Theory of Inhomogeneous Short Range Order and Calphad Modeling.

Part 4. Improved Combinatorial Factor

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Abstract

An improved combinatorial factor allows to reproduce the correct critical temperatures for the Ising lattices.

As result, the accuracy of thermodynamic values calculated near the critical point increases by the factor 2 - 3 for the most important lattice types.

It is shown why one-particle (Bragg-Williams) and two-particle (Quasichemical) approximations cannot be adequately applied for description of important nuances of interatomic interaction.

The problem of negative entropy values manifested at low temperatures and typical for model theories is discussed. It is being argued that this problem has to be treated as exaggerated.

Keywords: Combinatorial Factor; Miscibility Gap; Associated Solution Model; Quasichemical Theory; Frustrated Lattices; Cluster Site Approximation;

1 Introduction

The basis of the Theory of Inhomogeneous Short Range Order (TISR) [1] is its combinatorial factor (CF).

It has been shown [2] that this combinatorial factor, taken in its lowest approximation, reproduces the equations of Quasichemical Theory (QT) [3, 4] and therefore makes TISR a logical generalization of QT.

Both theories are asymptotically correct in the high temperature limit but become less and less reliable in the opposite case when temperature approaches the critical point of miscibility or ordering.

In particular, the error in estimation of upper critical solution temperature exceeds 10% for 3d lattices; the errors in the assessment of thermodynamic quantities can be about 10-20%.

Attempt to extend theory to even lower temperatures meets the supposedly disappointing discovery of possible negative values of configurational entropy of mixing [5].

The retro-analysis of the heuristic arguments that were used to derive the combinatorial factor of theory [1] shows the sensitive elements where this CF can be modified to serve better in the critical region. Following these hints we are capable [6] to choose the parameters of theory in a way that ensures reproduction the correct critical temperature and simultaneously provides significant precision improvements for all calculated thermodynamic values.

The analysis related to these modifications shows that the role of the above mentioned low-temperature negative values of configuration entropy is greatly exaggerated, although it remains an irritating attribute of formalism.

2 Improving the Combinatorial Factor

This article can be considered as direct continuation of [1] where all necessary abbreviations and details can be found.

As explained in [1] we are looking for a new choice of structural parameter γ that defines behavior of combinatorial factor K :

$$K = K_0 * \left(\frac{K_1}{K_0} \right)^\gamma \quad (1)$$

with

$$K_0 = \frac{N!}{N_1!N_2!} \quad (2)$$

$$K_1 \equiv K_1(M_{i\alpha}) = \frac{M!}{\prod_{i\alpha} (M_{i\alpha})!} \quad (3)$$

The "quasichemical" choice of value for γ was explained in [1]:

$$\gamma = (zN/2)/(mM) \quad (4)$$

where m is the number of links inside one cell. This choice ensures "quasichemical" precision of theory [2].

Based on the combinatorial factor (1), the expression for the free energy F can be written as:

$$\begin{aligned} F(N_j, M_{i\alpha}, \lambda_j) = & \beta \sum_{i\alpha} U_{i\alpha} M_{i\alpha} - \theta(1 - \gamma) \ln K_0 - \theta\gamma \ln K_1 \\ & + \lambda_1 \left(N_1 - \sum_{i\alpha} i M_{i\alpha} \right) + \lambda_2 \left(N_2 - \sum_{i\alpha} (k - i) M_{i\alpha} \right) \end{aligned} \quad (5)$$

We are looking for a new value for γ that would allow to reproduce the right critical temperature of alloy. The equation for miscibility curve was derived in [1]:

$$\frac{x_1(c)}{x_2(c)} \equiv \frac{\sum_i i W_i c^i}{\sum_i (k-i) W_i c^i} = c^{\frac{\gamma}{\gamma-1}} \quad (6)$$

together with the equation for the upper critical solution temperature:

$$\frac{\gamma}{\gamma-1} = \lim_{c \rightarrow 1} \frac{x_1(c) - x_2(c)}{(c-1)x_2(c)} \quad (7)$$

If the critical temperature is known (e.g. taken from the monograph [7] that collects results from the multiple sources) then the equation (7) can be used to obtain the value of γ which ensures that the correct critical temperature is reproduced.

Substituting the γ found in this way back into equation (6), we receive the equation, which determines the corrected miscibility curve.

For the case $k = 2$ (corresponding to the Quasichemical Theory [2]) the transcendent equation (6) can be transformed to relatively simple form:

$$\zeta \equiv \exp\left(-\frac{\beta U_{\Delta}}{\gamma \theta}\right) = \frac{c^{\frac{1}{\gamma-1}} - c}{1 - c^{\frac{\gamma}{\gamma-1}}} \quad (8)$$

Since the value of γ is assumed to be determined from the equation (7), we can consider the equation (8) as defining the parametric dependency of temperature θ from c and, therefore, from the directly related to c concentration x_1 .

Equation (7) also gets especially simple form in the case of cells-dimers:

$$\frac{\gamma}{\gamma-1} = \frac{2}{1 + \zeta_c} \quad (9)$$

where

$$\zeta_c \equiv \exp\left(-\frac{\beta U_{\Delta}}{\gamma \theta_c}\right)$$

and the value of critical temperature θ_c/U_{Δ} can be taken from monograph [7].

The explicit form of the equation (9) allows to make some important general conclusions. It is evident that the right side of this equation cannot exceed the value of 2; consequently, analyzing the left site of the equation we must conclude that $\gamma > 2$. It is the requirement that has to be satisfied for critical point to exist, as was already mentioned in [1].

In general case the value $\gamma = 1$ is the singularity point of the equation (6) where no solution is possible. If, nevertheless, we assume $\gamma = 1$ then no immiscibility effects can be described by such a theory.

The value $\gamma = 1$ still presents significant interest because the general expression for the combinatorial factor (1) converts at this condition into simple and extremely popular Bragg-Williams formula (3) for cells.

Table 1: Comparison of Critical Values calculated using Quasichemical (QT) and Improved Quasichemical Theory (IQT) with the best theoretical estimations [7]

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

In particular, this choice is made within the framework of Association Solution Model [8], which explains why this theory in its ideal version fails to describe correctly the systems with positive deviations from ideality.

As a general conclusion, it seems that we can apply the Bragg-Williams formula – albeit with relatively low accuracy – to evaluate the distribution statistics of individual atoms, but this formula should not be applied to *groups* of atoms.

The combinatorial factor from TISR (1) shows how this formula can be modified to be a reasonable approximation in general case.

Figure 1: Versions of Combinatorial Factor $g(\nu)$ for Square $2d$ lattice:

- Onsager solution – *red*
- Quasichemical approximation – *blue*
- Improved Quasichemical approximation – *green*
- Location of the critical point by Onsager – *red dot*
- Approximation by (16) – *dotted line*

To allow the comparison of different approximations described above, we presenting in the table.1 the values of some thermodynamic quantities calculated at critical point for a set of $2d$ and $3d$ lattices. Data values estimated using Bragg-Williams approximation (2) are included for reference, to make it evident the importance of short range order effects in estimating thermodynamic values.

The data in the table show that the "Improved Quasichemical Theory" (IQT) really provides significant improvements compared to the standard Quasichemical Theory (QT).

The ability to completely eliminate the error in determining the location of the critical point in the phase diagram should be considered extremely important if one remembers that the usual quasichemical 10% shift in the critical temperature value can mean a defect up to 100° (or even more) for typical metal melts.

Data in the table reveal another equally important fact: correction of the critical temperature value helps at the same time to reduce significantly the errors in the estimation of energy and entropy of the alloy.

This fact can be confirmed and clarified by the fig.1, which shows two different versions of the CF at $x = 1/2$, compared to the exact CF obtained in [9] from the Onsager solution [10] for square lattice.

High temperature corresponds to chaotic atom distribution (equivalent to $\nu = 1$ for the square lattice) and we can see from the picture that in this region the ordinary QT approximation is extremely close to the Onsager's solution.

When the temperature decreases and we approach the critical point of mixing, then the difference between QT and the exact curve sharply increases.

On the contrary, partially losing the quality of approximation in the high-temperature limit, IQT provides a more uniform (though hardly perfect) representation of the exact curve over the entire range from high temperatures to the critical point.

Exaggerating, we can say that QT is very good around one point, while IQT is reasonably good inside the whole physically meaning region. This is the real reason why all the related values improve as one moves from QT to IQT.

3 Multiatomic cells

The benefits of Improved Combinatorial Factor become especially important when we switching our attention from the $k = 2$ case (Quasichemical Theory) to multiatomic cells. As discussed in [2], the QT approximation has only one structural parameter – coordination number z – and cannot properly account for the topology or even dimensionality of underlying lattice.

By switching to the case of multiatomic cells, we receiving a tool that is much more sensitive to the structure of any particular grid, but the consideration has to be more accurate and more specific.

In particular, we must divide all existing lattice types into two categories.

Every lattice from the first category can be divided into two interlaced sublattices in such a way that any atom in one sublattice is surrounded only by atoms from the other sublattice.

Evident examples of this category are square $2d$, cubical, and BCC lattices.

As shown in [11], this type of grids has an additional type of symmetry, which, in particular, leads to the fact that the CF of ferromagnetic and antiferromagnetic interaction

behave in a similar way. CF developed for ferromagnetic case can be used (with some nuances in notation) for antiferromagnetic case.

For the case of lattices of first category (see fig.2) this type of symmetry can be expressed mathematically as

$$g(\nu) = g(\nu_{max} - \nu)$$

where ν_{max} is the maximal value of ν possible in lattice under consideration.

Figure 2: Versions of Combinatorial Factor $g(\nu)$ for Cubic Lattice:

Green lines – cells with $k = 2$

Red lines – cells with $k = 4$

Quasichemical approximation – *dotted* lines

Improved Quasichemical approximation – *solid* lines

Location of the critical point – *red dot*

Such structure provides a very favorable environment for realization the attractive interaction between distinct atoms. In the ground state one sublattice is populated by atoms of type a , while the second – by atoms of type b . In this configuration the proportion of attractive $a - b$ links reaches the maximal possible value of 100%.

Lattices from the second category are very different. No matter how you divide lattice into two sublattices, but every atom will have neighbors from both sublattices. As result,

the 100% limit for $a - b$ pairs cannot be reached. No matter how lattice is populated, some part of links will be of $a - a$ or $b - b$ type.

This category of grids is commonly known as geometrically frustrated [12] as the trend towards a favorable arrangement of atoms cannot be satisfied in the case of negative deviation from ideality.

Clearly, the existence of geometric frustrations cannot be recognized if the consideration is limited to groups of only two atoms. As a result, the CF provided by the classic QT for frustrated lattices should not be applied to describe any significant negative deviation from ideality (see fig.3).

Figure 3: Versions of Combinatorial Factor $g(\nu)$ for FCC Lattice:

Green lines – cells with $k = 2$

Red lines – cells with $k = 4$

Quasichemical approximation – *dotted* lines

Improved Quasichemical approximation – *solid* lines

Location of the critical point – *red dot*

Evident asymmetry of CF at $k > 2$ is very important. We can see that switching from $k = 2$ to $k = 4$ leads to the left curve branch going up and the right branch going down. We must expect that transition to even greater values of k will support this trend.

We can mimic this trend for the left branch by keeping $k = 4$, but replacing $\gamma = \gamma_{QC}$ with γ_{IQT} , where we know that $\gamma_{IQT} < \gamma_{QT}$ to allow left branch to go up.

Similarly, we should expect that for the right branch the improved value of γ will be *larger* than γ_{QT} . We need additional source – theoretical or empirical – to conclude what value of γ has to be used to reproduce the critical temperature of ordering in case of frustrated lattices.

In one of the forthcoming articles we will show that the Cluster Site Approximation (CSA) [13] can be considered as the partial case of TISR. No wonder, both theories were developed as multiatom generalization of QT.

Original version of CSA [14] was a direct generalization of Quasichemical Theory, but later the theory was modified [15] to reproduce correctly the results of Monte Carlo simulation [15]. This (pure formal) improvement was achieved by increasing one of the structural parameters of CSA by a factor 1.42.

In the planned articles we will show that these results precisely match the above discussion related to asymmetrical behavior of CF in the case of FCC lattices.

4 Negative Entropy Problem

Using the expression for the free energy (5) we can calculate the configurational entropy S of the system [11]:

$$S = -k_B \frac{\partial F}{\partial \theta} = k_B(1 - \gamma) \ln K_0 + k_B \gamma \ln K_1 = k_B N \ln g(\nu) \quad (10)$$

where a few additional abbreviations were introduced:

$$\nu = N_{12}/N \quad (11)$$

$$\ln g = \frac{1}{N} \ln K \quad (12)$$

We can see that the configurational entropy S of the system will become negative if $g(\nu) < 1$.

Negative combinatorial entropy at low temperatures is a physically meaningless value that indicates that the theory is being used outside the scope of applicability. Returning to fig.1-3 we can see that the CF (1) in all cases has the limiting value of $g(\nu)$ at $\nu \rightarrow 0$ less than 1. The only exclusion from this rule is the case $\gamma = 1$, but we have seen already that this version has very low accuracy and has other important disadvantages.

The named problem is not specific for QT or TISR. The Cluster Variation Method is another example of theories that meet the same difficulty and similar attention [15–18].

The obvious source of non-physical effects in model theories is the need to introduce some plausible but unproven assumptions when an exact solution is impossible. What is really important in such case, is the necessity to develop criteria clearly outlining the area of applicability.

Sometimes the defect can be fixed by introducing more or less significant modifications to the theory, but usually it creates problems in other places.

As an example, a few existing attempts to exclude negative values of configurational entropy in QT [9, 19] are based on some a priori modifications of the dependency of the CF on the composition and lead to highly nonlinear equations, which are unlikely to have ever been used to describe the real systems [20].

We will show now that:

- Even in the case of ordinary QT (the worst possible case) the negative values of CF are outside of physically meaningful region.
- TISR significantly improves the limiting behavior of CF presenting some remedy to the problem in general;

Indeed, we can see from the presented above pictures that in all cases the part of curve with $g(\nu) < 1$ is located *below* critical point (presented as large red spots in the fig.1-3).

It means that under conditions of thermodynamic equilibrium the negative value for CF cannot be reached. Below critical point the alloy will decay into two alloys of changed composition, so the entire branch below this point becomes irrelevant.

Certainly, this conclusion is valid only for equiatomic alloys presented in fig.1-3. It is still possible that even in this case the alloy will be found in a metastable state where we may find $g(\nu) < 1$.

To response to these concerns we will now calculate the entropy of the system along the spinodal [5] that presents the limiting curve separating stable and metastable compositions from completely unstable ones.

For this end we can use the equation for spinodal derived in[1]:

$$(1 - \gamma)k \sum_{i,l} (i - l)^2 W_i W_l c^{i+l} + 2\gamma \sum_i i W_i c^i \sum_l (k - l) W_l c^l = 0 \quad (13)$$

where k is the cell's size.

In the case of Quasichemical Theory ($k = 2$) W_1 is the only not trivial W_i variable in the equation (13) and this (quadratic) equation can be easily solved, defining W_1 as a function of c .

Using this solution we can calculate entropy S along spinodal (see fig.4 where S is presented as function of concentration x_1 rather than θ). Spinodal defines essential relationship between composition x_1 and temperature θ that allows this presentation.

The resulting figure provides visual proof that the negative values of configurational entropy remain outside of physically meaningful region.

To extend this conclusion on other versions of combinatorial factor we must to understand how this factor is changing from case to case.

We can see from fig.1-3 that transition from the QT case to IQT version provides some improvements in limiting behavior of CF. Both the width of the area where $g(\nu) < 1$ and the severity of the defect itself become smaller when switching from QT to IQT.

Additional improvements become evident when we switching from cells-dimers to cells containing more than two atoms.

The cumulative improvement effect is achieved when we switch to larger cells and simultaneously use parameter γ adjusted to the correct critical temperature.

Figure 4: Entropy S along spinodal for Cubic Lattice:
 Quasichemical approximation – blue line
 Improved Quasichemical approximation – red line

Based on this we can conclude that in all mentioned cases entropy calculated along the spinodal remains positive.

The fact that negative values of combinatorial factor are outside of physically accessible region is good known for the case of Quasichemical Theory [19]. We trying above to bring some arguments to extend this conclusion on IQT case.

However, [19] contains also an important assumption regarding systems with negative deviations from ideality, which we could not agree with.

According [19], in case of liquid alloys system will remain in the state described by the right branch of CF (see for example fig.2) even at extremely low temperatures because long range order (LRO) cannot be established in a liquid and therefore there is no concurrent phase to compete.

We would like to bring up immediately an example where this logic certainly fails.

If we consider, as example, system NaCl in liquid state, we know that LRO cannot exist, however we are sure that every cation is surrounded by anions and every anion – by cations. We have here case of SRO that is extremely close to LRO and it is a very

common picture for systems with very high negative deviations from ideality.

Two-sublattice model for liquid alloys is indeed meaningful and very useful. As example, we can point to other work of Hillert at all: [21].

Desire to find a form of CF that totally excludes negative values of combinatorial factor can be understood, though not very fruitful if we planning to extend formalism outside the Ising model. Nevertheless at the end of this section we would like to present one more attempt of this kind. It is possible thanks to the very specific form of CF (1) introduced by TISR.

Namely, in case of $2d$ square lattice, TISR allows for a very radical approach that could potentially kill non-physical values (but introduces some non-linearity that we consider too high a price).

Short description of this method may be still interesting.

To completely prevent the appearance of negative entropy values, the following limiting behavior of $g(\nu)$ should be ensured:

$$\lim_{\nu \rightarrow 0} g(\nu) = 1 \quad (14)$$

hoping that it will simultaneously exclude the values with $g(\nu) < 1$.

Using formula (1) for CF with $x_1 = x_2 = 1/2$ and applying it to the Quasichemical case we can bring (14) to the following form:

$$\lim_{\nu \rightarrow 0} \ln g(\nu) = (1 - \frac{\gamma}{2}) \ln 2 \quad (15)$$

If $\gamma = 1$, this expression (proportional to the entropy of alloy) occurs positive, confirming the above made conclusion that Bragg-Williams approximation, when applied to the groups of atoms, makes the alloy excessively stable and excludes therefore the immiscibility phenomenon.

Condition (15) is evidently satisfied at $\gamma = 2$.

At high temperatures, when ν approaches 1, we want γ to be close to the Quasichemical value $\gamma = z = 4$.

Based on these considerations we can try to introduce direct dependency of γ on ν . As shown, the resulting expression is supposed to have the specific limiting values when $\theta \rightarrow 0$ or $\theta \rightarrow \infty$ and the simplest formula of this type can be written as:

$$\gamma(\nu) = 4 - 2abs(\nu - 1)^{1.5} \quad (16)$$

This non-linear generalization of TISR seems quite convincing (see the dotted line in fig.1); however, we must understand that the inherited from QT primitive type of dependency of the CF on the composition will ultimately limit the quality of the obtained theory.

It is important also to understand that generalization of approximation (16) on multiatomic cells is quite problematic. Only at $k = 2$ the free energy can be expressed as explicit function of ν . In case of larger cells, both the free energy F and parameter ν (which can actually be considered as a dimensionless form of energy) should be considered as mathematical *functionals* depending on the complete distribution $\{M_{i\alpha}\}$ and

this pure mathematical fact will lead to extremely nonlinear equations, destroying all the advantages of theory.

5 Conclusion

Proposed in [1] combinatorial factor of multiatomic alloy is based on assumptions that are best satisfied at high temperatures and become less reliable when consideration approaches the upper critical solution temperature.

At the same time, the theory includes a structural parameter γ , closely related to the level of atomic correlations in the system. In [1] this parameter was selected according to the assumptions of the so-called "non-interference hypothesis" [3].

In current article, the parameter γ is chosen differently to improve the accuracy of the theory in the most physically significant area from the high temperatures to the critical point.

The result is a significant improvement, at least in some aspects:

- Theory reproduces the correct critical temperature of Ising alloy;
- The accuracy of thermodynamic values calculated near the critical point increases from 10 - 20% (and even worse for 2d structures) to 5 - 10%

These improvements are expected to be very important in the calculation of the phase diagrams, where the correct description of the critical point, if any, can determine the quality of the entire chart.

Improved values of γ are calculated for a few Ising lattices and several choices of cell's size, as presented in the table.1.

Data in the table show that increase in the size of cells doesn't have significant effect on the quality of approximation while the adjustment to correct critical temperature causes much more significant improvements.

At the same time usage of multiatomic cells is absolute necessity when considering negative deviations from the ideality inside frustrated lattices. Quasichemical approximation is qualitatively and quantitatively incorrect in this case.

Detailed analysis leads also to the very important conclusion that the Bragg-Williams approximation should never be applied to atomic clusters, but only to individual atoms.

Combinatorial factor from TISR is the correct alternative in both cases.

As good known, Quasichemical Theory predicts negative combinatorial entropy of mixing at low temperatures. This defect remains in place in all generalization cases, though in significantly reduced form.

Thorough investigation shows that in all considered cases negative values of combinatorial entropy are outside of physically accessible region and therefore cannot be considered as obstacle for successful usage of QT or TISR.

The improved values of structural parameter of theory γ are collected in the table.1 and can be directly applied to a solid mixtures. We meet some uncertainties when applying theory to a liquid alloy where "type of the lattice" or even "coordination number of lattice" have only conditional meaning.

In this case the only possible approach is to use γ as an adjustable parameter, as was already done in [22].

In general, it is important to understand that the improvements presented in this article are achieved without destroying the specific advantages of the theory: flexibility, minimalist set of adjustable parameters, and very reasonable level of precision in calculating the thermodynamic functions.

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