ISSN 2070-2051, Protection of Metals and Physical Chemistry of Surfaces, 2020, Vol. 56, No. 4, pp. 671–681. © Pleiades Publishing, Ltd., 2020.
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PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

Basics of Calculating the Surface Properties of Solid Solutions Taking the Ordering of Components into Account

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Received December 25, 2019; revised February 25, 2020; accepted March 3, 2020

Abstract—An approach for calculating the surface thermodynamic characteristics of solid solutions (alloys, salts, oxides, ferroelectrics, and nonstoichiometric compounds) with different degrees of ordering at the vapor–solid interface is formulated on the basis of the lattice gas model. This approach is the only one that makes it possible to describe the properties of phases and transition regions between equilibrium coexisting phases with equal accuracy. The model is constructed for the mixture components having comparable (but different) sizes with an arbitrary type of ordered structures in the bulk phase. The type of ordering is determined by some pattern formed by different sublattices periodically repeated in space. The transition region between the solid solution and vapor is a multilayered region with a variable density of components. Interatomic interaction potentials are taken into account in the approximation of pair contributions with preservation of direct correlation effects for several coordination spheres. A change of variables was used to reduce the equilibrium set of equations to component distributions, which allows one to reduce the problem to the dimensionality of the concentration profiles of components in the transition region. The case of nonequilibrium states of a solid solution and description of its evolution by kinetic equations are discussed. Finding the concentration profile of a solid solution allows one to evaluate the state of the interface roughness, the specific area of the rough surface, and the surface segregation of the solution components, and to analyze the effect of the surface segregation on the degree of ordering of the solution components in the transition region.

Keywords: surface tension of solid solutions, alloys, salts, oxides, ferroelectrics, nonstoichiometric compounds, surface segregation of components, interface roughness, lattice gas model

DOI: 10.1134/S2070205120040255

INTRODUCTION

The phenomenon of ordering is associated with the regular alternation of solid solution components that form the so-called “order” [1–4]. The emergence of ordering changes many physicochemical properties of solid solutions; therefore, their study is of great interest. It is well known that Landau’s phenomenological theory [5–10] based on the introduction of an order parameter is applied to this phenomenon, which is widely used for interpreting structural phase transitions in various compounds, salts, oxides, alloys, and ferroelectrics [11–13].

In parallel, model concepts regarding the microscopic nature of the processes of redistribution of components in solid solutions of different nature were being actively developed [1–3, 14–16]. These approaches were used to explain the experimental data on magnetic, electrical, mechanical, structural, and other bulk properties. Similarly, microscopic approaches were used to discuss the surface properties of solids [17–32].

However, thermodynamic approaches have been used and are being used to describe the surface properties of solids even more actively than microscopic approaches [33–36]. Let us remind that studies devoted to surface phenomena occupy an important place in the literature on thermodynamics of solids. Nevertheless, both purely thermodynamic and phenomenological approaches have turned out to be insufficiently substantiated and accurate. The most obvious example of such a discrepancy is the issue of the values and even the sign of the surface tension (ST) of solids. The source of this discrepancy is fundamental study [37] by Gibbs, who introduced the following two types of surface tension depending on the method of formation of a solid surface: surface tension due to mechanical disturbances that lead to the creation of a new surface and surface tension due to precipitation and crystallization processes that can be carried out under conditions that are close to equilibrium conditions.

It has been shown only recently that such a discrepancy is associated with strong nonequilibrium behavior of real solids, in which the surface formation process depends on the process conditions [38]. This means that it is impossible to take any mechanically stable state of a solid as an equilibrium state without experimental proof of its equilibrium. It is independence on the path of transition from the initial state to the final one that is the main indication of reaching equilibrium by the system and its existence in a state of equilibrium. Therefore, solids are in a nonequilibrium state in the vast majority of cases. It follows that the theory of solid–vapor interfaces should reflect the entire range of possible states of the system.

Thermodynamic equations do not depend on the aggregate state or phase state of the system [37]; therefore, Gibbs's thermodynamic definition for ST equally applies to all types of coexisting phases. A statistical approach was proposed in [39, 40] that satisfies the condition of complete phase equilibrium and Gibbs's definition for ST and is consistent with the ratio of relaxation times of the mass transfer and momentum transfer processes. Let us recollect that the condition of complete phase equilibrium means the presence of three types of partial equilibria, such as the mechanical (in pressure), thermal (in temperature), and chemical (in chemical potential) equilibria, each of which has its own relaxation time. The experimental data for these relaxation times correspond to relations $\tau_{\rm imp} \ll \tau_{\rm tem} \ll \tau_{\rm mas}$ [41, 42]; i.e., the relaxation time of the mass is much longer than the relaxation time of the momentum. An excess of free energy in coexisting phases rather than a hydrostatic approach with balancing stresses is taken as a basis for Gibbs's thermodynamic definition. In order for the transition region of the interface to exist, it is necessary to have exactly the same three partial equilibria inside each point of the transition region [39, 40], together with the need to use the equimolecular surface of the separating surface for a pure substance or its analogue in mixtures [33, 43].

The aim of this study is to develop a method for calculating the surface characteristics of solid solutions with consideration of the ordered state of solid solution components inside the bulk phases and their correlated distribution. To solve the problem of describing the interface between an ordered alloy and vapor, it is reasonable to take advantage of the molecular approach based on the lattice gas model (LGM) [28, 38, 44]. This approach covers the density of all three aggregate states, and this is the only approach enabling the self-consistent description of all three types of two-phase interfaces from a single point of view. It takes into account the interactions between the mixture components comparable in size. The LGM equations reflecting the discrete spatial distribution of the mixture components are constructed taking into account direct correlations in the modified quasi-chemical approximation (QCA), allowing for the inclusion of component oscillations. The theory also focuses on the description of the effects of the interface roughness, which allows one to estimate their specific surface areas, the surface segregation of components, the region of disappearance of ordering near the interface, etc.

The proposed approach differs from the existing level of studies by providing a possibility to describe in more detail the behavior of the thermodynamic characteristics of ordered systems at the interface. The phase-transition methods based on order parameters are analogous theoretical approaches that are widely known in the literature. They operate with approximations that ignore short-range correlations effects for ordered structures near the interface. In the systems under discussion, the methods of stochastic Monte Carlo simulation (compared to which the new theory is characterized not only by significant speed, but also greater accuracy) or the variational cluster method [45, 46] (compared to which our approach better describes the degree of defectiveness in the phase volume and the rough structure of interface) are also used.

Under real conditions, a lot of contacting phases with components that are not in equilibrium are present at the solid–vapor interface. These chemically nonequilibrium systems are in a state of mechanical equilibrium and an approach used in [39, 40] can also be applied to them, taking into account the fact that the evolution of the solid phase is described by kinetic equations and a thermodynamically equilibrated distribution of mobile phases and mechanical equilibrium are established in the solid phase and at its boundary at each point in time [38, 47]. In this case, one can use, instead of the equilibrium thermodynamic potentials, nonequilibrium analogues that have the same form as the equilibrium potentials through the unary and pairwise distribution functions. This allows us to formulate the following conditions for calculating nonequilibrium STs and other analogues of thermodynamic potentials: it is necessary to have equations for the concentration profile near the interface, and, for this purpose, it is necessary to have self-consistent kinetic equations that can be transformed, in the limit, into the equilibrium distributions of components at the interfaces.

Obviously, the derivation of equations begins with a strictly equilibrium case. A technique for such a derivation has been published [28, 29], and the main results are given here. We formulate a microscopic model that allows us to simultaneously take into account both the effects of ordering of solid solution components and nonuniform distribution of the components over the layers of the transition region between the vapor and the bulk phase of the solution. The obtained equations show how the surface characteristics depend on the microscopic distribution functions (DFs), the time dependence of which is described by kinetic equations.

LATTICE GAS MODEL

In the LGM, any volume V of the system is divided into cells with a size of about particle volume

$\nu_0 = \gamma_s\lambda^3$, where λ is the linear size of the cell, γ_s is the shape factor, and $V = N\nu_0$ (N is the number of cells (or lattice sites) in the system, which is equal to the maximum number of molecules under the close-packing condition). The number of different occupation states f of any site of the system is denoted by s; each site can contain only one molecule of type i (the center of mass of molecule i is inside the cell) or vacancy V. If there is a molecule of type i in the site, then site occupation states $1 \le f \le N$ are defined by γ_f^i values equal to $\gamma_f^i = 1$, where i corresponds to the mixture of molecules and vacancies comprised of $s - 1$ components; otherwise, $\gamma_f^i = 0$. Random variables obey the following relations: $\sum_{i=1}^{s} \gamma_f^i = 1$, $\gamma_f^i\gamma_f^j = \Delta_{ij}\gamma_f^i$, where Δ_{ij} is the Kronecker symbol, meaning that any site is necessarily occupied by any, but only one, particle (we will assign the last index, s, to free/vacant sites.)

Let N_i denote the number of molecules of type i in volume V. Then, $N = \sum_{i=1}^{s} N_i$, where N_i is the number of these molecules in volume V. The concentration of molecules of type i is $n_i = N_i/V$. In the LGM, the concentration of a mixture component is characterized by $\theta_i = \langle\gamma_f^i\rangle = N_i/N$ (symbol $\langle A\rangle$ means the A value averaged over the entire set of sites of the system). This connects the conventional and lattice concentrations of molecules of type i by relation $\theta_i = n_i\, v_0$. We will denote local density particles i in the cell under number f by θ_f^i, bearing in mind that normalization condition $\sum_{i=1}^{s} \theta_f^i = 1$ is fulfilled for any cell. In addition, total local concentration θ_f defined as $\theta_f = \sum_{i=1}^{s-1} \theta_f^i$ is introduced for the mixture. In the case of a homogeneous phase, the local θ_f^i and θ_f values and concentrations $\theta_i = \sum_{f=1}^{N} \theta_f^i / N$ and $\theta = \sum_{f=1}^{N} \theta_f / N$ averaged over the phase volume are identical for different sites.

In the LGM, the lattice structure in the bulk phase is characterized by number z of nearest neighbors. The lattice gas model implies the presence of mixture components with comparable (but different) sizes.

The distances between the sites of the lattice system are convenient to measure in coordination sphere (CS) numbers. We introduce the concept of CS radius ρ around the central particle as a set of sites located at a distance of ρ in the range of $1 \le \rho \le R_L$, where R_L is the radius of the Mie potential of lateral interactions (the R_L value corresponds to four or five CSs), around any selected site f within the range of $1 \le f \le N$. We denote the number of sites of coordination sphere ρ by $z(\rho)$.

In the general case, the populations of sites can be different because of internal interatomic interactions or external fields. This fact is characterized by the concept of type of sites with different numbers, but having the same properties.

This makes it possible to simplify the description by moving to group properties $\gamma_f^i = \gamma_q^i\eta_f^q$, where γ_q^i is a random variable that characterizes the occupation state of a site of type q (the properties of γ_q^i are similar to the projection properties of γ_f^i discussed above, i.e., $\sum_{i=1}^{s} \gamma_q^i = 1$ and $\gamma_q^i\gamma_q^j = \Delta_{ij}\gamma_q^i$), and the η_f^q value characterizes the type of site with number f. The η_f^q value is considered to be a value that is known and unchanged during the process of filling the lattice structure with molecules (nonrearranging structure) for $1 \le q \le t$, where t is the number of site types. If site f is a node of type q, then $\eta_f^q = 1$; otherwise, $\eta_f^q = 0$. The complete set of values $\{\eta_f^q\}$ for $1 \le f \le N$ uniquely defines the composition and arrangement of the structure, which can be random.

Averaged values $\langle\gamma_f^i\gamma_{g_\rho}^j\rangle = \theta_{fg}^{ij}(\rho)$ are pairwise probabilities of finding particles i and j at sites with numbers f and g at a distance of CS radius ρ. Normalization relations for pairwise functions $\sum_{j=1}^{s} \theta_{qp}^{ij}(\rho) = \theta_q^i$ are fulfilled for them.

For heterogeneous systems, the θ_f^i values for different cells f differ from each other; therefore, the values of local concentrations θ_f^i and volume averaged concentrations $\theta_i = \sum_{f=1}^{N} \theta_f^i / N = \sum_{q=1}^{t} F_q\theta_q^i$, where F_f is the fraction of sites of type q and $\sum_{q=1}^{t} F_q = 1$, are not identical. Here, in the second equality, we switched from site numbers to their types.

For heterogeneous systems, the lattice constant values become dependent on the type of inhomogeneity and are denoted by λ_{fg}. Accordingly, the partial contributions to lattice constant λ_{fg}^{ij} from neighboring pairs of molecules ij become dependent on the type of sites in which interacting pairs of molecules are located; $\lambda_{fg} = \sum_{ij} \lambda_{fg}^{ij}\theta_{fg}^{ij}$. Here, the θ_{fg}^{ij} function is the average fraction of the nearest ($\rho = 1$) pairs of neighboring molecules ij located at the pair of sites fg.

We denote the parameter of interaction between particles i and j located at sites with numbers f and g at a distance of ρ by $\varepsilon_{fg}^{ij}(\rho)$, where $\varepsilon_{fg}^{ij}(\rho) = 4\varepsilon_{fg}^{ij0}\{(\sigma_{ij}/r_{fg}^{ij}(\rho))^n - (\sigma_{ij}/r_{fg}^{ij}(\rho))^m\}$; $r_{fg}^{ij}(\rho)$ are the distances between particles i and j in different cells f and g at a distance of CS radius ρ within the range of $1 \le \rho \le R_L$, ε_{fg}^{ij0} and σ_{ij} are the parameters of the pairwise potential, and n and m are the parameters of the Mie potential ($n = 12$ and $m = 6$ correspond to the

Lennard–Jones potential). The interactions of particles with vacancies are equal to zero, i.e., $\varepsilon_{fg}^{iV}(\rho) = \varepsilon_{fg}^{Vj}(\rho) = \varepsilon_{fg}^{VV}(\rho)$. For a nonuniform lattice, the interaction parameter of particles i and j located at sites of type q and p with numbers f and g at a distance of ρ is denoted by $\varepsilon_{qp}^{ij}(\rho) = \varepsilon_{fg}^{ij}(\rho)$, since the site number and its type are uniquely related by η_f^q values.

In the general case of a heterogeneous system, the total energy of the system in the grand canonical ensemble is expressed as follows [28]:

$$H = \sum_f \sum_i \nu_q^i(\alpha)\gamma_f^i\eta_f^q - \frac{1}{2}\sum_{\rho=1}^{R}\sum_{f,g_\rho}\sum_{i,j}\varepsilon_{qp}^{ij}(\rho)\gamma_f^i\gamma_{g_\rho}^j\eta_f^q\eta_{g_\rho}^p, \tag{1}$$

where the $\nu_q^i(\alpha)$ value is the effective single-particle contribution of component i (for a vacancy, $\nu_f^s(\alpha) \equiv \nu_f^V(\alpha)$) to the energy of the system ($\nu_q^i(\alpha) = \nu_f^i(\alpha)$), which is determined by the interaction of a particle of type i with lattice site f ($1 \le f \le M$) or $\nu_f^i(\alpha) = -\beta^{-1}\ln(a_f^i(\alpha)P_i)$, where P_i is the partial pressure of component i in the thermostat, and by the ratio of partition functions of the particles located in the lattice system (Q_f^i) and thermostat ($Q_i^0(\alpha)$). Symbol α describes the relationship between the type of site f and the state of the environment of this central site. The occupancy states of the sites are characterized by local retention coefficients $a_f^i(\alpha) = \exp[\beta(\nu_f^i(\alpha) - \nu_f^s(\alpha))] = Q_f^i(\alpha)\beta\exp(\beta U_f^i)/Q_i^0(\alpha)$ of components i at site q (in adsorption and absorption, these are local partial Henry coefficients), where $\beta = 1/(k_BT)$; k_B is the Boltzmann constant; T is the temperature; $Q_f^i(\alpha)$ and $Q_i^0(\alpha)$ are the partition functions of particle i at site q and molecule i in the gas phase (thermostat), respectively; and U_f^i is the energy of the external field acting on particle i in site q (in adsorption, this is the wall potential). Specific formulas for these partition functions are given in [28, 48]. Energy (2) determines the partition function of the system; i.e., $Q = \sum_{f,i}\exp(-\beta H(\{\gamma_f^i\}))$, in which the sum is taken over all sites f of the system and all occupancy states i of its sites.

Ordered States of Solid Solutions in Bulk [49]

The lattice gas model reflects the case of an ordered state of components in the bulk phase [49]. In this case, the distribution of components becomes dependent on the site number in the unit crystallographic cell containing more than one site. Let the total number of sites be partitioned into δ_m sublattices, among which identical sublattices are possible. We denote the weight of the sublattice of type δ by F_δ for $1 \le \delta \le u$, where u is the number of sublattices of different types ($\sum_{\delta=1}^{u} F_\delta = \delta_m$). The nearest sites—one on each sublattice—form a unit cell translationally repeated throughout the entire lattice. Any node in the structure is defined by the following two indices (hk): cell number h and site number k inside the cell. Regarding the sublattice selection method, site number k is uniquely related to sublattice type δ. The structure of the ordered state is considered to be defined and characterized by the number of neighbors of sublattice site φ at a distance of ρ from sublattice site δ, i.e., $z_{\delta\varphi}(\rho)$. Hence, the total energy of the ordered system can be expressed as follows:

$$H = \sum_{(hk)}\sum_i \nu_\delta^i(\alpha)\gamma_{hk}^i - \frac{1}{2}\sum_{\rho=1}^{R}\sum_{(hk),(gn)_\rho}\sum_{i,j}\varepsilon_{\delta\varphi}^{ij}(\rho)\gamma_{hk}^i\gamma_{(gn)_\rho}^j. \tag{2}$$

The meaning of molecular parameters is preserved, taking into account the change in the meaning of the selected sublattice sites. Summation with respect to sites (hk) is performed over all lattice sites, and summation with respect to sites $(gn)_\rho$ is performed over structure sites located at a distance of ρ from sites (hk), including sites with $h = g$, but under condition $n \neq k$. Here, it is taken into account that each sublattice can contain its own number of components (s_δ) and internal degrees of freedom of the particle ($\nu_q^i(\alpha) = \nu_f^i(\alpha)$), and its interaction parameters $\varepsilon_{qp}^{ij}(\rho) = \varepsilon_{fg}^{ij}(\rho)$ depend on the type of sublattices [49].

Transition Region of the Interface of Isotropic Phases [38–40]

We restrict ourselves to the analysis of a planar interface between coexisting macroscopic phases. In this case, symbol $\gamma_f^i = \gamma_q^i\eta_f^q$ refers to the sites located in different monolayers. The properties of sites in the transition region are varied from a monolayer to a monolayer along the normal to the interface. The structure of the isotropic system is defined by the set of numbers of sites in the sites of monolayer p located at a distance of ρ from the site in monolayer q, i.e., by $z_{qp}(\rho)$. The total energy of the isotropic planar transition region of the system can be expressed as follows:

$$H = \sum_q\sum_i \nu_q^i(\alpha)\gamma_q^i - \frac{1}{2}\sum_{\rho=1}^{R}\sum_{q,p_\rho}\sum_{i,j}\varepsilon_{qp}^{ij}(\rho)\gamma_q^i\gamma_{p_\rho}^j. \tag{3}$$

It should be borne in mind here that neighbors of type p are in adjacent monolayers at a distance of ρ from the site in monolayer q; $1 \le q, p \le \kappa$, where κ is the width of the transition region of the interface, and $q - \delta_r \le p \le q + \delta_r$, where the δ_r values reflect the relationship between the distances along the monolayers and the distances separating the neighbors in different CSs; for example, in a cubic lattice, the first three neighbors are located in neighboring monolayers with $\delta_r = 1$, the fourth neighbors are in the second monolayer with $\delta_r = 2$, etc. Obviously, the δ_r value depends on the structure of the initial lattice and on the spatial orientation of the interface with respect to the initial lattice.

Transition Region of the Interface of Ordered Phases

In the case of analysis of the interface between ordered phases, it is necessary to simultaneously consider both the structure of ordering defined in the volume by a unit cell or a pattern composed of sublattices and changes in the properties of the system near the interface. From the formal point of view, this requires to combine features that distinguish different types of sites, such as the ordered state from the bulk to the interface and the change in the state of atoms of the solid in the transition region. The structure of the ordered system near the interface is determined by the set of numbers of sites at the sites of monolayer p, which are related to the sites of sublattices $(p,\varphi)_\rho$ and located at a distance of ρ from the site in monolayer q related to the sites of sublattices (q,δ), i.e., by $z_{(q,\delta)(p,\varphi)}(\rho)$. The total energy of the ordered macroscopic planar transition region of the system is expressed as follows:

$$\begin{aligned} H = {} & \sum_{(q,\delta)}\sum_{i} \nu_{\delta}^{i}(\alpha)\gamma_{q,\delta}^{i} \\ & -\frac{1}{2}\sum_{\rho=1}^{R}\sum_{(q,\delta),(p,\varphi)_\rho}\sum_{i,j}\varepsilon_{\delta\varphi}^{ij}(\rho)\gamma_{q,\delta}^{i}\gamma_{(p,\varphi)_\rho}^{j}. \end{aligned} \qquad (4)$$

This expression reflects the fact that the periodic structure of the ordered arrangement of sites of different sublattices near the interface requires refinement because of conjunction with the interface plane. Here, symbols q and p refer to transition region κ with $1 \le q$, $p \le \kappa$, which is determined solving an equation for the concentration profile of the distribution of atoms near the interface. In addition, the condition of consideration of the interparticle interaction inside R of CS, i.e., $q - \delta_r \le p \le q + \delta_r$, should be fulfilled. The meaning of the δ_r value is explained above.

Equations for the Distribution of Mixture Components

The cluster approach developed for an arbitrary type of heterogeneous systems [28] allows one to obtain, in the standard way, the following equations for the distribution of atoms in solid solutions in the form of local isotherms that fix the chemical potentials of components i at different sites of the system and for the relationship between pairwise distribution functions. The local partial isotherms for each monolayer q and the considered type of sublattice site (δ) as a function of the external pressure on set $\{P_j\}$ of partial pressures are of the following form:

$$a_{q,\delta}^{i}P_i = \theta_{q,\delta}^{i}\Lambda_{q,\delta}^{i}\big/\theta_{q,\delta}^{s},\ \Lambda_{q,\delta}^{i} = \prod_{\rho=1}^{R}\prod_{p=q-\delta_r}^{q+\delta_r}\left[\sum_{j=1}^{s}\hat\theta_{(q,\delta)(p,\varphi)}^{ij}(\rho)\exp[\beta\varepsilon_{(q,\delta)(p,\varphi)}^{sj}(\rho)]\big/\theta_{q,\delta}^{i}\right]^{z_{(q,\delta)(p,\varphi)}(\rho)}, \qquad (5)$$

where P_j is the pressure of component j with $1 \le j \le s_c$.

Excluding partial pressure values P_i from the left-hand sides, we obtain equations for the relative filling of sites of various types. For the bulk phase, the $a_q^i(\alpha)$ value—which represent the constant of retention by the lattice system or is an analog of the Henry coefficient in adsorption—is defined as ratio $a_q^i(\alpha) = F_q^{\,i}(\alpha)\big/F_i^{0}$ of the partition functions of the molecule in the lattice structure ($F_q^{\,i}$) and in the bulk phase (F_i^{0}) (for more details, see [48]). Here, $\Lambda_{q,\delta}^{i}$ is the imperfection function in the QCA; $\beta = (R_BT)^{-1}$, R_B is the gas constant; and $\theta_{qp}^{ij}(\rho)$ is the probability of finding the pair nearby, providing that component j is located in the cell of layer p and component i is located in the cell of layer q at a distance of ρ.

Pairwise functions are related to each other in the QCA by the following equation:

$$\begin{gathered} \hat\theta_{(q,\delta)(p,\varphi)}^{ij}(\rho)\hat\theta_{(q,\delta)(p,\varphi)}^{ml}(\rho) = \hat\theta_{(q,\delta)(p,\varphi)}^{il}(\rho)\hat\theta_{(q,\delta)(p,\varphi)}^{mj}(\rho), \\ \hat\theta_{(q,\delta)(p,\varphi)}^{ij}(\rho) = \theta_{(q,\delta)(p,\varphi)}^{ij}(\rho)\exp[-\beta\varepsilon_{(q,\delta)(p,\varphi)}^{ij}(\rho)], \end{gathered} \qquad (6)$$

which takes into account direct correlations between interacting particles.

The constructed set of equations reflects the following three situations indicated above: the ordered distribution of components in the bulk phase (if we neglect the transition region of the interface by omitting symbols q and p for layer numbers); the isotropic interface in the absence of ordering (if we neglect the bulk ordering by omitting symbols δ and φ for cell numbers and their sublattices); and the joint use of ordering indices and transition region numbers, which describes an ordered system near the interface. The absence of lower indices refers to a homogeneous dense phase without consideration of the ordering of components.

The system of equations (5) and (6) is solved using a change of variables, as specified in Appendix 1, which sharply reduces its dimension.

Knowing the concentration profile of the solid solution, it is possible to calculate all the surface characteristics necessary to obtain the values of thermodynamic functions and structural information about the transition region. In particular, it is possible to find the roughness characteristics of the interface from the concentration profile [50, 51], which allows one to estimate their specific surface areas, the surface segregation of components, the region of disappearance of ordering near the interface, etc.

Below, we simplify the method of defining the indices by returning to the original designation of sites by their numbers *f* and *g*, implying complete notations $f = q, \delta$ and $g = p, \varphi$.

FREE ENERGY AND SURFACE TENSION

Free Energy of the System

The expression for the Helmholtz free energy of a system comprised of *M* sites can be written as follows [52]: $F = E - TS$, where *E* is the energy of the system and *S* is the entropy of the system. The energy and entropy of the system is expressed via functions as follows:

$$\begin{aligned} E &= \sum_{f=1}^{M}\sum_{i=1}^{s-1}\Big[\theta_f^i\beta^{-1}\ln(a_f^i(\alpha)) + \frac{1}{2} \\ &\quad\times\sum_{\rho=1}^{R} z_{fg}(\rho)\sum_{j=1}^{s-1}\varepsilon_{fg}^{ij}(\rho)\theta_{fg}^{ij}(\rho)\Big], \\ S &= k\sum_{f=1}^{M}\sum_{i=1}^{s}\Big\{\theta_f^i\ln(\theta_f^i) + \frac{1}{2}\sum_{\rho=1}^{R} z_{fg}(\rho) \\ &\quad\times\sum_{j=1}^{s}\Big[\theta_{fg}^{ij}(\rho)\ln\theta_{fg}^{ij}(\rho) - \theta_f^i\theta_g^j\ln(\theta_f^i\theta_g^j)\Big]\Big\}. \end{aligned} \tag{7}$$

The use of expressions for $\nu_q^i(\alpha)$ in the internal energy allows one to take into account the internal motions of components together with their interparticle interactions. Another way,

$$\begin{aligned} F &= \sum_{f=1}^{M}\sum_{i=1}^{s}\theta_f^i M_f^i, \quad M_f{}^i = \nu_q^i(\alpha) + kT\ln\theta_f^i \\ &\quad+ \frac{kT}{2}\sum_{\rho=1}^{R_L}\sum_{g\in q\pm\delta_r} z_{fg}(\rho)\ln[\hat{\theta}_{fg}^{ii}(\rho)\,\hat{\theta}_{fg}^{ik}/(\theta_f^i)^2\,\hat{\theta}_{fg}^{ki}], \end{aligned} \tag{8}$$

where index *k* is any component of the system—it is chosen on the basis of the convenience of operation (usually, it is a symbol for the vacancy).

In the volume of an isotropic homogeneous solution, this formula can be rewritten as follows:

$$\begin{aligned} F_0 &= M\sum_{i=1}^{s}\theta_i M_i, \quad M_i = \nu_i(\alpha) + kT\ln\theta_i \\ &\quad+ kT\sum_{\rho=1}^{R_l} z(\rho)\ln[\hat{\theta}_{ii}(\rho)/(\theta_i)^2]/2, \end{aligned} \tag{9}$$

where $z(\rho)$ is the number of neighbors in the bulk phase at a distance of CS radius ρ.

Surface Tension

Using the definition for ST as an excess of free energy in the transition region [38–40], we obtain

$$\begin{aligned} \sigma(R)A &= \sum_{\mathrm{f}=2}^{\kappa-1}[\mu_{\mathrm{f}}^V - \mu_V]\theta_{\mathrm{f}}^V, \\ \mu_f^V &= kT\ln\theta_f^V + \frac{kT}{2} \\ &\quad\times\sum_{\rho=1}^{R_L}\sum_{g\in q\pm\delta_r} z_{fg}(\rho)\ln[\theta_{fg}^{VV}(\rho)/(\theta_f^V\theta_g^V)]. \end{aligned} \tag{10}$$

Provided that

$$\begin{aligned} &\sum_{i=1}^{s_c}(M_f^i - M_f^V)\Gamma_i = 0, \\ &\Gamma_i = \sum_{q=2}^{\kappa-1}\Big[\theta_q^i - \theta_\alpha^i\Big|_{q=1}^{q=\rho_e} - \theta_\beta^i\Big|_{q=\rho_e+1}^{q=\kappa}\Big], \end{aligned} \tag{11}$$

where Γ_i is the usual Gibbs excess of component *i* for a planar interface. Condition (11), which determines the position of the separating surface, coincides with the traditional requirement [43] for an analog of the equimolecular separating surface in a multicomponent mixture. Formula (10) is defined at any density of the mixture.

Mechanical Equilibrium

Helmholtz free energy derivative $dF_{lat}/dV_{loc|T,\mathbf{N}} = -P_{loc}$ with respect to some local volume V_{loc} gives local pressure P_{loc} for any phase state of the system. These relations can be used to search for local lattice parameters λ_{fg} by means of the Gibbs–Duhem microscopic equation [38, 39]. The local pressure is expressed through the Gibbs–Duhem microscopic equation in the integral form as $\mathrm{P}_f = \int_0^{\theta_f}\frac{1}{\nu_f}\sum_{i=1}^{s_c}\theta_f^i d(\mu_f^{is})$, where P_f is the total local mechanical pressure at site *q*, including the consideration of changes in the volume of vacancies due to deformation of cell *f* of the system and due to a change in their number upon isothermal particle exchange with a thermostat tank. There is difference $\mu_f^{is} = M_f^i - M_f^s$ in the $d(\mu_f^{is})$differential. For more details, see [38, 39]. The condition of local mechanical stability of the molecules has the following form:

$$\frac{F_{fg}^{ij}\partial\lambda_{fg}^{ij}}{S_{fg}\partial\lambda_{fg}} = -P_{fg}^{ij}, \quad P_{fg}^{ij} = \beta^{-1}\int_{0}^{\theta_f}\frac{1}{v_f} \times\left[\Delta_{ij}\theta_f^i\frac{d(\ln(\theta_f^i/\theta_f^s))}{d\theta_f} + \frac{d\ln\hat{\Lambda}_f^i(\alpha)}{d\lambda_{fg}^{ij}}\frac{d\lambda_{fg}^{ij}}{d\theta_f}\right]d\theta_f, \tag{12}$$

where $F_{fg}^{ij} = \partial F_{lat}/\partial\lambda_{fg}^{ij}$ and $\partial\nu_f = S_{fg}\partial\lambda_{fg}$, ν_f is the average volume of cell *f*, which is connected with lattice parameters through expression $\nu_f = \gamma_s\prod_{\sigma}\lambda_{f,\sigma}$; $\lambda_{f,\sigma} = [\lambda_{ff-1,\sigma} + \lambda_{ff+1,\sigma}]/2$; symbols $ff \pm 1,\sigma$ refer to neighboring sites in direction $\sigma = x, y, z$; and S_{fg} is the area of cell *f* to the normal along the *fg* bond. The introduced $\lambda_{ff\pm1,\sigma}$ values are the distances between pairs of sites of type *fg* along the σ axis. Here, renormalized imperfection function $\hat{\Lambda}_f^i$ means the ratio of quantities from equation (5), calculated by formula $\hat{\Lambda}_f^i(\alpha) = \Lambda_f^i/a_f^i(\alpha)$ taking into account the interactions of all components. Free energy minimization makes it possible to determine lattice parameters λ_{fg} of a heterogeneous system.

NONEQUILIBRIUM STATE OF SOLIDS

The physical cause of the nonequilibrium state of solids is the diffusive inhibition of the redistribution of components in local volumes of solids. The evolution of such processes is described by kinetic equations of the diffusion type. The kinetic approach reflects its dynamic nature, which is the most important property of an equilibrium state. The LGM provides the construction of kinetic equations on all time scales and is applicable for all aggregate states of substances [38]. Within the QCA, all the probabilities of multiparticle configurations, which describe the effect of surrounding particles on the rates of elementary processes, are expressed via local concentrations θ_f^i and pairwise functions $\theta_{fg}^{\mathrm{in}}$. The structure of the closed system of equations for unary and pairwise correlators corresponding to the nearest neighbors is expressed as follows (here, symbol α refers to the step number of the multistep process):

$$\begin{aligned} \frac{d}{dt}\theta_f^i &= \sum_{\alpha} P_f^i(\alpha)(U_f^i(\alpha), U_{fg}^{ij}(\alpha)), \\ \frac{d}{dt}\theta_{fg}^{ij} &= \sum_{\alpha} P_{fg}^{ij}(\alpha)(U_f^i(\alpha), U_{fg}^{ij}(\alpha)). \end{aligned} \tag{13}$$

The right-hand sides of Eqs. (13) contain contributions $P_f^i(\alpha)$ and $P_{fg}^{ij}(\alpha)$ from the rates of elementary steps, namely: $U_f^i(\alpha) = U_f^i(\alpha|\theta_f^i, \theta_{fg}^{in})$, i.e., the rates of elementary one-site processes $i \leftrightarrow b$ at sites of type *f*; and $U_{fg}^{ij}(\alpha) = U_{fg}^{ij}(\alpha|\theta_f^i, \theta_{fg}^{in})$, i.e., the rates of elementary two-site processes $i + j_\alpha \leftrightarrow b + d_\alpha$ at pairs of neighboring sites *fg*. The structure of Eqs. (13) is explained in more detail in Appendix 2.

The presence of pairwise functions θ_{ij} makes it possible to take into account the process prehistory, which is determined not only by the initial distribution of concentrations, but also by the initial values of the pairwise distribution functions. Pairwise functions play a key role in kinetic equations; in particular, they not only describe the process prehistory in its dynamics, but also provide self-consistency to the description of the equilibrium and rates of elementary steps in the equilibrium state [28, 38].

Nonequilibrium Thermodynamic Potentials

Knowing the solution of kinetic equations (13) with respect to θ_f^i and θ_{fg}^{in}, any thermodynamic functions that depend on them as functions on arguments, including nonequilibrium thermodynamic potentials, can be calculated at any point in time. The equations constructed above for equilibrium distributions through unary and pairwise functions preserve their form in nonequilibrium states. Therefore, expressions (7) serve as formulas for the Helmholtz nonequilibrium energy at any point in time, including also the equilibrium state of the system. If nonequilibrium states of solids are present, then in such situations we can speak of nonequilibrium analogues of the equilibrium potentials of the contacting solid and mobile phases, as shown in [47]. In the LGM, a theoretical description at the microscopic level leads to the situation when all thermodynamic potentials are equally expressed via unary and pairwise DFs, regardless of the state of the system. The difference between the equilibrium and dynamics consists in the way of describing the unary and pairwise DFs themselves. In the equilibrium state, unary and pairwise DFs are related by equations that do not contain time (thus, above, Eqs. (5) and (6) give an algebraic relationship between them.) In the dynamics, unary and pairwise DFs are explicitly related by kinetic equations via time (time argument). Detailed diffusion-type equations that describe processes in solid-state matrices were constructed in [28, 38].

Thus, all the above-described equations for the free energy and ST are expressions for calculating the nonequilibrium ST at the interfaces in the process of solid body evolution. The redistribution of components is described by equations of type (13), and the corresponding values of unary and pairwise DFs at each point in time make it possible to find the ST values.

CONCLUSIONS

The constructed equations for the distribution of mixture components with comparable sizes, which take into account interparticle interaction and internal motions, enable a microscopic description of planar macroscopic interfaces between ordered solid solutions and vapor.

The developed theory makes it possible to simultaneously take into account two main factors of the interfaces between solids, which are related to the ordering of components in bulk phases and to their nonequilibrium state determined by formation prehistory of the material. Each of the factors plays an important role in understanding the interaction of the material with the environment and in the preservation or targeted change of this state. It provides a closed system of equations for the concentration profile of solid solution components, which reflects the effects of short-range order against the background of long-range order in the bulk phase.

Two methods introduced by Gibbs for calculating the ST is directly related to the following versions of its description: the strictly equilibrium version of the theory (Appendix 1) and the nonequilibrium version of the theory (Appendix 2). We pay attention to the difference in the dimensions of the equation sets describing the interface according to whether the system is in an equilibrium or nonequilibrium state. In an equilibrium state, pairwise variables are reduced (Appendix 1), but this does not happen in a nonequilibrium state (Appendix 2) as long as the local equilibrium is not established (in the local equilibrium, pairwise functions are in equilibrium with densities). This is possible in bulk phases when describing diffusion processes, but this is not possible in regions near interfaces, since a sharp change in the density requires a more detailed description of the pairs.

The found concentration profiles can be used to calculate the entire range of surface characteristics, starting from the internal and free energies and ending with the surface tension, as well as to analyze the degree of roughness of the interface under consideration (as in [50, 51, 54]). Concomitantly, the degree of surface segregation of solution components and the nature of order disappearance near the interface are estimated. This kind of information is important for the kinetics of various surface processes.

The theory is intended to describe a wide range of solid solutions and compounds. The scope of the developed approach is extended to numerous alloys, oxides, salts, ferroelectrics, and nonstoichiometric compounds, which form the basis of various materials used in numerous catalytic, membrane, and adsorption technologies.

APPENDICES

Appendix 1. Reducing the dimension of the system of nonlinear equations for the distribution of components

An increase in the number of system components increases the dimension of the system of equations for the unary (θ_f^i) and pairwise (θ_{fg}^{ij}) functions. The number of equations for θ_f^i increases linearly as s increases, and the number of equations of pairwise functions $\theta_{fg}^{ij}(\rho)$ increases even faster as s(s – 1)/2. An increase in the number of calculated monolayers κ (the system has a nonuniform distribution of the density) gives rise to a further increase in the dimension of the equation set [28, 53].

To reduce the dimension, the system of equations is constructed with respect to the functions of conditional probability t_{gf}^{si}. The change of variables consists in the fact that $u_{fg}^i = t_{gf}^{si}$ are selected as independent variables; $\sum_{i=1}^{s} u_{fg}^i = 1$. Conditional probabilities t_{gf}^{si} can be expressed through equations $\theta_{fg}^{ij}\theta_{fg}^{ss} = \theta_{fg}^{is}\theta_{fg}^{sj}e^{\beta\varepsilon_{fg}^{ij}}$—which reflect the essence of the QCA—as $t_{fg}^{ij} = \dfrac{\theta_{fg}^{is}\theta_{fg}^{sj}}{\theta_f^i\theta_{fg}^{ss}}e^{\beta\varepsilon_{fg}^{ij}} = \dfrac{u_{fg}^i u_{gf}^j \theta_f^s}{\theta_f^i u_{gf}^s}e^{\beta\varepsilon_{fg}^{ij}}$. In that case, unary functions θ_f^i are calculated through given desired variables u_{fg}^i, instead of set of equations (5), by the following formula:

$$\theta_f^i = \frac{u_{fg}^i \xi_{fg^*}^i}{\psi_f}, \quad \xi_{qp}^i = 1 + \sum_{j=1}^{s-1} u_{gf}^j(\exp\{\beta\varepsilon_{fg}^{ij}\} - 1),$$
$$\psi_f = u_{fg^*}^s + \sum_{i=1}^{s-1} u_{fg^*}^i \xi_{fg^*}^i, \tag{A1.1}$$

where *fg** is a pair conditionally called the “reference pair,” which extends from site *f* and possesses the highest interaction energy between the components located at sites of the pair. Using conditional densities in sites *fg**, unary functions θ_f^i and pairwise functions θ_{fg}^{ij} are recalculated.

Remaining functions θ_f^s, θ_{fg}^{sj}, and θ_{fg}^{is} are determined from the following normalizations:

$$\sum_{i=1}^{s}\theta_f^i = 1, \quad \sum_{j=1}^{s} t_{fg}^{ij} = 1 \Rightarrow \sum_{i=1}^{s}\sum_{j=1}^{s}\theta_{fg}^{ij} = 1. \tag{A1.2}$$

In the QCA, each coordination sphere is analyzed independently; therefore, the above expressions for the nearest neighbors are supplemented by similar expressions for subsequent neighbors.

Appendix 2. Basics of the kinetic approach

In a nonequilibrium state, total distribution function $P(\{\gamma_f^i\},\tau)$ varies because of a certain process. Let the total process consist of many steps, and let the step number of the elementary process be denoted by α [28, 29]. The main kinetic equation for the evolution of the total distribution function of the system in state {I} (for brevity, notation $\{I\} \equiv \{\gamma_f^i\}$ is used) can be written, owing to implementation of α elementary processes in condensed phases, in the following fashion:

$$\begin{aligned}&\frac{d}{d\tau}P(\{\mathrm{I}\}),\tau)\\&=\sum_{\alpha,\{\mathrm{II}\}}[W_a(\{\mathrm{II}\}\to\{\mathrm{I}\})P(\{\mathrm{II}\},\tau),\\&\quad-W_a(\{\mathrm{I}\}\to\{\mathrm{II}\})P(\{\mathrm{I}\},\tau)],\end{aligned}\tag{A2.1}$$

where $W_\alpha(\{\mathrm{I}\} \to \{\mathrm{II}\})$ is the probability of implementation of elementary process α (the probability of transition through channel α), as a result of which the system passes from state {I} to state {II} at time point τ. The sum with respect to index α is taken over all possible transitions for all realizable states of the system.

If the elementary process proceeds at one site, then the lists of occupancy states {I} and {II} of the system sites differ only for this site. One-site processes are the processes associated with a change in the internal degrees of freedom of a particle, with the adsorption and desorption of nondissociating molecules, and with a reaction proceeding by a shock mechanism. If the elementary process proceeds at two neighboring sites of the lattice, then the lists of states {I} and {II} differ in the occupancy states of these two sites. Two-site processes are the exchange reactions, the adsorption and desorption of dissociating molecules, the migration processes by vacancy and exchange mechanisms, etc. The partition function of state {II} corresponds to the change in the occupancy states of all lattice sites. The relationship between states {I} and {II} depends on the process mechanism, which determines the set of elementary steps α.

Equation (A2.1) is written in the Markov approximation, for which it is believed that the relaxation processes of the internal degrees of freedom of all particles proceed faster than the processes of changing the occupancy states.

Transition probabilities α obey the following condition of detailed equilibrium:

$$\begin{aligned}&W_a(\{\mathrm{I}\}\to\{\mathrm{II}\})\exp(-\beta\mathrm{H}(\{\mathrm{I}\}))\\&=W_a(\{\mathrm{II}\}\to\{\mathrm{I}\})\exp(-\beta\mathrm{H}(\{\mathrm{II}\})),\end{aligned}\tag{A2.2}$$

where $\mathrm{H}(\{\mathrm{I}\})$ is the total energy of the lattice system in state {I}.

Within the QCA, all probabilities of the multiparticle configurations describing the influence of surrounding particles on the rates of elementary processes are expressed through unary (θ_f^i) and pairwise correlators. A closed system of equations for the unary and pairwise correlators can be written in general form as follows [28]:

$$\begin{aligned}\frac{d}{dt}\theta_f^i&=\sum_\alpha\left[U_f^b(\alpha)-U_f^i(\alpha)\right]\\&+\sum_h\sum_j\sum_\alpha\left[U_{fh}^{bd}(\alpha)-U_{fh}^{ij}(\alpha)\right],\end{aligned}\tag{A2.3}$$

$$\frac{d}{dt}\theta_{fg}^{ij}=\sum_\alpha\left[U_{fg}^{bd}(\alpha)-U_{fg}^{ij}(\alpha)\right]+P_{fg}^{ij}+P_{gf}^{ji},\tag{A2.4}$$

$$\begin{aligned}P_{fg}^{ij}&=\sum_\alpha\left[U_{fg}^{(b)j}(\alpha)-U_{fg}^{(i)j}(\alpha)\right]\\&+\sum_h\sum_m\sum_\alpha\left[U_{hfg}^{(cb)j}(\alpha)-U_{hfg}^{(mi)j}(\alpha)\right],\end{aligned}\tag{A2.5}$$

where unknown unary and pairwise functions obey normalization conditions (A1.2), which are fulfilled for any point in time. The right-hand sides of Eqs. (A2.3)–(A2.5) contain the rates of elementary steps. The presence of equations for pairwise correlators makes it possible to reflect any nonequilibrium state of the components and provides a description of the effect of the prehistory of the system state on the process dynamics.

Rates of elementary steps. In Eq. (A2.3), $U_f^i(\alpha)$ are the rates of elementary two-site processes $i \leftrightarrow b$ (here, $h \in z_f$), $U_{fg}^{ij}(a)$ are the rates of elementary two-site processes $i + j_\alpha \leftrightarrow b + d_\alpha$ ($h \in z_f^*$) at neighboring sites, and the second term in (A2.5) describes step $i + m \leftrightarrow b + c$ at neighboring sites f and h.

All rates $U_f^i(\alpha)$ and $U_{fg}^{ij}(r|\alpha)$ of elementary steps are calculated within the theory of absolute reaction rates for nonideal reaction systems, which are written in the QCA considering the interparticle interaction [28, 29, 49]. The properties of the activated complex (AC) in the theory of absolute reaction rates for nonideal reaction systems depend on the interaction between particles in the transition and ground states. This requires, in addition to knowledge of the ε_{ij} values in the ground state, knowledge of interparticle interactions ε_{ij}^* in the transition state. Therefore, the formulas for rates $U_f^i(\alpha)$ and $U_{fg}^{ij}(r|\alpha)$ depend on both ε_{ij} and energy ε_{ij}^*.

As an example, we give the following expressions for diffusion shift rates $U_{fg}^{iV}(\alpha)$ taking into account the interaction of nearest neighbors (the general case is given in [49]):

$$U_{fg}^{iV}(\alpha)=K_{fg}^{ij}(\alpha)\theta_{fh}^{iV}\prod_{\eta\in z_f^*}S_{f\eta}^i\prod_{\chi\in z_g^*}S_{g\chi}^V,\tag{A2.6}$$

where $K_{fh}^{ij}(\alpha)$ is the rate constant of the elementary step of migration, $S_{f\eta}^i=\sum_{m=1}^s\theta_{f\eta}^{im}\times\exp[\beta(\varepsilon_{f\eta}^{im*}-\varepsilon_{f\eta}^{im})]/\theta_f^i$, and $S_{h\chi}^V=\sum_{m=1}^s\theta_{h\chi}^{Vm}\times$

$\exp(\beta\varepsilon_{h\chi}^{im*})/\theta_f^V$ is the factor of the imperfection function for the hop rate. The product in (A2.6) is taken with respect to neighboring sites η (for central site *f*) and χ (for central site *g*) by excluding bond *fg*, which is indicated by asterisks in z_f* and z_g*.

Equations (A2.4) contain terms $U_{fg}^{(i)j}(\alpha)$ and $U_{hfg}^{(mi)j}(\alpha)$ related to one- ($i''b$) and two-site ($i + m''b + c$) reactions of particle *i* in the presence of neighbor particle *j*. In this case, particle *j* itself does not take part in elementary process α, but changes the value of the activation barrier for reacting particle *i* in the case of a one-site process and for reacting particles *i* and *m* in the case of a two-site process. In the QCA, terms $U_{fg}^{(i)j}(\alpha)$ and $U_{hfg}^{(mi)j}(\alpha)$ are closed through functions θ_f^i and $\theta_{fg}^{in}(r)$, and no new unknown correlators appear. For example (A2.6), the $U_{hfg}^{(VA)A}$ functions in Eqs. (A2.4) have the following form: $U_{hfg}^{(ij)A} = U_{hf}^{ij} Y_{fg}^{jA}$, $\Psi_{fg}^{jA} = t_{hg}^{jA}\exp(\beta\delta\varepsilon_{fg}^{jA})/S_{fg}^{j}$, where $S_{fg}^{j} = \sum_k t_{hg}^{jk} \times$ $\exp(\beta\delta\varepsilon_{fg}^{jk})$, and $t_{hg}^{jk} = q_{hg}^{jk}/q_h^j$.

In the limit of large times, system of kinetic equations (A2.4) transforms into Eqs. (6) for the equilibrium distribution of components.

FUNDING

This study was performed within the framework of a state order to the Institute of General and Inorganic Chemistry, Russian Academy of Sciences, in the field of fundamental studies.

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Translated by O. Kadkin