The consideration of virial corrections in the diffusion equations

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Abstracts. The diffusion phenomenon is known to be a universal physical process and the basis of many industrial technologies for advanced materials. Abnormalities of diffusion have been observed which cannot be described by existing theory. The diffusion of atoms of the introduction (boron) possessing great energy of dissolution, results in significant deformation of the crystal lattice of iron in the radius of the first coordination spheres.

Mayer’s approach to the solution of the problem of getting diffusion equation with viral corrections, indicating the account of interparticle interaction in these systems, has been offered in this work. In the ongoing project the model of diffusion of boron impurities, strongly interacting with the lattice has been described. Further directions in the solution of this problem have been suggested. To explain the anomalies observed in the diffusion mechanism of implementation a comparison of theoretical calculations has been attempted, in particular, in the system iron-boron.

1. Introduction
Diffusion is one of the most general physical processes and phenomena underlying at the basis a lot of transformations and processes in solids. The ordinary diffusion theory does not explain a number of effects during the diffusion of the interstitial atoms with high dissolution energy, causing a considerable deformation of the crystal lattice in the first coordination spheres. Such atoms strongly interact with the nearby atoms of the solvent crystal lattice and with each other, that becomes considerably apparent in a number of special effects [1], particularly, these are anomalies of atom redistribution within the diffused zone, a special character of the influence of lattice defects on the diffusion kinetics, diffusion under tension and so on. The account of the interatomic interaction influence on the diffusion kinetics is of great significance due to the small sizes of the diffused zones with great magnitudes of concentration gradients, typical of diffusion processes on a micro- and submicron-scale.

At present there are some experimental diffusion data in the systems with limited solubility Fig.1 [1, 2]. In the systems with even little chemical impurity concentration one should not neglect the interaction of the impurity atoms with each other. It is necessary to take into account the interaction of the solvent atoms, forming the crystal lattice in which the diffusion process takes place.

Indeed, in many cases, by the study of diffusion redistribution of components of the solid solution anomalies have been detected which haven’t been received with help of existing diffusion theory. For example, in the references [1, 2] the results obtained in the system with limited solubility iron-boron have been presented. While on one hand, in [1] it hasn’t been revealed two phases. Having been shown in Fig. 1 the section of the diffusion zone is a solid solution and ‘the jump’ on C(x) can’t be explained within the theory of diffusion.

The objective of this work is to identify models of impurity diffusion, strongly interacting with the lattice while on one hand, on the other hand the clarification of the connection diffusion equation by the configuration integral and the interatomic interaction. An attempt has been made to compare
theoretical calculations for the explanation of the anomalies observed in the diffusion of interstitial mechanism (the system iron-boron).

2. Theory

To study the diffusion processes in the complex systems, which properties are obviously different from the model of ideal gas, a number of approaches has been developed by present time. For example, in accordance with the theory of Mayer for concentrated solid solutions [3] the expression for the chemical potential is used

\[ \mu(T, p, n_i) = \mu^0_i(T, p) + kT \ln a(n_i), \]  

where instead of the concentration of \( n_i \) the activity of component \( a(n_i) \) has been introduced, depending on the concentration of \( n_i \) and other state parameters and the standard chemical potential \( \mu^0_i \) is the function that depends on the temperature \( T \) and pressure \( p \).

Being based on Mayer approach [3], the expression for the chemical potential of such systems was obtained, which must contain, in addition summand chemical potential of an ideal classical gas, the member, expressing the interatomic interaction. The eq. of state in the form of a virial expansion is known [3, 4] to have the form of eq.

\[ \frac{pV}{\theta} = 1 - \sum_{n=1}^{N} \frac{n}{n+1} \beta_n \rho^n, \]  

where \( \rho = \frac{N}{V} \) is the density of particles (atoms), \( \beta_n \) are the irreducible group integrals (virial coefficients), \( p \) is the pressure, \( \theta = kT \), where \( k \) is Boltzmann's constant.

Virial coefficients correspond to the interactions between two, three, etc. molecules sequentially. We have reduced the problem of virial equation of state for solid solution consisting of \( N \) particles to the number of special problems of interaction between two, three particles, and etc., similarly as the problems with gases are solved.

Our calculation has been limited with the first virial coefficient, considering only pairwise interactions. According to [3] the chemical potential in the form of a virial decomposition has the form

\[ \mu = \mu_0 - \theta \sum_{n=1}^{N} \beta_n \left( \frac{N}{V} \right)^n, \]
where $\mu_0 = \theta \ln C$ is the standard chemical potential, $C = \frac{N}{V}$ the concentration of the substance.

Solid implementation solutions with bcc lattice on the basis of $\alpha$-Fe, metals V and VI groups are characterized with a strong distortion created by the interstitial atoms and significantly features of its mechanical and physical properties [5].

The Morse potential has been chosen alternatively the potential of the Lennard-Jones (LJ). The potential of LJ is two-parameter, so it has very limited possibilities for variations of the macroscopic parameters of the simulated material. In fact, it can satisfy the value of only one macroscopic parameter. It can be, for example, the modulus of elasticity or ultimate strength in statics, the speed of propagation of longitudinal waves etc. On the other hand, this potential describes the properties of some substances (primarily crystalline inert gases) and the interaction strength of the Van der Waals forces very accurately. The potential of LJ is widely used as a classical model potential, especially in the works, which main objective is the study of General physical laws without getting the exact quantitative results.

The Morse potential has three parameters that allows to satisfy the value of two independent macroscopic parameters, such as modulus of elasticity and ultimate strength in statics. The simplicity and clarity of calculating the parameters of the potential makes it very convenient to use. Another advantage compared with the potential of LJ is faster decay at a distance, which is handy if you are modeling it is necessary to consider the interaction of only the nearest particles. The Morse potential is given by formula [5]:

$$
\Phi(r) = D \left[ e^{-2N(r-1)} - 2e^{-N(r-1)} \right].
$$

(4)

This potential is different from LJ potential by a faster (exponential instead of power) decrease up to the infinity, it has’nt singular point in zero, but what is more important in the considered case is the presence of the dimensionless parameter $N$. The definition of all three parameters of the (4): $N$ defines the width of the potential well, $D$ is the depth of the potential well (the minimum potential energy of interaction between two atoms of boron), $b$ is the minimum distance between a pair of particles, when the force of interaction is zero, i.e., $b = r_{\text{min}}$.

According to [2] the second group of the integral is defined by expression:

$$
b_2 = \frac{1}{2} \cdot 4\pi \int_0^\infty r^2 f(r) dr,
$$

where $f(r) = e^{-\Phi(r)/\theta} - 1$ - Mayer function. $\Phi(r)$ is the Morse potential.

Performing Mayer function expansion, we have transformed the expression, standing under the integral to mind

$$
r^2 f(r) = \sum_{n=1}^\infty \frac{r^2}{\theta^n} \cdot \frac{\Phi^n(r)}{n!}.
$$

Performing some mathematical calculations, we have obtained the expression for the first virial coefficient

$$
\beta_1 = 2b_2 = -\frac{4\pi b^3}{N^3} S ,
$$

(5)

$$
S = \sum_{(n)} \frac{(-1)^n D^n}{\theta^n} \sum_{k=0}^{n-1} \frac{(-2)^{k+1}}{k!(n-k)!(2n-k)!} e^{2n(2k+1)}
$$

and the symbol $\sum_{(n)}$ denotes summation over nearest environment of the boron atom in the bcc lattice of iron.

According to (3) the chemical potential of our system will be determined
\[ \mu = \theta \ln C + \frac{4\pi b^3 \theta}{N^3} S \cdot C, \]  
\[ \text{(6)} \]
i.e., the expression (6) can be represented in the form
\[ \mu = kT \ln C - kT \beta_1 C. \]  
\[ \text{(7)} \]

Using formulas, which relate the concentration in mass percent concentration in mass relative units, we have found the number of boron atoms in 1 m$^3$ of iron. The minimum distance between B atoms in the lattice of Fe has been found by the formula:
\[ r_{\text{min}} = \sqrt[3]{\frac{1 \text{m}^3}{N_B}} = 2.604 \cdot 10^{-9} \text{ m}, \]
where $N_B = 5.66 \cdot 10^{25}$ is the number of boron atoms in the lattice of iron, $r_{\text{min}} > a$ where a is the lattice parameter of iron, $a = 2.866$ Å [6].

As a variant of the consideration of interaction of the boron atom with neighboring atom of iron we have chosen the Morse potential (with the introduction of additional screened multiplier for forces of attraction).

Researching convergence of these series (5) we can see, that d’Alamberts criterion must converge. But in (5) we get divergent series. Which feature is that by involution $\Phi(r)$ in $n$ the (5) contains multiplier $e^{N(2n-k)}$ increases with $n$ ($n \geq k$). To construct a integrand function $r^2 f(r)$, we shall see a big and thin peak by $r = r_{\text{min}}$. Considering its area we get a very big value, that we can’t accept because it hasn’t got any physical sense. As a rule for Morse’s potential cut-off radius is entered, that means that the distance where there is an interaction, it is zero. Using cut-off radius that decreases the number of neighbours, interacting with every atom.

We do screening of Morse's potential (multiply component, which is responsible for attracting forces to screened multiplier $e^{-\lambda r}$). Such interstitial impurity like boron, creates very strong mechanical tensions in crystal lattice of iron [2, 7]. Radius of action of these tensions are several $r_{\text{min}}$, the interaction of the atoms is assumed to depend from the interatomic distances [8]. That’s why by numerical calculations $\beta_1$ we must do the integration to non-infinitum, but to the order $r = 3r_{\text{min}}$. The calculation from the three spheres is optimal, because the energy contribution over three spheres is very small [8, 9]. In this case the procedure of numerical calculation in Maple allows to our mind, not to miss this peak, because it is very narrow. Taking the screening for (4) we have been got
\[ \Phi(r) = D \left[ e^{-2N\frac{r-1}{r_{\text{min}}}} - 2e^{-N\frac{r-1}{r_{\text{min}}}} \cdot e^{-\lambda r} \right], \]  
\[ \text{(8)} \]
Where $D$ is the minimal potential energy of interaction between boron atom and iron atom. In studying of sources, we haven’t identified any specific values for the minimum potential energy of interaction between atoms of iron and boron. But on the basis the average interaction energy, we have assumed that $D = 10 \cdot 10^{-19}$ J [10, 11]. Parameter $\lambda$ is found by inspection. Grüneisen constant is known [5] to be connected with parameter $\Sigma$ by the relation $\Gamma = \frac{\Sigma}{2}$. Taking for boron $\Gamma = 3$, then $\Sigma$ has been used by the simulation $\Sigma = 2\Gamma = 6$.

The calculation has been performed in Maple. Let us choose $\lambda = 1.95 \cdot 10^7$, $\beta_1 = 212.3916$. The graphics of potential $\Phi(r)$ (8) and the integrand function $r^2 f(r)$ are presented in Fig. 2 and 3. $\beta_1$ corresponding to the interaction between the iron atom and boron is $\sim 10^{14}$, so that we neglect this interaction.
3. Results

According to the chosen approach, the diffusion equation has the form

\[ \frac{\partial C}{\partial t} = D \frac{\partial}{\partial x} \left( (1 - \beta_1 C) \frac{\partial C}{\partial x} \right). \]  

(9)

The initial and boundary conditions have the form

\[ C(x, 0) = \begin{cases} C_1, & x \leq 0 \\ 0, & x > 0 \end{cases}; \quad C(0, t) = C_1, \quad C(1, t) = 0. \]

The solution of (9) is presented in Fig. 4. When the initial concentration impurity is \( C_1 = 5 \cdot 10^{-3}, 5 \cdot 10^{-4}, \) respectively.

Its solution is slightly different from Fick's diffusion equation. In the framework of this model a linear dependence of the diffusion coefficient on the concentration has been obtained. We have restricted by the pair interaction, i.e. in the virial series is one component of \( \beta_1. \) This result is evident in the approximation of weak interaction of the diffusion of atoms with the atoms of the lattice. For calculating a diffusion coefficient of boron in iron \( D = 2.7 \cdot 10^{-10} \text{ m}^2/\text{s} \) has been taken [12]. In our calculation \( \beta_1 C \ll 1. \)
4. Conclusions

The problem of the interaction between the two boron atoms among the atoms of iron must be considerate. These two atoms are not neighbors, i.e. they do not interact directly. This problem is described in the framework of a phenomenological theory of diffusion, we have used the same Mayer approach to calculate the chemical potential of the impurity atom and the virial coefficient of this impurity in a solid. The procedure for obtaining expressions for \( \mu = \left( \frac{\partial F}{\partial N} \right)_{\mu} \) and \( F \) is the free energy should be modified for the case of a solid body. Our next task is to obtain expressions virial coefficient in the solid, but on the basis of the statistical sum of a defect-free crystal (for phonon gas), considering that during the interaction of phonons contribute to the interaction of atoms.

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