda, p_{ij\alpha}, \theta) \\
= \beta M \sum_{i\alpha} U_{ij\alpha} p_{ij\alpha} - \theta(1 - \gamma) \ln K_0 - \theta\gamma \ln K_1 \\
+ \lambda_1 N \left(x_1 - \sum_{ij\alpha} \frac{i}{k_1} p_{ij\alpha} \right) + \lambda_2 N \left(x_1 - \sum_{ij\alpha} \frac{j}{k_2} p_{ij\alpha} \right) \\
+ \lambda N \left(1 - \sum_{ij\alpha} p_{ij\alpha} \right)
\end{aligned} \tag{1}$$

where, in particular, we assume that every atom of the system is included in a cell, and only in one cell:

$$\begin{aligned}
k_1 &= z \\
k_2 &= 1; \quad k = k_1 + k_2 = z + 1 \\
M &= \frac{N}{k} = \frac{N}{z + 1} \\
\beta &= \frac{Nz}{2Mz} = \frac{z + 1}{2}
\end{aligned} \tag{2}$$

θ is a temperature factor – composition of absolute temperature and the Boltzmann constant k_B [14].

The Lagrange multipliers λ_1 and λ_2 ensure that the probability to find atom a as "central" atom and the probability to find it as part of "shell" is the same and is equal to x_1 .

The described collection of M cells is named *ensemble*. Different types of cells inside of ensemble are described using three indexes. In particular, $M_{ij\alpha}$ is the number of cells with j ($j = 0, 1$) atoms of type a in the center, i ($i = 0, 1, \dots, z$) such atoms in the shell, while α numbers all available for the cell of specified composition configurations:

$$\alpha = 1, 2, \dots, C_z^i$$

where C_z^i is the number of distinguishable allocations of i atoms a in a shell.

Combinatorial factor K of the system is [15]:

$$K = K_0 * \left(\frac{K_1}{K_1^\infty} \right)^\gamma \tag{3}$$

where

$$\ln K_1 = \ln \frac{M!}{\prod_{ij\alpha} (M_{ij\alpha})!} = -M \sum_{ij\alpha} p_{ij\alpha} \ln p_{ij\alpha} \tag{4}$$

and it can be shown [15] that

$$K_1^\infty \equiv \lim_{\theta \rightarrow \infty} K_1 = K_0 = \frac{N!}{N_1!N_2!} \quad (5)$$

The structural parameter γ , when taken in the quasichemical approximation [6], is equal to β

$$\gamma = \beta = \frac{z+1}{2} \quad (6)$$

The minimization of the free energy (1) results in

$$p_{ij\alpha} = \exp\left(-\frac{\beta U_{ij\alpha}}{\theta\gamma}\right) b_1^i b_2^j b \quad (7)$$

where b and b_j are defined through

$$b_j = \exp\left(\frac{\lambda_j}{\theta\gamma} \frac{k}{k_j}\right) \quad (8)$$

$$b = \exp\left(\frac{\lambda k}{\theta\gamma}\right)$$

As was shown in [13] (or can be calculated independently),

$$\begin{aligned} \mu_1 &= \frac{\partial F}{\partial N_1} = \theta(1-\gamma) \ln x_1 + \lambda + \lambda_1 + \lambda_2 \\ \mu_2 &= \frac{\partial F}{\partial N_2} = \theta(1-\gamma) \ln x_2 + \lambda \end{aligned} \quad (9)$$

Until now we did not imposed any restrictions on the dependence of cells energy on the composition. But since we are interested in comparison of combinatorial factors only, from this moment on we will assume that the energy of cells follows strongly the rules of the Ising model:

$$U_{i0\alpha} = U_\Delta i; \quad U_{i1\alpha} = U_\Delta(z-i) \quad (10)$$

where U_Δ is the energy of one link $a-b$.

This assumption cannot influence the combinatorial factor, that depends on the geometrical structure of the lattice only, but significantly simplifies and clarifies our work by reducing both models to the ordinary Quasichemical Theory – some simplification that is certainly impossible in the general case when the energy of "surrounded atom" is a nonlinear functional of the composition.

As the result of the assumption (10), and as it follows from (7), we can see immediately that the probabilities $p_{ij\alpha}$ are independent of α , so we can introduce new variables p_{ij} :

$$p_{ij} = \sum_{\alpha} p_{ij\alpha} = C_z^i p_{ij1} \quad (11)$$

The notations used by SAM and TISR are significantly different and have to be brought to the common basis for comparison.

In particular, the ensemble of "surrounded atoms" consists of N elements, while TISR ensemble includes only $N/(z+1)$ elements.

This difference has to be taken in the account when comparing the calculated values.

The variables describing cells are defined differently inside SAM [16], where n_{Ai} denotes the number of atoms a surrounded by i atoms b , and n_{Bi} denotes the number of atoms b surrounded by i atoms a :

$$\begin{aligned} n_{Ai} &= Np_{(z-i)1} = NC_z^i p_{(z-i)11} \\ n_{Bi} &= Np_{i0} = NC_z^i p_{i01} \end{aligned} \quad (12)$$

The critical point where difference between TISR and SAM becomes evident is the expression for the combinatorial factor, namely, the part of the expression for the free energy (1) that includes K_1 :

$$\begin{aligned} \gamma \ln K_1 &= -\gamma M \sum_{ij\alpha} p_{ij\alpha} \ln p_{ij\alpha} \\ &= -\frac{z+1}{2} \frac{N}{z+1} \sum_{ij} C_z^i p_{ij1} \ln p_{ij1} \\ &= \frac{1}{2} \left(\ln N! - \ln \prod_i (n_{Ai}/C_z^i!)^{C_z^i} - \ln \prod_i (n_{Bi}/C_z^i!)^{C_z^i} \right) \end{aligned} \quad (13)$$

This expression contains an extra multiplier $1/2$, compared to [16].

The same problem can be indicated in the expression for the internal energy of the system:

$$\begin{aligned} E &= \beta M \sum_{i\alpha} U_{ij\alpha} p_{ij\alpha} \\ &= \frac{z+1}{2} \frac{N}{z+1} \sum_i C_z^i (U_{i01} p_{i01} + U_{i11} p_{i11}) \\ &= \frac{1}{2} \sum_i (U_{i01} n_{Bi} + U_{(z-i)11} n_{Ai}) \end{aligned} \quad (14)$$

Again, we have here extra factor $1/2$ that is missing in SAM [16]. It means that the equations of SAM can be formally received from the equations of TISR if we replace γ by the value that is two times larger.

The source of this difference is easy to understand.

Parameter γ is defined in [15] by the condition

$$\gamma(Mm) = \frac{zN}{2} \quad (15)$$

where Mm is the number of interatomic links belonging to the ensemble of cells [15] (described at the beginning of this section), while $zN/2$ is the total number of links in the system.

We can say that γ is selected to ensure that every *link* in the system is counted in the combinatorial factor precisely one time.

Combinatorial factor in SAM is constructed [16, 17] by treating the "surrounded atoms" as independent entities, rather than pairs.

It looks natural but it is the source of the difference.

Let us consider an arbitrary pair of atoms $m - m'$. We can consider the "surrounded atom" where m is the central atom and m' is located in its shell.

We can consider also the "surrounded atom" where m' is the central atom and m is located in its shell.

But it means that when calculating the combinatorial factor, the pair $m - m'$ is taken into account *twice*, while in TISR, as we have seen, every pair is taken into account only *ones*.

As mentioned above, it is the source of the difference.

We should like to evaluate quantitatively the role of indicated discrepancy by comparing the results of the two theories.

The necessary calculations become simpler thanks to our assumption that atom interactions follow the rules of the Ising model (10).

Considering an arbitrary cell we know that permutations of atoms inside its shell do not affect the count of pairs $a - b$ for this cell, so we conclude that under the assumptions of Ising model the energy of the system is simply the number of pairs $a - b$ in the system, multiplied by the energy of one such pair U_{Δ} .

This energy can be calculated directly, by counting the number of pairs $a - b$, OR, calculating first the number of distinct "surrounded atoms" and then taking in the account the numbers of pairs $a - b$ inside every "surrounded atom".

The same is correct for the combinatorial factor. We can consider permutations of pairs, as usual in Quasichemical Theory, OR, consider permutations of "surrounded atoms" along with permutations of pairs inside every "surrounded atom".

As a result (as shown formally in the appendix A) the equations of SAM are indeed reduced to the equations of Quasichemical Theory when we accepting the Ising-like form of the interatomic interaction, however SAM has a double value for the parameter γ .

3. Surrounded Atom Model and TISR comparison

After all the above preparatory work, we can now compare the results of SAM and TISR.

The usual method for assessing the accuracy of a statistical-thermodynamic model is based on comparing the results calculated near the critical point with those known from the literature sources [18] for the Ising model.

Since we had assumed that the rules of the Ising model were fulfilled, we know that the free energy curve is symmetrical with respect to the $x_1 = 1/2$ composition.

It means also that the immiscibility curve (binodal [5]) can be described as not trivial ($x \neq 0.5$) solution of the equation

$$\frac{\partial f}{\partial x_1} \equiv \mu_1(x_1) - \mu_2(x_1) = 0 \quad (16)$$

Using expressions (9) for the chemical potentials of components and notations (7) we can reduce this equation to the form

$$(1 - \gamma) \ln \frac{x_1}{x_2} + \frac{\gamma z}{z + 1} \ln b_1 + \frac{\gamma}{z + 1} \ln b_2 = 0 \quad (17)$$

or

$$\ln \frac{x_1}{x_2} = \frac{\gamma}{(z + 1)(\gamma - 1)} \ln (b_1^z b_2) \quad (18)$$

To handle this equation we will use the parametric solution of "two-sub-cells" TISR model produced in [13], section 3. Assumptions of the Ising model allow to simplify this solution and present necessary expressions in reduced form, though the intermediate transformations are a little bit cumbersome and are detailed in the appendix (A).

As a result of these transformations all variables are expressed as functions of the parameter b_1 only.

As can be seen from (29), the critical point corresponds to $x_1 = 0.5$ when $b_1 = b_2 = 1$. At these conditions the equation (18) turns into identity. To get the equation defining the critical point we must resolve this uncertainty:

$$\lim_{b_1 \rightarrow 1} \frac{x_1(b_1) - x_2(b_1)}{(b_1 - 1)x_2(b_1)} = \frac{\gamma}{(z + 1)(\gamma - 1)} \lim_{b_1 \rightarrow 1} \frac{b_1^z b_2 - 1}{b_1 - 1} \quad (19)$$

and coming to the equation that allows to calculate the critical temperature:

$$\frac{U_\Delta}{\theta_c} = -\frac{\gamma}{\beta} \ln \frac{\gamma z - (z + 1)}{\gamma z} \quad (20)$$

If we accepting the following from TISR condition $\gamma = (z + 1)/2$ then the above equation reduces to the derived in [19] equation for the critical point in the Quasichemical Theory:

$$\frac{U_\Delta}{\theta_{QC}} = -\ln \frac{z - 2}{z} \quad (21)$$

We will receive a little bit different equation for the critical temperature if we accepting the provided by SAM value $\gamma = z + 1$:

$$\frac{U_\Delta}{\theta_{SAM}} = -2 \ln \frac{z - 1}{z} \quad (22)$$

Using these critical values together with the presented by (9) and (30) expressions for the thermodynamic variables, we can immediately show that while TISR version is precisely equivalent to the ordinary Quasichemical Theory, SAM can ensure only the precision that is intermediate between Bragg-Williams approximation and Quasichemical Theory.

To make it evident, the results of calculations are collected in the table.1 along with the multiple results derived in [19] for different approximations and accompanied by the best theoretical estimations from [18].

The comparison shows immediately that SAM provides surprisingly low level of precision in the description of the short range order effects.

Table 1: Critical Values (per atom) calculated using Surrounded Atom Model (SAM), Quasichemical (QT) and Improved Quasichemical Theory (IQT) [19] along the best theoretical estimations [18]

LATTICE		BW	SAM	QT	IQT	IQT2	[18]
2d square	k	1	5	2	2	4	
	γ	1	5	4	2.784	1.608	
	U_{Δ}/θ_c	0.500	0.575	0.693	0.882	0.882	0.882
	E/U_{Δ}	1.000	0.857	0.667	0.439	0.412	0.292
	S/k_B	0.693	0.652	0.580	0.461	0.430	0.306
2d triangular	k	1	7	2	2	3	
	γ	1	7	6	3.002	1.956	
	U_{Δ}/θ_c	0.333	0.365	0.405	0.549	0.549	0.549
	E/U_{Δ}	1.500	1.364	1.200	0.751	0.715	0.501
	S/k_B	0.693	0.668	0.633	0.497	0.471	0.330
cubical	k	1	7	2	2	8	
	γ	1	7	6	4.440	1.673	
	U_{Δ}/θ_c	0.333	0.365	0.405	0.443	0.443	0.443
	E/U_{Δ}	1.500	1.364	1.200	1.064	1.051	0.966
	S/k_B	0.693	0.668	0.633	0.598	0.588	0.541
BCC	k	1	9	2	2	4	
	γ	1	9	8	5.234	2.729	
	U_{Δ}/θ_c	0.250	0.267	0.288	0.315	0.315	0.315
	E/U_{Δ}	2.000	1.867	1.714	1.528	1.524	1.452
	S/k_B	0.693	0.675	0.652	0.619	0.617	0.585
FCC	k	1	13	2	2	4	
	γ	1	13	12	5.845	2.566	
	U_{Δ}/θ_c	0.166	0.174	0.182	0.204	0.204	0.204
	E/U_{Δ}	3.000	2.870	2.727	2.381	2.362	2.270
	S/k_B	0.693	0.682	0.668	0.630	0.623	0.597

4. Conclusions

Equations of Surrounded Atom Model (SAM) are derived from the equations of Theory of Inhomogeneous Short Range Order being applied to the corresponding atom groups ("surrounded atoms").

Lengthy calculations show that the combinatorial factor used by SAM may be significantly improved by using the approach provided by TISR.

Attempt of SAM to use large groups of atoms as basis of consideration is basically spoiled down by a not trivial error in the combinatorial factor and by accepting a primitive one-parameter form of dependence of "surrounded atoms" energy on composition.

This approach artificially excludes from the consideration the systems described by Ising model or close to such systems – assumption that cannot be proved by experiment.

In general, the choice of "surrounded atoms" as basis of considerations cannot be considered as good choice by a few reasons:

- Only interactions between central atom and the shell are considered, while interactions between atoms in the shell are neglected. It automatically means that the configurational factor used by SAM is sensitive to the only structural parameter – coordination number – and is not capable to distinguish $3d$ and $2d$ dimensional systems if the coordination numbers coincide.

It is theoretically possible to include the omitted links in the consideration, but this approach would make the calculations excessively complicated.

- SAM introduces potentially very detailed description of Short Range Order but in reality never uses it to the full extent, making therefore the calculations more complicated than necessary.

As is evident from the above considerations, TISR can easily be applied to "surrounded atoms" but this possibility presents a restricted interest. TISR provides much better methods of description the multicomponent systems, while still using extremely small number of adjustable parameters.

Numerous examples of successful use of TISR formalism can be found in [15], [6], [20].

In [19] it is shown how several known models – including SAM – can be dramatically refined by using an Improved Combinatorial Factor – important result that would be really difficult to achieve outside the scope of TISR.

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A. Reduction to Quasichemical Theory

We would like to show now that the equations of SAM can be reduced to the results of Quasichemical Theory if we assume that the interatomic interactions follow the rules of the Ising model.

This requires some lengthy (though simple) calculations but can streamline the comparison of results provided by SAM and TISR.

As follows from (10)

$$W_{i0} = C_z^i \eta^i; \quad W_{i1} = C_z^i \eta^{(z-i)} \quad (23)$$

where

$$W_{ij} = \sum_{\alpha} W_{ij\alpha}; \quad \eta = \exp\left(-\frac{\beta U_{\Delta}}{\gamma \theta}\right) \quad (24)$$

Based on (23) we can now calculate a few sums defined in [13] (formula (31)):

$$\begin{aligned} S_0 &= \sum_i W_{i0} b_1^i = \sum_i C_z^i \eta^i b_1^i = (1 + \eta b_1)^z \\ S_1 &= \sum_i W_{i1} b_1^i = \sum_i C_z^i \eta^{(z-i)} b_1^i = (\eta + b_1)^z \end{aligned} \quad (25)$$

$$\begin{aligned} S_0^a &= \sum_i \frac{i}{z} W_{i0} b_1^i = \frac{b_1}{z} \frac{d}{db_1} (1 + \eta b_1)^z = \eta b_1 (1 + \eta b_1)^{z-1} \\ S_1^a &= \sum_i \frac{i}{z} W_{i1} b_1^i = \frac{b_1}{z} \frac{d}{db_1} (\eta + b_1)^z = b_1 (\eta + b_1)^{z-1} \end{aligned} \quad (26)$$

$$\begin{aligned} S_0^b &= S_0 - S_0^a = (1 + \eta b_1)^z - \eta b_1(1 + \eta b_1)^{z-1} = (1 + \eta b_1)^{z-1} \\ S_1^b &= S_1 - S_1^a = (\eta + b_1)^z - b_1(\eta + b_1)^{z-1} = \eta(\eta + b_1)^{z-1} \end{aligned} \quad (27)$$

$$\begin{aligned} R &= S_0 S_1^b + S_1 S_0^a = (1 + \eta b_1)^z \eta(\eta + b_1)^{z-1} + (\eta + b_1)^z \eta b_1(1 + \eta b_1)^{z-1} \\ &= \eta(1 + \eta b_1)^{z-1}(\eta + b_1)^{z-1}(1 + 2\eta b_1 + b_1^2) \end{aligned}$$

$$\begin{aligned} b &= \frac{S_1^b}{R} = \frac{\eta(\eta + b_1)^{z-1}}{\eta(1 + \eta b_1)^{z-1}(\eta + b_1)^{z-1}(1 + 2\eta b_1 + b_1^2)} = \frac{1}{(1 + \eta b_1)^{z-1}(1 + 2\eta b_1 + b_1^2)} \\ b_2 &= \frac{S_0^a}{S_1^b} = \frac{b_1(1 + \eta b_1)^{z-1}}{(\eta + b_1)^{z-1}} \end{aligned} \quad (28)$$

$$x_1 = \frac{S_1 S_0^a}{R} = \frac{(\eta + b_1)^z \eta b_1(1 + \eta b_1)^{z-1}}{\eta(1 + \eta b_1)^{z-1}(\eta + b_1)^{z-1}(1 + 2\eta b_1 + b_1^2)} = \frac{b_1(\eta + b_1)}{(1 + 2\eta b_1 + b_1^2)} \quad (29)$$

$$x_2 = 1 - x_1 = \frac{1 + \eta b_1}{1 + 2\eta b_1 + b_1^2}$$

Energy E of the system is, according (1):

$$\begin{aligned} E &= \beta M \sum_{i\alpha} U_{ij\alpha} p_{ij\alpha} \\ &= \frac{N}{2} b \sum_i (i U_\Delta W_{i0} b_1^i + (z - i) U_\Delta W_{i1} b_1^i b_2) \\ &= \frac{N}{2} U_\Delta b (k_1 S_0^a + z b_2 S_1 - k_1 b_2 S_1^a) \\ &= N U_\Delta z \frac{S_1^b S_0^a}{R} \end{aligned} \quad (30)$$

Non negative solution of any of the equations (29) is:

$$b_1 = \eta \frac{r - x_2 + x_1}{2x_2} = \frac{2x_1}{\eta(r + x_2 - x_1)} \quad (31)$$

where

$$r = \sqrt{(x_2 - x_1)^2 + \frac{4x_1 x_2}{\eta^2}} \quad (32)$$

The found value for b_1 has to be substituted into few typical combinations:

$$\begin{aligned} \eta + b_1 &= \frac{\eta(r + 1)}{2x_2} \\ 1 + \eta b_1 &= \frac{r + 1}{r + x_2 - x_1} \end{aligned} \quad (33)$$

Using (29) we can simplify expressions for b and b_2 :

$$\begin{aligned} b &= \frac{x_2}{(1 + \eta b_1)^z} = \frac{x_2(r + x_2 - x_1)^z}{(1 + r)^z} \\ b_2 &= b_1 \left(\frac{2x_2}{\eta(r + x_2 - x_1)} \right)^{z-1} \end{aligned} \quad (34)$$

Expression for μ_1 includes the following combination:

$$\begin{aligned} bb_2b_1^z &= \frac{x_2(r + x_2 - x_1)^z}{(1 + r)^z} b_1 \left(\frac{2x_2}{\eta(r + x_2 - x_1)} \right)^{z-1} b_1^z \\ &= \frac{(2x_2)^z(r + x_2 - x_1)}{2(1 + r)^z} \frac{2x_1}{\eta(r + x_2 - x_1)} \frac{1}{\eta^{z-1}} b_1^z \\ &= x_1 \left(\frac{2x_2}{\eta(1 + r)} \right)^z \left(\eta \frac{r - x_2 + x_1}{2x_2} \right)^z = x_1 \left(\frac{r - x_2 + x_1}{1 + r} \right)^z \end{aligned} \quad (35)$$

Using the equations (9) we can now calculate the chemical potential of components:

$$\begin{aligned} \mu_1 &= -\theta(\gamma - 1) \ln x_1 + \frac{\theta\gamma}{z+1} \ln b + \frac{\theta\gamma z}{z+1} \ln b_1 + \frac{\theta\gamma}{z+1} \ln b_2 \\ &= \theta \ln x_1 - \theta\gamma \ln x_1 + \frac{\theta\gamma}{z+1} \ln x_1 \left(\frac{r - x_2 + x_1}{1 + r} \right)^z \\ &= \theta \ln x_1 + \frac{\theta\gamma z}{z+1} \ln \frac{r - x_2 + x_1}{x_1(1 + r)} \\ \mu_2 &= -\theta(\gamma - 1) \ln x_2 + \frac{\theta\gamma}{z+1} \ln b \\ &= \theta \ln x_2 + \frac{\theta\gamma}{z+1} (-(z+1) \ln x_2 + \ln x_2 + z \ln \frac{r + x_2 - x_1}{r + 1}) \\ &= \theta \ln x_2 + \frac{\theta\gamma z}{z+1} \ln \frac{r + x_2 - x_1}{x_2(r + 1)} \end{aligned} \quad (36)$$

We can see now that in the case of "surrounded atoms" the provided by TISR value $(z+1)/2$ for γ reduces the above expressions to the form identical to the expressions for the chemical potentials of components known from the Quasichemical Theory [3, 6, 21].

It is important to remember that the named reduction of SAM model to Quasichemical Theory can happen only when we assuming the typical for Ising model purely pair-like form of interatomic interaction.

Introduction of non-linear dependence of energy of "surrounded atoms" on composition cannot fix the problem with the combinatorial factor but still allows to extend theory beyond usual limitations of Quasichemical Theory.