Generalized Lattice Model of Multi-Component Systems with Internal Degrees of Freedom. I. General consideration

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Abstract

The paper contains the generalization of usual lattice model of multicomponent systems. The generalization is related to account the following factors: 1. The short-range parts of interatomic repulsions. These repulsions are not identical for different pairs of atoms, therefore it is impossible to take into account the repulsions by means of usual ideal lattice introduction. 2. The long-range interatomic potentials take into account by means of effective fields approximation. 3. The presence the interatomic potentials depending on some inner degrees of freedoms such as atomic electric and/or magnetic momentum. The Helmholtz free energy functional in the generalized lattice model is reduced to the Ginzburg-Landau-Cahn-Hilliard-like (GLCH) form. The connection between the interatomic potentials characteristics and the parameters of the GLCH-like functional is obtained. The equations for both full and partial equilibrium distributions of the species in multicomponent systems are derived.

PACS numbers: 05.20.-y, 05.70.-a, 82.65.+r

Keywords: Lattice model, Free energy, Phase equilibrium, Long-range and short-range interatomic potentials, Cahn-Hilliard and Ginzburg-Landau models

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I. INTRODUCTION

The problem of quantitative description of multicomponent systems is interesting from both theoretical and practical points of view. The theoretical description of real systems from “first principles” is now impossible because of absence of constructive methods of partition functions calculations for realistic models. Therefore the only way of the realistic models investigations is the phenomenological approach based on some additional assumptions. One of the most popular phenomenological approaches to statistical thermodynamics of condensed systems is the Cahn-Hilliard and Ginzburg-Landau approximation. Application of these very attractive models has some well known restrictions. Most essential of these restrictions is absence of concrete relations between models parameters and characteristics of constituents and their interactions.

At construction of the theory of these structures there is a lot of the difficulties caused by absence of constructive methods of the analysis of realistic models of substance from “first principles”. Therefore it is necessary to be content with development of phenomenological models. The examples of such models are Ginzburg-Landau [1], Cahn-Hilliard [2, 3, 4] models and the various variants of lattice and cell models [5, 6, 7, 8].

The basic idea of lattice models consists on introduction of some ideal lattice on which sites atoms of components are distributed. This idea allows to consider the identical short-range repulsions between atoms, but does not allow to consider differences in repulsions of the components. Most essential disadvantages of the lattice models are well known:

1. The assumption of some lattice existing independently of difference between components proper atomic sizes. This assumption is comparatively plausible by the condition of vanishingly small difference of the components atomic sizes. As a rule, this condition takes no place. Really, introduction of lattice is the way the short-range parts of interatomic potentials account. Difference of short-range parts of components interatomic potentials leads to lattice distortions and the notion of the lattice, strictly speaking, in this case becomes invalid.

2. The postulate on Fermi-like functional form of distribution function for average occupations numbers has not any theoretical justification — there are infinitely many functions with range of values [0; 1].

3. Interatomic potentials in lattice-like models of condensed systems, as a rule, cannot be described with small number of parameters, such as interaction energy of nearest neighbors interactions. The unavoidable lattice distortions lead to the changes of interatomic distances and short-range parts of interatomic potentials are not slowly changing functions.

4. The assumption on pair-wise interatomic potentials is not very convincing, because all the interatomic interactions appear as result of the averaging over fast electronic degrees of freedom in system. These degrees of freedom are very sensitive to atom coordination environment.

Ginzburg-Landau and Cahn-Hilliard models contain a set of phenomenological parameters which connections with real physical characteristics of the components and their interactions remains hidden.

The generalized lattice model (GLM) of multicomponent condensed systems (such as solid or liquid solutions) was proposed in papers [9, 10, 11] and developed in [12, 13, 14]. In
contradistinction to usual lattice model (see for example [5, 6, 7, 8]), the GLM takes into account the following factors:

1. The short-range interatomic repulsions [9]. These repulsions are not identical for different pair of atoms, therefore it is impossible to take into account the repulsions by means of lattice introduction (at best, the lattice model can be considered as method of short-range interactions account in the case of one-component system and that with some essential restriction, related in particular to thermal defects).

2. The presence of the local fields due to the long-range parts of the interatomic potentials [10]. These fields have the essential influence on both equilibrium properties [9] and non-equilibrium processes [11] on the corresponding scales.

3. The connection between the GLM and the Ginzburg-Landau approximation is obtained in paper [12]. The relation of some characteristics of the components and their interatomic potentials with Ginzburg-Landau parameters is established. This relation makes possible to use the mathematical tools of the Ginzburg-Landau and Cahn-Hilliard approximations for the GLM research.

4. The existence of comparatively stable polyatomic complexes that manifest itself in both thermodynamics and kinetics as one and indivisible particles [13].

The present paper contains further development of the GLM. In addition to the previous results it takes into account the following factors:

1. Existence of the internal atomic degrees of freedom such as atomic electric and magnetic moments. These degrees of freedom are responsible for the local magnetization and local electric polarization in the system.

2. Reduction of the GLM to the Ginzburg-Landau-Cahn-Hilliard-like (GLCH) functional form. In contrast to the GLCH theory, this functional contains the well defined parameters that have direct connections with the characteristics of the constituents and their interactions.

3. Colossal times of the structure transformation and the equilibrium reaching. Real condensed systems are, as a rule, essentially non-equilibrium systems.

4. The presence of the hierarchy of relaxation times in real condensed systems and related partially equilibrium states of the systems. The evoluntional processes rearrangements in such systems have multi-stepped character.

5. Absence of full thermodynamic equilibrium in the system.

All the results are formulated on the basis of the unified mathematical apparatus and the common physical ideas. All the approximations have clear physical sense, well foundations, and strictly based conditions of the applicability.
II. GENERALIZED LATTICE MODEL — THE BASIC NOTIONS AND RELATIONS

A. Conditions for free energy

The basic idea of the lattice models is the assumption that particles are located in sites of some ideal lattice. This assumption is incompatible with differences of atomic sizes of the components and with presence of the various kinds defects in real condensed systems.

Therefore let us introduce instead of the ideal lattice the connections between local densities of the components with a view to take into account the differences of the atomic sizes of the components and the various kinds of defects in the system.

It should be noted that the short-range repulsive parts of the interatomic potentials lead, in particular, to some restriction on the local densities $n_i(r)$ of the constituents particles numbers in the system

$$n_i(r) \leq \frac{1}{\omega_i},$$

where $\omega_i$ is the inverse value of the maximal local density of $i$-th component ($i = 1 \div m$, $m$ is the number of the components in the system). The quantity $\omega_i$ has dimensionality of volume and henceforth will called as the specific atomic volume of $i$-th component. As far as the quantity $\omega_i n_i(r)$ is the local volume fraction of $i$-th component at the point $r$, then we have the restrictions on the local densities of the components for all points in the system:

$$\sum_{i=1}^{m} \omega_i n_i(r) \leq 1. \quad (2)$$

Let us introduce the additional component — the vacancies (or holes) with their proper volume $\omega_0$ and local density $n_0(r)$. Suppose the holes do not interact with real components but they fill all the unavoidably existent vacant places in the system (such as thermal or radiation defects). With account of the vacancies we have the following the packing condition:

$$\sum_{i=0}^{m} \omega_i n_i(r) - 1 = 0. \quad (3)$$

The minimization of free energy should be realized under the packing condition, which takes into account the short-range parts of the interatomic potentials in the system. Hence the interatomic potentials should be included into the free energy with cutting out their the short-range parts:

$$K_{ij}(r) = \begin{cases} W_{ij}(r), & \text{if } |r| \geq a_{ij}, \\ 0, & \text{otherwise,} \end{cases} \quad (4)$$

where $W_{ij}(r)$ is “true” interaction potential between $i$-th and $j$-th components, $a_{ij}$ are the cutting parameters, related to the specific atomic volumes of the components by the relations

$$a_{ij} \simeq \left[ (\omega_i)^{1/3} + (\omega_j)^{1/3} \right]. \quad (5)$$

Beyond the packing condition (3) the numbers $N_i$ of components atoms in the system should be fixed at the free energy minimization. These conditions have the following form:

$$\int_{(V)} n_i(r) \, dr - N_i = 0, \quad i = 0 \div m. \quad (6)$$
The packing condition (3) and condition of numbers particles conservation (6) should be satisfied for any form of the configuration part of the free energy.

B. Configuration part of free energy

Denote by $K_{ij}(\mathbf{r} - \mathbf{r}')$ the long-range part of the independent of the inner degrees of freedom (such as their electric and magnetic moments) potential energy of $i$-th and $j$-th interacting particles located in points $\mathbf{r}$ and $\mathbf{r}'$, respectively.

The number of $i$-th kind particles in an infinitesimal volume $d\mathbf{r}$ near a point $\mathbf{r}$ is $n_i(\mathbf{r}) d\mathbf{r}$. Similarly, the number of $j$-th kind particles in infinitesimal volume $d\mathbf{r}'$ near a point $\mathbf{r}'$ is $n_j(\mathbf{r}') d\mathbf{r}'$. Then the full energy of interactions between these particles near points $\mathbf{r}$ and $\mathbf{r}'$ is

$$n_i(\mathbf{r}) d\mathbf{r} \ K_{ij}(\mathbf{r} - \mathbf{r}') n_j(\mathbf{r}') d\mathbf{r}'.$$  \(7\)

Hence the inner degrees of freedom independent part energy of the system have a form:

$$U_1 = \frac{1}{2} \sum_{i,j=1}^{m} \iint_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}'.$$  \(8\)

The similar way leads to expression for configuration part of the free energy with account of the atomic electric and magnetic moments of the components:

$$U = \frac{1}{2} \sum_{i,j=1}^{m} \iint_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' +$$

$$+ \frac{1}{2} \sum_{i,j=1}^{m} \iint_{(V)} Q_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{D}_i(\mathbf{r}) \cdot \mathbf{D}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}' +$$

$$+ \frac{1}{2} \sum_{i,j=1}^{m} \iint_{(V)} R_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{M}_i(\mathbf{r}) \cdot \mathbf{M}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}' +$$

$$+ \frac{1}{2} \sum_{i,j=1}^{m} \iint_{(V)} S_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{D}_i(\mathbf{r}) \cdot \mathbf{M}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}',$$  \(9\)

where $\mathbf{D}_i(\mathbf{r})$ and $\mathbf{M}_i(\mathbf{r})$ are electric and magnetic atomic moments of $i$-th components, located at the point $\mathbf{r}$, $K_{ij}(\mathbf{r} - \mathbf{r}')$, $Q_{ij}(\mathbf{r} - \mathbf{r}')$, $R_{ij}(\mathbf{r} - \mathbf{r}')$ and $S_{ij}(\mathbf{r} - \mathbf{r}')$ are long-range parts of the relevant two-body interatomic potentials.

It should be noted that the vacancies do not contribute into the configuration free energy, but their contribution into the free energy due to entropy term:

$$S = -\sum_{i=0}^{m} \int_{(V)} n_i(\mathbf{r}) \ln \left( \frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) d\mathbf{r},$$  \(10\)

where $n(\mathbf{r})$ is the summarized local density of the particles and vacancies

$$n(\mathbf{r}) = \sum_{j=0}^{m} n_j(\mathbf{r}).$$  \(11\)
Thus, the Helmholtz free energy $F$ of the system with account of the non-uniform external electric $\mathbf{E}(\mathbf{r})$ and magnetic $\mathbf{H}(\mathbf{r})$ fields has the following form:

\begin{equation}
F = \frac{1}{2} \sum_{i,j=1}^{m} \int_{(V)} K_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \sum_{i,j=1}^{m} \int_{(V)} Q_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{D}_i(\mathbf{r}) \cdot \mathbf{D}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \sum_{i,j=1}^{m} \int_{(V)} R_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{M}_i(\mathbf{r}) \cdot \mathbf{M}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}' + \frac{1}{2} \sum_{i,j=1}^{m} \int_{(V)} S_{ij}(\mathbf{r} - \mathbf{r}') n_i(\mathbf{r}) n_j(\mathbf{r}') (\mathbf{D}_i(\mathbf{r}) \cdot \mathbf{M}_j(\mathbf{r}')) d\mathbf{r} d\mathbf{r}' + \sum_{i=1}^{m} \int_{(V)} (\mathbf{E}(\mathbf{r}) \cdot \mathbf{D}_i(\mathbf{r})) n_i(\mathbf{r}) d\mathbf{r} + \sum_{i=1}^{m} \int_{(V)} (\mathbf{H}(\mathbf{r}) \cdot \mathbf{M}_i(\mathbf{r})) n_i(\mathbf{r}) d\mathbf{r} + T \sum_{i=0}^{m} \int_{(V)} n_i(\mathbf{r}) \ln \left( \frac{n_i(\mathbf{r})}{n(\mathbf{r})} \right) d\mathbf{r},
\end{equation}

where $T$ is absolute temperature in energetic units.

The equilibrium space distributions of components is determined by minimum of Helmholtz free energy functional with account of the conditions (3) and (9). But it should be noted that beyond this condition we need some additional conditions connecting all the electric $\mathbf{D}_i(\mathbf{r})$ and magnetic $\mathbf{M}_i(\mathbf{r})$ moments with the external fields. Suppose that external fields influence on the orientations of related moments but do not influence on their magnitudes. Hence we have

\begin{equation}
(\mathbf{D}_i(\mathbf{r}))^2 - D_i^2 = 0; \quad (\mathbf{M}_i(\mathbf{r}))^2 - M_i^2 = 0.
\end{equation}

C. The Lagrange functional and full equilibrium in the system

For the minimization of the Helmholtz free energy (12) at the conditions (3), (9), (13) let us introduce the Lagrange functional $\mathcal{L}$ depending on the local densities $n_i(\mathbf{r})$ of the components, their electric and magnetic moments $\mathbf{D}_i(\mathbf{r})$, $\mathbf{M}_i(\mathbf{r})$, the external fields $\mathbf{E}(\mathbf{r})$, $\mathbf{H}(\mathbf{r})$, and the Lagrange multipliers $\Psi(\mathbf{r})$, $\lambda_i(\mathbf{r})$, $\nu_i(\mathbf{r})$, $\mu_i$:

\begin{equation}
\mathcal{L}\{n_i(\mathbf{r})\}, \{\mathbf{D}_i(\mathbf{r})\}, \{\mathbf{M}_i(\mathbf{r})\}, \{\lambda_i(\mathbf{r})\}, \{\nu_i(\mathbf{r})\}, \{\Psi(\mathbf{r})\}, \{\mu_i\} =
\end{equation}

\begin{equation}
= F - \sum_{i=0}^{m} \mu_i \int_{(V)} n_i(\mathbf{r}) \, d\mathbf{r} - N_i - \sum_{i=1}^{m} \int_{(V)} \frac{\lambda_i(\mathbf{r})}{2} \left[ (\mathbf{D}_i(\mathbf{r}))^2 - D_i^2 \right] \, d\mathbf{r} - \sum_{i=1}^{m} \int_{(V)} \frac{\nu_i(\mathbf{r})}{2} \left[ (\mathbf{M}_i(\mathbf{r}))^2 - M_i^2 \right] \, d\mathbf{r} - \int_{(V)} \Psi(\mathbf{r}) \left( \sum_{i=0}^{m} \omega_i n_i(\mathbf{r}) - 1 \right) \, d\mathbf{r}.
\end{equation}
The necessary condition or the extremum of the Lagrange functional is vanishing of the ordinary and functional derivatives with respect to $n_i(r)$, $D_i(r)$, $M_i(r)$, $\Psi(r)$, $\lambda_i(r)$, $\nu_i(r)$, $\mu_i$:

\[
\begin{aligned}
\frac{\delta L}{\delta n_i(r)} &= 0; \\
\frac{\delta L}{\delta D_i(r)} &= 0; \\
\frac{\delta L}{\delta M_i(r)} &= 0; \\
\frac{\delta L}{\delta \Psi_i(r)} &= 0; \\
\frac{\partial L}{\partial \mu_i(r)} &= 0; \\
\frac{\delta L}{\delta \lambda_i(r)} &= 0; \\
\frac{\delta L}{\delta \nu_i(r)} &= 0.
\end{aligned}
\]  

(15)

Simple calculations lead to following system of equations:

\[
\frac{\delta L}{\delta n_i(r)} = 0 \implies \mu_i = -\omega_i \Psi(r) + T \ln \left( \frac{n_i(r)}{n(r)} \right) + \sum_{j=1}^{m} \int_{(V)} K_{ij}(r - r') n_j(r') \, dr' + \\
+ \sum_{j=1}^{m} \int_{(V)} Q_{ij}(r - r') (D_i(r) \cdot D_j(r')) n_j(r') \, dr' + \\
+ \sum_{j=1}^{m} \int_{(V)} R_{ij}(r - r') (M_i(r) \cdot M_j(r')) n_j(r') \, dr' + \\
+ \sum_{j=1}^{m} \int_{(V)} S_{ij}(r - r') \left\{ (D_i(r) \cdot M_j(r')) + (M_i(r) \cdot D_j(r')) \right\}_2 n_j(r') \, dr' + \\
+ (E(r) \cdot D_i(r)) + (H(r) \cdot M_i(r));
\]

(16)

\[
\frac{\delta L}{\delta D_i(r)} = 0 \implies \\
\sum_{j=1}^{m} \int_{(V)} n_i(r) Q_{ij}(r - r') n_j(r') D_j(r') \, dr' + \\
+ \frac{1}{2} \sum_{j=1}^{m} \int_{(V)} n_i(r) S_{ij}(r - r') n_j(r') M_j(r') \, dr' - \lambda_i(r) D_i(r) + E(r) n_i(r) = 0;
\]

(17)
\[
\frac{\delta \mathcal{L}}{\delta M_i(r)} = 0 \implies \sum_{j=1}^{m} \int_{(V)} n_i(r) R_{ij}(r - r') n_j(r') M_j(r') \, dr' + \frac{1}{2} \sum_{j=1}^{m} \int_{(V)} n_i(r) S_{ij}(r - r') n_j(r') D_j(r') \, dr' - \nu_i(r) M_i(r) + H(r)n_i(r) = 0; \tag{18}
\]

\[
\frac{\delta \mathcal{L}}{\delta \Psi_i(r)} = 0 \implies \sum_{i=0}^{m} \omega_i n_i(r) - 1 = 0; \tag{19}
\]

\[
\frac{\partial \mathcal{L}}{\partial \mu_i(r)} = 0 \implies \int_{(V)} n_i(r) \, dr - N_i = 0; \tag{20}
\]

\[
\frac{\delta \mathcal{L}}{\delta \lambda_i(r)} = 0 \implies (D_i(r))^2 - D_i^2 = 0; \tag{21}
\]

\[
\frac{\delta \mathcal{L}}{\delta \nu_i(r)} = 0 \implies (M_i(r))^2 - M_i^2 = 0. \tag{22}
\]

This system of integral equations (16-22) describes the space distributions of the components as well electric and magnetic moments in the system with account of both short-range and long-range parts on interatomic potentials in presence of the external fields. This system of equations take place for the case of full thermodynamic equilibrium in the systems.

Unfortunately, at present there are no effective methods of such kind equations solutions for kernel \(K_{ij}(r), Q_{ij}(r), R_{ij}(r), S_{ij}(r)\) of general form. But under the some conditions this system of equations can be reduced to a system of the partial differential equations. Instead of the interatomic potentials \(K_{ij}(r), Q_{ij}(r), R_{ij}(r), S_{ij}(r)\), the system of partial differential equations contains a set of integral characteristics of the potentials.

III. GINZBURG-LANDAU-CAHN-HILLIARD-LIKE APPROXIMATION

A. Reduction of the Generalized lattice model to Ginzburg-Landau-Cahn-Hilliard-like approximation

There are at least three scales of the sizes in the system:

1. atomic sizes \(a_0\);

2. range of actions of long-range parts of the interatomic potentials \(r_0\);
3. distances $b_0$ on which changes local compositions and/or local moments of the components in the system.

Suppose these parameters obey the inequalities:

$$a_0 \lesssim r_0 \ll b_0. \quad (23)$$

Let us transform the expression for moments-independent part of the configuration energy in (12):

$$F_1 = \frac{1}{2} \sum_{i,j=1}^{m} \int \int_{(V)} K_{ij}(r - r') n_i(r)n_j(r') \, dr \, dr'. \quad (24)$$

With regard to condition

$$|r - r'| \ll b_0 \quad (25)$$

we have

$$n_j(r') \approx n_j(r) + \sum_{s=1}^{3} \frac{\partial n_j(r)}{\partial x_s} (x'_s - x_s) + \frac{1}{2} \sum_{s_1, s_2=1}^{3} \frac{\partial^2 n_j(r)}{\partial x_{s_1} \partial x_{s_2}} (x'_{s_1} - x_{s_1})(x'_{s_2} - x_{s_2}), \quad (26)$$

where $x_s$ and $x'_s$ denote Cartesian components of the vectors $r$ and $r'$, respectively. Substitution of (26) into (24) lead to the result:

$$F_1 (\{n_k(r)\}) = \int_{(V)} \left\{ \frac{1}{12} \sum_{i,j=1}^{m} K_{ij}^{(2)} n_i(r) \Delta n_j(r) + \frac{1}{2} \sum_{i,j=1}^{m} K_{ij}^{(0)} n_i(r) n_j(r) \right\} \, dr, \quad (27)$$

where $\Delta$ is the Laplace operator, $K_{ij}^{(p)}$ are some integral characteristics of the interatomic potentials

$$K_{ij}^{(p)} = \int_{(V)} K_{ij}(r') |r'|^p \, dr'. \quad (28)$$

The expressions for moment-depending parts of configuration energy in (12) can be transformed by analogy:

$$F_2(\{n_k(r)\}, \{D_k(r)\}) = \int_{(V)} \left\{ \frac{1}{12} \sum_{i,j=1}^{m} Q_{ij}^{(2)} (D_i(r)n_i(r) \cdot \Delta [D_j(r)n_j(r)]) + \frac{1}{2} \sum_{i,j=1}^{m} Q_{ij}^{(0)} (D_i(r) \cdot D_j(r)) n_i(r) n_j(r) \right\} \, dr, \quad (29)$$

$$F_3(\{n_k(r)\}, \{M_k(r)\}) = \int_{(V)} \left\{ \frac{1}{12} \sum_{i,j=1}^{m} R_{ij}^{(2)} (M_i(r)n_i(r) \cdot \Delta [M_j(r)n_j(r)]) + \frac{1}{2} \sum_{i,j=1}^{m} R_{ij}^{(0)} (M_i(r) \cdot M_j(r)) n_i(r) n_j(r) \right\} \, dr, \quad (30)$$
\[ F_d(\{n_k(r)\}, \{D_k(r)\}, \{M_k(r)\}) = \int_{(V)} \left\{ \frac{1}{12} \sum_{i,j=1}^{m} S_{ij}^{(q)} (D_i(r)n_i(r) \cdot \Delta [M_j(r)n_j(r)]) + \right. \]
\[ + \frac{1}{2} \sum_{i,j=1}^{m} S_{ij}^{(p)} (D_i(r) \cdot M_j(r)) n_i(r) n_j(r) \right\} \, dr, \tag{31} \]

where \( Q_{ij}^{(q)}, R_{ij}^{(q)} \) and \( S_{ij}^{(p)} \) are the integral characteristics of the moment-depending parts of the interatomic potentials determined by perfect analogy with \([28]\).

Substitute \([28], [29], [30]\) and \([31]\) into \([12]\):

\[ F(\{n_k(r)\}, \{D_k(r)\}, \{M_k(r)\}) = \int_{(V)} \left\{ \frac{1}{12} \sum_{i,j=1}^{m} \left[ K_{ij}^{(2)} n_i(r) \Delta n_j(r) + \right. \right. \]
\[ + Q_{ij}^{(2)} (D_i(r)n_i(r) \cdot \Delta [D_j(r)n_j(r)]) + R_{ij}^{(2)} (M_i(r)n_i(r) \cdot \Delta [M_j(r)n_j(r)]) + \]
\[ + S_{ij}^{(2)} (D_i(r)n_i(r) \cdot \Delta [M_j(r)n_j(r)]) \right\} + \]
\[ + \frac{1}{2} \sum_{i,j=1}^{m} \left[ K_{ij}^{(0)} + Q_{ij}^{(0)} (D_i(r) \cdot D_j(r)) + R_{ij}^{(0)} (M_i(r) \cdot M_j(r)) + \right. \]
\[ + S_{ij}^{(0)} (D_i(r) \cdot M_j(r)) \right] n_i(r) n_j(r) + \]
\[ + \sum_{i=1}^{m} \left[ (E(r) \cdot D_i(r)) n_i(r) + (H(r) \cdot M_i(r)) n_i(r) + T n_i(r) \ln \left( \frac{n_i(r)}{n(r)} \right) \right] \right\} \, dr. \tag{32} \]

The next step is using the Green formula

\[ \int_{(V)} u(r) \Delta v(r) \, dr = - \int_{(V)} (\nabla u(r) \cdot \nabla v(r)) \, dr, \tag{33} \]

that has place if the functions \( u(r), v(r) \) and their gradients \( \nabla u(r), \nabla v(r) \) vanish on the boundary of domain \( V \). Using this formula, the terms with Laplacians in \([32]\) take the following forms:

\[ \int_{(V)} n_i(r) \Delta n_j(r) \, dr = - \int_{(V)} (\nabla n_i(r) \cdot \nabla n_j(r)) \, dr, \tag{34} \]

\[ \int_{(V)} (D_i(r)n_i(r) \cdot \Delta [D_j(r)n_j(r)]) \, dr = - \int_{(V)} \sum_{\alpha=1}^{3} \left( \nabla [D_{i\alpha}(r)n_i(r)] \cdot \nabla [D_{j\alpha}(r)n_j(r)] \right) \, dr, \tag{35} \]
\[ \int_{V} (\mathbf{M}_i(r) n_i(r) \cdot \Delta [\mathbf{M}_j(r) n_j(r)]) \, dr = - \int_{V} \sum_{\alpha=1}^{3} (\nabla [M_{i\alpha}(r) n_i(r)] \cdot \nabla [M_{j\alpha}(r) n_j(r)]) \, dr, \]  

(36)

\[ \int_{V} (\mathbf{D}_i(r) n_i(r) \cdot \Delta [\mathbf{M}_j(r) n_j(r)]) \, dr = - \int_{V} \sum_{\alpha=1}^{3} (\nabla [D_{i\alpha}(r) n_i(r)] \cdot \nabla [M_{j\alpha}(r) n_j(r)]) \, dr, \]  

(37)

where \( D_{i\alpha}(r) \) and \( M_{i\alpha}(r) \) denote components of the vectors \( \mathbf{D}_i(r) \) and \( \mathbf{M}_i(r) \), respectively.

As a result, we have the following expression for the Helmholtz free energy functional:

\[
F \left( \{n_k(r)\}, \{\mathbf{D}_k(r)\}, \{\mathbf{M}_k(r)\} \right) = \int_{V} \left\{ -\frac{1}{12} \sum_{i,j=1}^{m} \left[ K_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla n_j(r)) + \right. \right.
\]

\[ + Q_{ij}^{(2)} \sum_{\alpha=1}^{3} (\nabla [D_{i\alpha}(r) n_i(r)] \cdot \nabla [D_{j\alpha}(r) n_j(r)]) + \]

\[ + R_{ij}^{(2)} \sum_{\alpha=1}^{3} (\nabla [M_{i\alpha}(r) n_i(r)] \cdot \nabla [M_{j\alpha}(r) n_j(r)]) + \]

\[ + S_{ij}^{(2)} \sum_{\alpha=1}^{3} (\nabla [D_{i\alpha}(r) n_i(r)] \cdot \nabla [M_{j\alpha}(r) n_j(r)]) + \right. \right\} \]

\[ \left. \frac{1}{2} \sum_{i,j=1}^{m} \left[ K_{ij}^{(0)} + Q_{ij}^{(0)} (\mathbf{D}_i(r) \cdot \mathbf{D}_j(r)) + R_{ij}^{(0)} (\mathbf{M}_i(r) \cdot \mathbf{M}_j(r)) + \right. \right. \]

\[ + S_{ij}^{(0)} (\mathbf{D}_i(r) \cdot \mathbf{M}_j(r)) \right) n_i(r) n_j(r) + \]

\[ + \sum_{i=1}^{m} \left[ (\mathbf{E}(r) \cdot \mathbf{D}_i(r)) n_i(r) + (\mathbf{H}(r) \cdot \mathbf{M}_i(r)) n_i(r) + T n_i(r) \ln \left( \frac{n_i(r)}{n(r)} \right) \right] \right\} \, dr. \]

This functional is similar to Ginzburg-Landau and Cahn-Hilliard functionals, but in contrast to these functionals formula (38)

1. is not restricted by the polynomial over order parameters in the integrand;
2. all the parameters in (38) have clear physical sense.

The functional (38) has some essential advantages over the more exact functional (12):

- The expression (38) does not contain any unknown functions of general form (such as interatomic potentials), but contains the finite set of their simple characteristics (numerical parameters) \( K_{ij}^{(p)} \) (28);
Analysis and solution of differential equations, that can be obtained from functional (38), are much more simple problems as solution of non-linear integral equations (16–22) for general case;

The inverse problem — search of parameters using some experimental data (such as phase diagrams) — is the immense problem from the integral equations (16–22), but quite realistic one from the functional (38);

At last, the solution, based on the functional (38), can be used as well initial approximation for much more complicated problems, related to functional (16–22).

There is the necessary condition of the mathematical correctness for the functional (38). The necessity of the fluctuations suppression in the system means that all the matrices $K_{ij}^{(2)}$, $Q_{ij}^{(2)}$, $R_{ij}^{(2)}$, $S_{ij}^{(2)}$ must be negative-definite.

B. The Lagrange functional for GLCH-like approximation and full equilibrium in the system

It should be noted the conditions (3), (6), (13) must satisfied not only for functional (12), but also for functional (38). Let us introduce the Lagrange functional $\mathcal{L}_1$, corresponding to the GLCH-like Helmholtz free energy functional (38), by analogy with (14):

$$\mathcal{L}_1(\{n_k(r)\}, \{M_k(r)\}, \{D_k(r)\}, \{\lambda_k(r)\}, \{\nu_k(r)\}, \{\Psi(r)\}, \mu_k) =$$

$$= F(\{n_k(r)\}, \{D_k(r)\}, \{M_k(r)\}) -$$

$$- \sum_{i=0}^m \mu_i \left[ \int (V) n_i(r) \, dr - N_i \right] - \sum_{i=1}^m \int (V) \frac{\lambda_i(r)}{2} \left[ (D_i(r))^2 - D_i^2 \right] \, dr -$$

$$- \sum_{i=1}^m \int (V) \frac{\nu_i(r)}{2} \left[ (M_i(r))^2 - M_i^2 \right] \, dr - \int (V) \Psi(r) \left( \sum_{i=0}^m \omega_i n_i(r) - 1 \right) \, dr. \quad (39)$$

This functional has the following form:

$$\mathcal{L}_1(\{n_k(r)\}, \{M_k(r)\}, \{D_k(r)\}, \{\lambda_k(r)\}, \{\nu_k(r)\}, \{\Psi(r)\}, \mu_k) =$$

$$= \tilde{\mathcal{L}}_1 + \tilde{\mathcal{L}}_1, \quad (40)$$

where

$$\tilde{\mathcal{L}}_1 = \sum_{i=1}^m \left[ \mu_i N_i + \frac{D_i^2}{2} \int (V) \lambda_i(r) \, dr + \frac{M_i^2}{2} \int (V) \nu_i(r) \, dr \right] + \int (V) \Psi(r) \, dr \quad (41)$$
is the second part of the functional (39), which does not depend in explicit form on functions $D_i(r)$, $M_i(r)$, $n_i(r)$,

$$
\widetilde{L}_1 (\{n_k(r)\}, \{D_k(r)\}, \{M_k(r)\}) = F (\{n_k(r)\}, \{D_k(r)\}, \{M_k(r)\}) - 
- \int (V) \left\{ \sum_{i=1}^{m} \left[ \mu_i n_i(r) + \frac{\lambda_i(r)}{2} D_i^2(r) + \frac{\nu_i(r)}{2} M_i^2(r) + \Psi(r) \omega_i n_i(r) \right] \right\} \, dr \quad (42)
$$

is the second part of the functional (39), which depends on $n_i(r)$, $D_i^\alpha(r)$, $M_i^\alpha(r)$ in explicit form. The last functional has a form

$$
\widetilde{L}_1 (\{u_s(r)\}) = \int (V) \Lambda (u_s(r), \nabla u_s(r)) \, dr, \quad (43)
$$

where $u_s(r)$ denotes all the functions $n_i(r)$, $D_i^\alpha(r)$, $M_i^\alpha(r)$ and

$$
\Lambda (u_s(r), \nabla u_s(r)) = - \frac{1}{12} \sum_{i,j=1}^{m} \left[ K_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla n_j(r)) + Q_{ij}^{(2)} \sum_{\alpha=1}^{3} (\nabla [D_i^\alpha(r)n_i(r)] \cdot \nabla [D_j^\alpha(r)n_j(r)]) + R_{ij}^{(2)} \sum_{\alpha=1}^{3} (\nabla [M_i^\alpha(r)n_i(r)] \cdot \nabla [M_j^\alpha(r)n_j(r)]) +
+ \sum_{i,j=1}^{m} \left[ K_{ij}^{(0)} + Q_{ij}^{(0)} (D_i(r) \cdot D_j(r)) + R_{ij}^{(0)} (M_i(r) \cdot M_j(r)) +
+ S_{ij}^{(0)} (D_i(r) \cdot M_j(r)) \right] n_i(r) n_j(r) +
+ \sum_{i=1}^{m} \left[ (E(r) \cdot D_i(r)) n_i(r) + (H(r) \cdot M_i(r)) n_i(r) + \frac{1}{2} \left[ \lambda_i(r) D_i^2(r) + \nu_i(r) M_i^2(r) \right] +
+ T \ln \left( \frac{n_i(r)}{n(r)} \right) - \mu_i - \Psi(r) \omega_i \right] n_i(r) \right].
$$

The solution of the variational problem for functional (39) is equivalent to solution of the variation problem for functional (12) with conditions (3), (6), (13). Thus, the equilibrium
distributions of the components and their electric and magnetic moments obey the Lagrange-Euler system of equations for functional (43):

$$\frac{\partial \Lambda}{\partial u_s(r)} - \left( \nabla \cdot \frac{\partial \Lambda}{\partial (\nabla u_s(r))} \right) = 0,$$

(45)

together with conditions (3), (6), (13).

Using the Lagrange-Euler equation for $u_s(r) = n_i(r)$ gives the equation:

$$\sum_{j=1}^{m} \left[ K_{ij}^{(0)} + Q_{ij}^{(0)} (D_i(r) \cdot D_j(r)) + R_{ij}^{(0)} (M_i(r) \cdot M_j(r)) + S_{ij}^{(0)} (D_i(r) \cdot M_j(r)) \right] n_j(r) +$$

$$+ \sum_{j=1}^{m} \sum_{\alpha} \left[ Q_{ij}^{(2)} (\nabla D_i^\alpha(r) \cdot \nabla [D_j^\alpha(r)n_j(r)]) + R_{ij}^{(2)} (\nabla M_i^\alpha(r) \cdot \nabla [M_j^\alpha(r)n_j(r)]) +$$

$$+ \frac{1}{2} \left[ S_{ij}^{(2)} (\nabla D_i^\alpha(r) \cdot \nabla [M_j^\alpha(r)n_j(r)]) + S_{ij}^{(2)} (\nabla M_i^\alpha(r) \cdot \nabla [D_j^\alpha(r)n_j(r)]) \right] +$$

$$+ \left[ (E(r) \cdot D_i(r)) + (H(r) \cdot M_i(r)) + T \ln \left( \frac{n_i(r)}{n(r)} \right) \right] - \mu_i + \omega_i \Psi(r) =$$

$$= - \frac{1}{6} \sum_{j=1}^{m} \left[ K_{ij}^{(2)} n_j(r) + \sum_{\alpha} Q_{ij}^{(2)} (\nabla \cdot \{ D_i^\alpha(r) \nabla (D_j^\alpha(r)n_j(r)) \}) +$$

$$+ \sum_{\alpha} R_{ij}^{(2)} (\nabla \cdot \{ M_i^\alpha(r) \nabla (M_j^\alpha(r)n_j(r)) \}) +$$

$$+ \frac{1}{2} \sum_{\alpha} S_{ij}^{(2)} \left\{ (\nabla \cdot \{ D_i^\alpha(r) \nabla (M_j^\alpha(r)n_j(r)) \}) + (\nabla \cdot \{ M_i^\alpha(r) \nabla (D_j^\alpha(r)n_j(r)) \}) \right\} \right];$$

(46)

Using the Lagrange-Euler equation for $u_s(r) = D_i^\alpha(r)$ gives the equation:

$$\sum_{j=1}^{m} \left\{ Q_{ij}^{(0)} D_j^\alpha(r) + \frac{1}{2} S_{ij}^{(0)} M_j^\alpha(r) \right\} n_i(r) n_j(r) + E^\alpha(r) n_i(r) + \lambda_i(r) D_i^\alpha(r) -$$

$$- \frac{1}{6} \sum_{j=1}^{m} \left\{ Q_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla [D_j^\alpha(r)n_j(r)]) + \frac{1}{2} S_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla [M_j^\alpha(r)n_j(r)]) \right\} =$$

$$= - \frac{1}{6} \nabla \cdot \sum_{j=1}^{m} \left\{ Q_{ij}^{(2)} n_i(r) \nabla [D_j^\alpha(r)n_j(r)] + \frac{1}{2} S_{ij}^{(2)} n_i(r) \nabla [M_j^\alpha(r)n_j(r)] \right\};$$

(47)

Similarly, using the Lagrange-Euler equation for $u_s(r) = M_i^\alpha(r)$ gives the equation:

$$\sum_{j=1}^{m} \left\{ R_{ij}^{(0)} M_j^\alpha(r) + \frac{1}{2} S_{ij}^{(0)} D_j^\alpha(r) \right\} n_i(r) n_j(r) + H^\alpha(r) n_i(r) + \nu_i(r) M_i^\alpha(r) -$$

$$- \frac{1}{6} \sum_{j=1}^{m} \left\{ R_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla [M_j^\alpha(r)n_j(r)]) + \frac{1}{2} S_{ij}^{(2)} (\nabla n_i(r) \cdot \nabla [D_j^\alpha(r)n_j(r)]) \right\} =$$

$$= - \frac{1}{6} \nabla \cdot \sum_{j=1}^{m} \left\{ R_{ij}^{(2)} n_i(r) \nabla [M_j^\alpha(r)n_j(r)] + \frac{1}{2} S_{ij}^{(2)} n_i(r) \nabla [D_j^\alpha(r)n_j(r)] \right\}. $$

(48)

The system of equations (46, 47, 48) with conditions (3), (6), (13) describes space distributions of the components and local electric and magnetic moments for the case of full thermodynamic equilibrium in the system.
C. Partial equilibrium in the system

It should be noted that in view of colossal times of relaxations for solid state systems, the full thermodynamic equilibrium as a rule does not realizable. In the best way, there are the particular equilibriums in real solid state structures.

In particular, for inhomogeneous layered systems with electric and magnetic degrees of freedom relaxation times related to electric and magnetic degrees of freedom are short whereas times of redistribution of the components have a colossal scales. Thus, the order parameters related to slow degrees of freedom, are not equilibrium parameters. They predetermine by the prehistory of the samples and should be preassigned.

Suppose that the slow variables in the system are space distributions of the components \( n_i(r) \), whereas distributions of the electric \( D_i(r) \) and magnetic \( M_i(r) \) moments are the fast variables. Then the functions \( n_i(r) \) should be prescribed, but the functions \( D_i(r) \) and \( M_i(r) \) obey the equations (47, 48) and (3, 6, 13).

IV. CONCLUSION

This paper sets as a goal development the unified theoretical approach to both statistical thermodynamics and kinetic phenomena in microheterogeneous systems with account their most essential real peculiarities:

1. Presence of some inner degrees of freedom of constituent atoms (such as their atomic electric and magnetic moments);

2. Presence of the competitive short-range and long-range parts of the components interatomic potentials;

3. Presence of essential difference of the components atomic sizes. In particular, owing to this difference there are no ideal lattices in the real condensed matter.

It should be noted that such peculiarities as misfits on the phases boundaries, deformations fields, and local elastic properties of the matter in microheterogeneous systems are caused mainly by the interatomic potentials. Therefore, the correct account of the indicated peculiarities of the real systems should be as basis for the adequate model of the real microheterogeneous systems, especially for the layered and composite systems with essential magnetoelectric interaction.

There are many works dealing with theoretical research of microheterogeneous systems with the magnetoelectric effect. The reviews of some results on the subject my be find in papers [15, 16, 17, 18]. Most of the theoretical papers are based on the phenomenological Ginzburg-Landau-like free energy functional with additional terms considering lattices distortions and misfits on the interphase boundaries [19, 20]. There is a series of the papers by Khachaturyan with co-workers [21, 22] based on the phase field approach to composites. As a rule the nature of the phenomenological parameters remains hidden.

It should be noted the very interesting works on the statistical properties and random geometry of inhomogeneous systems [23].

The present paper contains the other approach to statistical thermodynamics of the multicomponent condensed matter. The main peculiarities of this approach consist of following.
1. Instead of the ideal lattices we introduce the packing condition [3]. This condition allows to take into account essential differences of the components atomic sizes.

2. We take into account the long-range parts of the interatomic potentials by means of the effective fields approximation. Owing to packing condition the GLM as a whole falls outside the limits of the effective fields approximation.

3. We take into account the interatomic potentials depending on inner degrees of freedoms such as atomic electric and/or magnetic momentum. The magnetoelastic interactions are included in the implicit form.

4. The Helmholtz free energy functional for the generalized lattice model with account of electric and magnetic atomic moments is reduced to GLCH-like form. The connection between the interatomic potentials and parameters of the GLCH-like functional is established.

One of the most interesting applications of the GLM is research of layered structures with alternation of magnetic and ferroelectric layers. In particular, this approach permits

- to take into account lattices misfits on the interphases without any auxiliary assumptions;
- to impart the physical interpretation to the phenomenological models like GLCH;
- to find the ways for prognosis of the layered structures.

These results will be presented in the next papers.

Acknowledgments

The work was partially supported by the Program of Russian Ministry of Education and Science.

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