STATISTICAL THEORY OF DIFFUSION
IN CONCENTRATED ALLOYS

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The earlier-suggested master equation approach is used to develop the statistical theory of steady-state diffusion in concentrated substitution alloys considering FCC alloys with the nearest-neighbor pairwise interactions as an example. General expressions for the Onsager coefficients in terms of microscopic interatomic interactions and some statistical averages are presented. We discuss methods of calculations of these averages using various statistical approximations and various approximations for description of vacancy correlations, with the full taking into account the vacancy-solute interactions. Our simplest statistical approximation, called the "kinetic mean-field approximation" (KMFA), corresponds to using the mean-field approximation for statistical averages and the pair-cluster approximation (PCA) for calculations of thermodynamic parameters; for dilute alloys, the KMFA is exact. To describe vacancy correlation effects at any concentrations, we develop both the nearest-neighbor-jump approximation and the second-shell-jump approximation. We also describe methods to take into account fluctuations in statistical averages using the PCA, and to describe non-pairwise vacancy-solute correlations using the triple vacancy-solute correlation model. For each of approximations and methods developed, we derive expressions for the Onsager coefficients at any composition of an alloy. For binary alloys, we also present expressions for the diffusion coefficients. The results obtained can provide a basis for microscopic calculations of diffusion coefficients at any composition of an alloy.

1. INTRODUCTION

The existing microscopic theories of diffusion in alloys based on the random walk theory and the "vacancy-solute association-dissociation" models (to be called "traditional" theories) have been developed only for dilute alloys [1–9]. For the concentrated alloys, diffusion is usually described using various phenomenological approaches [10–12], and some authors believe that "the nature of concentration dependence" of diffusion coefficients "has never been fully explained and there does still not exist any adequate theories for describing such a dependence" [11]. Even for a dilute binary alloy AB with a low solute fraction $c_B \ll 1$, calculations of linear in c_B terms in diffusion coefficients ("enhancement factors") for both chemical and tracer solute diffusion seem to be not performed, while existing calculations

of tracer solvent enhancement factors (which are used, in particular, to estimate the microscopic parameters important for diffusion in real alloys [8, 9]) contain significant errors discussed in Ref. [13].

The recently-suggested master equation approach [14–21] provides opportunities for fully microscopic treatments of diffusion at any composition of an alloy. This approach enables to explicitly express the Onsager and diffusion coefficients via microscopic interatomic interactions and some statistical averages. These interactions can be calculated using *ab initio* methods, while statistical averages can be evaluated using well-elaborated methods of statistical physics. As the level of accuracy and reliability of both *ab initio* calculations [22, 23] and statistical methods [24–28] is steadily increasing, the master equation approach seems to be prospective for developments of non-empirical and predictive theories of diffusion in concentrated alloys.

At the same time, previous applications of the master equation approach to diffusion theory made by Nas-

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tar et al. [16–19] (and called by these authors "the self-consistent mean-field theory") include a number of shortcomings. As discussed below in Sec. 7.3, many equations used in [16–19] are cumbersome, implicit, employ unreliable approximations, and include errors, in particular, those mentioned in [21]. It hinders the further development of the theory.

In this work we present the formulation of the master equation approach to diffusion theory free from shortcomings mentioned. We aim to develop the statistical theory which can describe the steady-state diffusion in substitution alloys of any composition as fully and consistently as the canonical Gibbs theory describes properties of equilibrium systems. Our basic equations are simple and explicit, they can be solved using the standard methods of statistical physics, and their possible generalizations (for example, to the case of not-nearest or non-pairwise interactions) are evident.

To be definite, we illustrate our approach by consideration of FCC alloys with the nearest-neighbor pairwise interactions. For a binary alloy, such a model is equivalent to the well-known "five-frequency model" [1–9], but we also consider the multi-component alloys and take into account the solute-solute interactions not considered in the standard five-frequency model.

The important general feature of our approach is the proper description of effects of vacancy-solute interaction (or "vacancy-solute binding energy" [1–9]) related to the thermodynamic activity of vacancies. As discussed in Refs. [13, 21] and in Sec. 7.3, this contribution was usually missed in the previous calculations of diffusion coefficients, in particular, in all calculations of the tracer self-diffusion enhancement factor b_{A*}. This led to spreading of a pessimistic opinion that the "diffusion experiments by themselves are not sufficient to determine this binding energy" [9]. We show that this opinion is wrong, and in Ref. [13] we estimate this binding energy for several alloys for which necessary experimental data are available.

The paper is organized as follows. In Sec. 2, we present main equations of the master equation approach needed for what follows. In Sec. 3, these equations are used to derive general expressions for Onsager coefficients describing steady-state diffusion in a substitution alloy. In Sec. 4, we discuss both the exact relations and the methods of approximate calculations of Onsager coefficients in alloys of any composition. Here we also describe the kinetic mean-field approximation (KMFA) in calculations of statistical averages, as well as the nearest-neighbor-jump approximation (NNJA) and the second-shell jump approximation (SSJA) in description of vacancy correlation effects. In Sec. 5, we

discuss taking into account the fluctuative terms in statistical averages using the pair-cluster approximation (PCA) described in Refs. [24–26]. In Sec. 6, we discuss the general microscopic expressions for diffusion coefficients in a binary alloy and define the "correlative Onsager coefficients" and correlation factors for a concentrated alloy. In Sec. 7, we present explicit expressions for the Onsager and diffusion coefficients in a binary alloy using the NNJA-KMFA and the SSJA-KMFA. We also show that for the case of a dilute alloy, these expressions turn into those obtained in traditional theories [8]. In Sec. 8, we discuss the non-pairwise vacancy-solute correlation considering model when such correlations act only between three nearest neighbors in the FCC lattice. Our main results are summarized in Sec. 9.

2. GENERAL EQUATIONS OF DIFFUSIONAL KINETICS IN A SUBSTITUTION ALLOY

General equations of the master equation approach for the diffusional kinetics of alloys and their applications to studies of diffusion in interstitial alloys have been discussed earlier [15, 20]. In this section, we present the basic relations from Ref. [20] needed for what follows. We consider a substitution alloy with $(m + 1)$ components p' which include host atoms denoted by index h, solute atoms denoted by Greek letters α, β, λ, μ, ν, and vacancies denoted by v. Latin letters p, q, r will denote all kinds of atoms, both h and α, while Greek letters ρ, σ, τ will denote both solute atoms α and vacancies v, thus the whole set p' can be written either as $\{p, v\}$ or as $\{h, \rho\}$. Distributions of atoms over lattice sites i are described by the different occupation number sets $\{n_i^{p'}\}$ where the operator $n_i^{p'}$ is 1 when the site i is occupied by a p'-species component, and 0 otherwise. At each i, these operators obey the identity $\sum_{p'} n_i^{p'} = 1$. Hence, only m of them are independent, and one of these operators can be expressed via other ones. We eliminate operator n_i^h corresponding to a host atom writing it as

$$n_i^h = \left(1 - \sum_\rho n_i^\rho\right). \tag{1}$$

This is convenient to describe real alloys where the vacancy site fractions are very low: $\langle n_i^v \rangle \ll \langle n_i^\alpha \rangle$, while Nastar et al. [16–19] eliminate operators n_i^v for vacancies.

We use the pairwise interaction model for which the total configurational Hamiltonian H^t can be expressed via $n_i^{p'}$ and couplings $V_{ij}^{p'q'}$ as follows:

$$H^t = \sum_{ij} \left(\frac{1}{2} \sum_{pq} V_{ij}^{pq} n_i^p n_j^q + \right.$$
$$\left. + \sum_p V_{ij}^{pv} n_i^p n_j^v + \frac{1}{2} V_{ij}^{vv} n_i^v n_j^v \right). \quad (2)$$

After elimination of operators n_i^h according to Eq. (1), the Hamiltonian H^t takes the form:

$$H^t = E_0 + \sum_{\rho i} \varphi_\rho n_i^\rho + H_{int}. \quad (3)$$

Here constants E_0 and φ_ρ yield some insignificant shifts in the total energy and chemical potentials, while the interaction Hamiltonian H_{int} can be written as

$$H_{int} = \sum_{\alpha\beta, i>j} v_{ij}^{\alpha\beta} n_i^\alpha n_j^\beta + \sum_{\alpha, ij} v_{ij}^{\alpha v} n_i^\alpha n_j^v, \quad (4)$$

where terms $v_{ij}^{vv} n_i^v n_j^v$ with vacancy-vacancy interactions are neglected, and the configurational interaction $v_{ij}^{\alpha\rho}$ is expressed via couplings $V_{ij}^{p\,q'}$ in (2) as follows:

$$v_{ij}^{\alpha\rho} = (V^{\alpha\rho} - V^{\alpha h} - V^{h\rho} + V^{hh})_{ij}. \quad (5)$$

The fundamental master equation for the probability P of finding an occupation number set $\{n_i^\rho\} = \xi$ can be written as [15]:

$$\frac{dP(\xi)}{dt} = \sum_\eta [W(\xi, \eta)P(\eta) - W(\eta, \xi)P(\xi)] \equiv \hat{S}P, \quad (6)$$

where $W(\xi, \eta)$ is the $\eta \to \xi$ transition probability per unit time. Adopting for probabilities W the conventional "transition state" model [15, 22], we express the transfer matrix $\hat{S}$ in (6) in terms of the probability of an elementary inter-site atomic exchange ("jump") $pi \rightleftharpoons vj$ between neighboring sites i and j per unit time:

$$W_{ij}^{pv} = n_i^p n_j^v \omega_{pv}^{eff} \exp[-\beta(\hat{E}_{pi,vj}^{SP} - \hat{E}_{pi,vj}^{in})]. \quad (7)$$

Here $\beta = 1/T$ is the reciprocal temperature, $\hat{E}_{pi,vj}^{SP}$ is the saddle point energy, $\hat{E}_{pi,vj}^{in}$ is the initial (before the jump) configurational energy of a jumping atom and a vacancy, and the factor ω_{pv}^{eff} can be written as

$$\omega_{pv}^{eff} = \omega_{pv} \exp\left(\Delta S_{pi,vj}^{SP}\right), \quad (8)$$

where ω_{pv} is the attempt frequency (which has the order of magnitude of a mean frequency of vibrations of a jumping atom in an alloy), and $\Delta S_{pi,vj}^{SP}$ is the entropy difference between the saddle-point and initial alloy states.

The saddle point energy $\hat{E}_{pi,vj}^{SP}$ in (7) depends in general on the atomic configuration near the ij bond.

We describe this dependence by the pairwise interaction model and write this energy as [22]:

$$\hat{E}_{pi,vj}^{SP} = E_h^p + \sum_{\lambda l} \Delta_{p,ij}^{\lambda l} n_l^\lambda, \quad \Delta_{p,ij}^{\lambda l} = (\varepsilon_{p,ij}^{\lambda l} - \varepsilon_{p,ij}^{hl}). \quad (9)$$

Here E_h^p is the saddle point energy for a p-species atom in the pure host metal, the parameter $\Delta_{p,ij}^{\lambda l}$ (to be called the "saddle-point interaction") describes changes in this energy due to a possible substitution of a host atom in site l by a λ-species solute atom, while $\varepsilon_{p,ij}^{\lambda l}$ and $\varepsilon_{p,ij}^{hl}$ are microscopic parameters which can be calculated using either *ab initio* [22] or model [20] calculations.

The most general expression for the probability P in (6) can be written as [15, 16]

$$P\{n_i^\rho\} =$$
$$= \exp\left[\beta\left(\Omega + \sum_{\rho i} \lambda_i^\rho n_i^\rho - H_{int} - \hat{h}_{eff}\right)\right], \quad (10)$$

$$\hat{h}_{eff} = \frac{1}{2} \sum_{\rho\sigma, ij} h_{ij}^{\rho\sigma} n_i^\rho n_j^\sigma +$$
$$+ \frac{1}{6} \sum_{\rho\sigma\tau, ijk} h_{ijk}^{\rho\sigma\tau} n_i^\rho n_j^\sigma n_k^\tau + \ldots \quad (11)$$

Here parameters λ_i^ρ (which are both time- and space-dependent, in general) can be called "site chemical potentials" for an α-species atom or a vacancy with respect to a host atom. These parameters are related to the local chemical potentials μ_i^ρ and μ_i^h as [26]:

$$\lambda_i^\rho = (\mu_i^\rho - \mu_i^h). \quad (12)$$

Quantities $h_{i\ldots j}^{\rho\ldots\sigma}$ in (11) (to be called "effective interactions" [16–18]) describe renormalizations of configurational interactions (5) in the course of kinetic processes, and they can depend on both time and space, too. Constant Ω is determined by normalization.

Multiplying Eq. (6) by operators n_i^ρ and summing over all configurations $\{n_j^\lambda\}$, we obtain equations for the mean occupations of site ("local site fractions") $c_i^\rho = \langle n_i^\rho \rangle$:

$$dc_i^\rho/dt \equiv \dot{c}_i^\rho = \langle n_i^\rho \hat{S} \rangle, \quad (13)$$

where $\langle (\ldots) \rangle$ means averaging over distribution (10), e. g.:

$$c_i^\rho = \langle n_i^\rho \rangle = \sum_{\{n_j^\sigma\}} n_i^\rho P\{n_j^\sigma\}. \quad (14)$$

For simplicity, in Secs. 2–7 we consider the case of presence in (11) of only pairwise effective interactions $h_{ij}^{\rho\sigma}$ which is sufficient for dilute alloys; the non-pairwise effective interactions will be considered in Sec. 8. Then after some algebraic manipulations described in [20], Eqs. (13) can be written similarly to Eqs. (28)–(34) in [20]:

$$
\begin{aligned}
\dot{c}_i^\alpha &= \sum_{j(i)} \Big\langle \gamma_{\alpha v} \hat{b}_{ij}^\alpha \Big\{ \exp\Big[\beta\Big(\lambda_j^\alpha + \lambda_i^v - h_{ji}^{\alpha v} - \\
&\quad - \sum_{\lambda l}(h_{jl}^{\alpha\lambda} + h_{il}^{v\lambda})n_l^\lambda\Big)\Big] - \{i \to j\}\Big\}\Big\rangle, \\
\dot{c}_i^h &= \sum_{j(i)} \Big\langle \gamma_{hv} \hat{b}_{ij}^h \Big\{ \exp\Big[\beta\Big(\lambda_i^v - \sum_{\lambda l} h_{il}^{v\lambda}n_l^\lambda\Big)\Big] - \\
&\quad - \{i \to j\}\Big\}\Big\rangle,
\end{aligned}
\tag{15}
$$

where we also correct some misprints made in [20] and use the identity $(c_i^v + \sum_\alpha c_i^\alpha) = (1 - c_i^h)$. In Eqs. (15), symbol $j(i)$ means summation over sites j being nearest neighbors of site i, while the factor γ_{pv} can be called "the activation frequency" for a $p \to v$ exchange in a pure host metal which can be written similarly to Eq. (7):

$$
\gamma_{pv} = \omega_{pv}^{eff}\exp(-\beta E_{ac}^{pv}). \tag{16}
$$

Here ω_{pv}^{eff} is the same as in (8), while E_{ac}^{pv} is the effective activation energy which is linearly expressed via the saddle point energy E_h^p in (9) and couplings $V_{ij}^{pp'}$ in (2) [20]. The operator $\hat{b}_{ij}^p$ in (15) (to be called "correlation operator" [29]) describes influence of neighboring solute atoms on the probability of a $pi \rightleftharpoons vj$ jump. It can be written as:

$$
\begin{aligned}
\hat{b}_{ij}^p &= n_i^h n_j^h \times \\
&\times \exp\Big[\sum_{\alpha l}\beta(u_{il}^\alpha + u_{jl}^\alpha)n_l^\alpha - \sum_{\alpha l}\beta\Delta_{p,ij}^{\alpha l}n_l^\alpha\Big], \quad (17)
\end{aligned}
$$

where $\Delta_{p,ij}^{\alpha l}$ is the same as in Eq. (9), while parameters u_{il}^α (to be called "kinetic interactions" [29]) are expressed via V_{ij}^{pq} in (2) as follows:

$$
u_{il}^\alpha = (V_{il}^{h\alpha} - V_{il}^{hh}). \tag{18}
$$

We note that the kinetic interaction u_{il}^α in (17) and (18) does not depend on the kind p of a jumping atom, unlike the saddle-point interaction $\Delta_{p,ij}^{\alpha l}$ in (9).

Using operator identities

$$
n_l^\alpha n_l^\beta = n_l^\alpha \delta_{\alpha\beta}, \quad \exp(xn_l^\alpha) = 1 + n_l^\alpha f(x), \tag{19}
$$

where $\delta_{\alpha\beta}$ is the Kroneker symbol and $f(x)$ is $(e^x - 1)$, we can explicitly write the operator $\hat{b}_{ij}^p$ (17) as follows:

$$
\hat{b}_{ij}^p = n_i^h n_j^h \prod_l (1 + f_{p\Delta,ij}^{\alpha l}n_l^\alpha), \tag{20}
$$

$$
f_{p\Delta,ij}^{\alpha l} = [\exp(\beta u_{il}^\alpha + \beta u_{jl}^\alpha - \beta\Delta_{p,ij}^{\alpha l}) - 1]. \tag{21}
$$

3. GENERAL EQUATIONS FOR ONSAGER COEFFICIENTS

3.1. Method of calculations of Onsager coefficients in the master equation approach

The steady-state diffusion is commonly described in terms of Onsager coefficients L_{pq} which relate the atomic flux density $\mathbf{J}_p$ to the chemical potential gradients $\nabla\mu_q$ supposed to be small and constant. These chemical potentials can be counted off the vacancy chemical potential μ_v (which is zero for the usual condition of diffusion when vacancies are in equilibrium [8]), and in cubic crystals where diffusion is isotropic, Onsager relations can be written as:

$$
\mathbf{J}_p = -\sum_q L_{pq}\nabla\mu_q. \tag{22}
$$

In a nonuniform alloy, local values $\mu_i^{qv} = (\mu_i^q - \mu_i^v)$ are related to λ_i^ρ defined by Eqs. (12) as follows:

$$
\mu_i^{\alpha v} = (\lambda_i^\alpha - \lambda_i^v), \quad \mu_i^{hv} = -\lambda_i^v. \tag{23}
$$

Below we use the methods of calculations of Onsager coefficients suggested by Nastar et al. [16–18]. The steady-state diffusion corresponds to a weakly nonuniform alloy for which the local chemical potential difference $\delta\lambda_{ji}^\rho = (\lambda_j^\rho - \lambda_i^\rho)$ in Eqs. (15) is small, while the effective interactions $h_{ij}^{\alpha\rho}$ (called also "fields" for short) are proportional to these differences. Linearizing Eqs. (15) in $\delta\lambda_{ji}^\rho$ and $h_{ij}^{\alpha\rho}$ and expressing $\delta\lambda_{ji}^\rho$ via $\delta\mu_{ji}^p = (\mu_j^p - \mu_i^p)$ according to (23), we obtain:

$$
\begin{aligned}
\dot{c}_i^p &= \\
&= \beta\sum_{j(i)}\Big\langle\gamma_{pv}\exp(\beta\lambda_\alpha + \beta\lambda_v)\hat{b}_{ij}^p\Big[\delta\mu_{ji}^p + (h_{ij}^{pv} - h_{ji}^{pv}) - \\
&\quad - \sum_{\lambda l}(h_{il}^{v\lambda} - h_{jl}^{v\lambda})n_l^\lambda + \sum_{\lambda l}(h_{il}^{p\lambda} - h_{jl}^{p\lambda})n_l^\lambda\Big]\Big\rangle. \quad (24)
\end{aligned}
$$

Here and below, λ_α or λ_v without a site index i or j means the equilibrium value of this chemical potential, while averaging is made over the equilibrium distribution P described by Eq. (10) with $\lambda_i^\rho = \lambda_\rho$ and

$\hat{h}_{eff} = 0$. In accordance with the definition (11), fields $h_{ij}^{p\lambda}$ are nonzero only when index p corresponds to a solute atom α, while $h_{ij}^{h\lambda} = 0$ (which is also illustrated by Eqs. (15)). For the given j, each term in the right-hand side of (24) has evidently the meaning of an atomic flux $J_{j\to i}^{p}$ through bond ij. It enables to write the linear relation between these fluxes and quantities $\delta\mu_{ji}^{p}$ and $h_{ij}^{p\rho}$ in (24). It was also noted in [16, 17] that for the steady-state diffusion, fields $h_{ij}^{\alpha\rho}$ are antisymmetric in indices i and j:

$$h_{ji}^{\alpha v} = -h_{ij}^{\alpha v}, \quad h_{ji}^{\alpha\beta} = -h_{ij}^{\alpha\beta}. \tag{25}$$

Denoting also site i by index "0" and site j by index "1", we can write the above-mentioned fluxes $J_{0\to1}^{p}$ as follows:

$$J_{0\to1}^{p} = -\beta\left[\overline{w}_p(\delta\mu_p + 2h_1^{pv}) - \right.$$
$$\left. - \sum_{\lambda l} \nu_p^{\lambda l}(h_{0l}^{v\lambda} - h_{1l}^{v\lambda} - h_{0l}^{p\lambda} + h_{1l}^{p\lambda})\right], \quad (26)$$

where $\delta\mu_p$ is $(\mu_1^p - \mu_0^p)$, h_1^{pv} is the nearest-neighbor effective interaction (being nonzero only at $p \neq h$), and $\overline{w}_p$ and $\nu_p^{\lambda l}$ are statistical averages:

$$\overline{w}_p = \langle\hat{w}_{01}^p\rangle, \quad \nu_p^{\lambda l} = \langle\hat{w}_{01}^p n_l^\lambda\rangle. \tag{27}$$

Here operator $\hat{w}_{01}^p$ is the product of the operator $\hat{b}_{01}^p$ given by Eq. (17) or (20) and the constant factor Γ_p which enters into Eqs. (24):

$$\begin{aligned} &\hat{w}_{01}^p = \Gamma_p \hat{b}_{01}^p, \\ &\Gamma_\alpha = \gamma_{\alpha v} \exp(\beta\lambda_\alpha + \beta\lambda_v), \quad \Gamma_h = \gamma_{hv} \exp(\beta\lambda_v). \end{aligned} \tag{28}$$

Taking into account the presence of factor $n_i^h n_j^h$ in the operator $\hat{b}_{ij}^p$ (20) and the relations (65) below for λ_α and λ_v in (28), we see that the average $\overline{w}_p$ in (27) is proportional to the site fraction c_p of p-species atoms. Thus this average can be written as

$$\overline{w}_p = c_p\,\omega_p, \tag{29}$$

where ω_p has evidently the meaning of the mean frequency of $p \leftrightarrows v$ jumps for a p-species atom. Therefore, Eq. (29) provides the statistical definition of this frequency, and below we mainly discuss frequencies ω_p rather than averages $\overline{w}_p$.

Fields $h_{ij}^{\alpha\rho}$ in Eqs. (26) can be found from the stationarity condition for two-site averages [16, 17]:

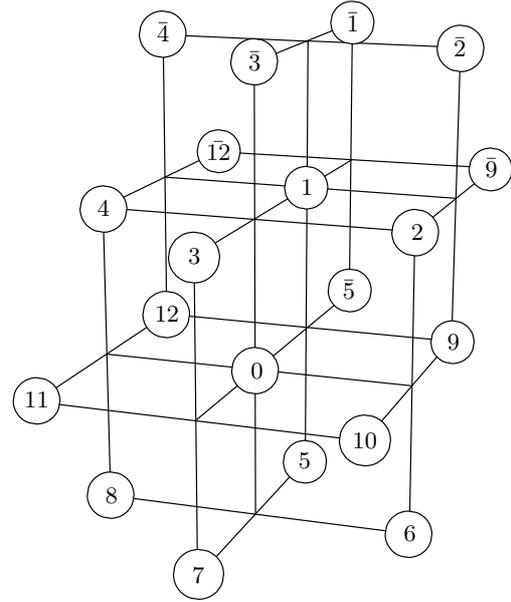$$(d/dt)\langle n_0^\alpha n_j^p\rangle = 0, \tag{30}$$

Fig. 1. Bond (0,1) in the FCC lattice and its nearest neighbors, sites k and $\bar{k}$ discussed in the text

which yields the following equations for $h_{ij}^{\alpha\rho}$ [15–17]:

$$\sum_{k\neq0\neq j}\left[m_{\alpha,0k}^{pj}(\delta\mu_{k0}^\alpha + 2h_{0k}^{\alpha v}) - \sum_{\lambda l}t_{\alpha,0k}^{pj,\lambda l}(h_{0l}^{v\lambda} - h_{kl}^{v\lambda} - \right.$$
$$- h_{0l}^{\alpha\lambda} + h_{kl}^{\alpha\lambda}) + m_{p,jk}^{\alpha 0}(\delta\mu_{kj}^p + 2h_{jk}^{pv}) -$$
$$\left. - \sum_{\lambda l}t_{h,jk}^{\alpha 0,\lambda l}\left(h_{jl}^{v\lambda} - h_{kl}^{v\lambda} - h_{jl}^{p\lambda} + h_{kl}^{p\lambda}\right)\right] = 0, \quad (31)$$

where

$$m_{p,ik}^{qj} = \langle\hat{w}_{ik}^p n_j^q\rangle, \quad t_{p,ik}^{qj,\lambda l} = \langle\hat{w}_{ik}^p n_j^q n_l^\lambda\rangle. \tag{32}$$

Following Nastar et al. [16], we consider diffusion along z-axis of an FCC alloy when chemical potentials $\mu_i^p = \mu^p(\mathbf{R}_i)$ depend only on z_i. Let us denote positions of sites 0 and 1 in Eqs. (26) as $\mathbf{R}_0 = (0, 0, 0)$ and $\mathbf{R}_1 = (0, a_0/2, a_0/2)$ where a_0 is the FCC lattice constant, while sites near the bond $(0, 1)$ are numbered as shown in Fig. 1. Quantity $\delta\mu_p$ in Eqs. (26) is the difference of chemical potentials between neighboring atomic planes along z axis: $\delta\mu_p = \mu_p(a_0/2) - \mu_p(0)$. The field $h_{0l}^{p\lambda} = h^{\rho\lambda}(\mathbf{R}_{0l})$ does not change under rotations of vector $\mathbf{R}_{0l} = (x_{0l}, y_{0l}, z_{0l})$ around z-axis, and it changes sign under reflection with respect to (x, y)-plane: $h^{\rho\lambda}(x_{0l}, y_{0l}, -z_{0l}) = -h^{\rho\lambda}(x_{0l}, y_{0l}, z_{0l})$. For brevity, we denote the set of crystallographically equivalent sites with the same positive value $z_{0l_n} > 0$ as l_n^+, the similar set with the negative value $z_{0l_n} = -z_{l_n}$,

as l_n^-, and fields $h^{\rho\lambda}(\mathbf{R}_{l_n^+})$ or $h^{\rho\lambda}(\mathbf{R}_{l_n^-})$ corresponding to the set of sites l_n^+ or l_n^-, as $h_n^{\rho\lambda}$ or $(-h_n^{\rho\lambda})$. Index n which numbers different sets of equivalent sites, l_n^+ and l_n^-, is supposed to increase with the distance $|\mathbf{R}_{0l}|$, and for a given $|\mathbf{R}_{0l}|$, it increases with the z_{0l} value. Thus $n = 1$ corresponds to the nearest-neighbor field $h_1 = h(\mathbf{R}_{01})$, and Eqs. (26) can be concisely written as:

$$J_{0\to1}^p = -\beta \left[\overline{w}_p(\delta\mu_p + 2h_1^{pv}) + \right.$$
$$\left. + \sum_\lambda \sum_{n=1}^{n_{max}} l_{p,n}^\lambda (h_n^{\lambda v} - h_n^{\lambda p}) \right]. \quad (33)$$

Here n_{max} is the maximum number of fields $h_n^{\rho\lambda}$ taken into account, and increase of n_{max} corresponds to a more accurate description of vacancy correlation effects [16]. Coefficients $l_{p,n}^\lambda$ in (33) are defined as follows:

$$l_{p,n}^\lambda = \sum_{l_n^+, l_n^-} \langle \hat{w}_{01}^p (n_{l_n^+} - n_{l_n^-} - n_{1,l_n^+} + n_{1,l_n^-})^\lambda \rangle. \quad (34)$$

Here index λ at brackets means that it should be put at each term within brackets, e. g., $(n_{l_n^+} + \dots)^\lambda = (n_{l_n^+}^\lambda + \dots)$, and we use the following notation:

$$n_{l_n^\pm} = n(\mathbf{R}_{l_n^\pm}), \quad n_{1,l_n^\pm} = n(\mathbf{R}_{l_n^\pm} + \mathbf{R}_1). \quad (35)$$

Using the same notation as in (33)–(35), we can concisely write Eqs. (31) similarly to (33):

$$m_{\alpha,n}^p(\delta\mu_\alpha + 2h_1^{\alpha v}) - m_{p,n}^\alpha(\delta\mu_p + 2h_1^{pv}) +$$
$$+ \sum_\lambda \sum_{m=1}^{n_{max}} \left[(t_{\alpha,nm}^{p\lambda} - t_{p,nm}^{\alpha\lambda}) h_m^{\lambda v} - t_{\alpha,nm}^{p\lambda} h_m^{\lambda\alpha} + \right.$$
$$\left. + t_{p,nm}^{\alpha\lambda} h_m^{\lambda p} \right] = 0, \quad (36)$$

where coefficients $t_{p,nm}^{q\lambda}$ and $m_{p,n}^q$ are defined as follows:

$$t_{p,nm}^{q\lambda} =$$
$$= \sum_{k=1}^{12} \sum_{l_m^+, l_m^-} \langle \hat{w}_{0k}^p n_{n,1}^q (n_{l_m^+} - n_{l_m^-} - n_{k,l_m^+} + n_{k,l_m^-})^\lambda \rangle, \quad (37)$$
$$m_{p,n}^q = \sum_{k=1}^{4} \langle (\hat{w}_{0k}^p - \hat{w}_{0,k+4}^p) n_{n,1}^q \rangle.$$

Here $n_{l_m^+}$ and $n_{l_m^-}$ are the same as in (34); operator $n_{n,1}^q = n^q(\mathbf{R}_{n,1})$ corresponds to the vector $\mathbf{R}_{n,1}$ chosen as "the first one" in the set of vectors $\mathbf{R}_{l_n^+}$; $n_{k,l_n^\pm}$ defined similarly to $n_{1,l_n^\pm}$ in Eq. (35) is $n(\mathbf{R}_{l_n^\pm} + \mathbf{R}_k)$; and we took unto account symmetry or antisymmetry of each average in (36) with respect to reflections $\mathbf{R}_{n,1} \to (-\mathbf{R}_{n,1})$.

Equation (36) enables to express all fields $h_n^{\alpha\rho}$ as linear combinations of $\delta\mu_q$. Then substitution of these expressions into Eq. (33) yields the linear relation between the flux $J_{0\to1}^p$ and differences $\delta\mu_p$:

$$J_{0\to1}^p = \sum_q A_{pq}\delta\mu_q, \quad (38)$$

where parameters A_{pq} are some functions of coefficients $l_{p,n}^\lambda$, $m_{p,n}^q$ and $t_{p,n}^{q\lambda}$ in Eq. (36). To relate parameters A_{pq} in (38) to the Onsager coefficients L_{pq} in (22), we note that the flux density J_p along z axis can be found as the ratio of the total flux through one site lying in the plane $(0,0,0)$ to the area $S = a_0^2/2$ corresponding to this site, while the difference $\delta\mu_p$ in Eq. (38) is simply expressed via $\nabla\mu_q = (0,0,d\mu_q/dz)$:

$$J_p = 4J_{0\to1}^p/S = 8J_{i\to j}^p/a_0^2, \quad (39)$$

$$\delta\mu_p = (d\mu_p/dz)a_0/2. \quad (40)$$

Substituting these relations into (38) and comparing the result with a z-component of Eq. (22), we find:

$$L_{pq} = -4A_{pq}/a_0 = -na_0^2 A_{pq}, \quad (41)$$

where $n = 4/a_0^3$ is the atomic density in the FCC lattice.

3.2. Model of nearest-neighbor kinetic and saddle-point interactions

Below we consider the model when both the saddle-point and the kinetic interactions, $\Delta_{p,ij}^\lambda$ and u_{il}^λ in Eqs. (9), (17), (20) and (21), are nonzero only for the nearest-neighbors. This corresponds to the standard "five-frequency model" for FCC alloys [1–9]. For this model, the operator $\hat{b}_{01}^p$ and the mean frequency ω_p in Eqs. (20), (28) and (29) take the form:

$$\hat{b}_{01}^p = n_0^h n_1^h \prod_l \left(1 + \sum_\mu n_l^\mu f_{p\Delta}^\mu \right) \times$$
$$\times \prod_m \left(1 + \sum_\nu n_m^\nu f_u^\nu \right), \quad (42)$$
$$\omega_p = (\Gamma_p/c_p)\langle \hat{b}_{01}^p \rangle.$$

Here indices l and m indicate sites differently positioned with respect to the bond $(0,1)$, as shown in Fig. 1. In this figure, sites with positions $\mathbf{R}_k$ for k between 1 and 12 correspond to the nearest neighbors of site "0" positioned at $\mathbf{R}_0 = 0$, while sites positioned at $\mathbf{R}_{\bar{k}} \equiv \mathbf{R}_{1,k} = (\mathbf{R}_1 + \mathbf{R}_k)$ correspond to the nearest

neighbors of site "1" with $\mathbf{R}_1 = (0, a_0/2, a_0/2)$. The evident relations

$$\bar{7} \equiv 0, \quad \bar{6} \equiv 9, \quad \bar{8} \equiv 12, \quad \overline{10} \equiv 2, \quad \overline{11} \equiv 4 \quad (43)$$

are also taken into account.

In Eq. (42), index l in the first product takes four values: 2, 4, 9 or 12, which correspond to the nearest neighbors of bond (0,1), i. e., of both site 0 and site 1. Index m in the second product corresponds to the nearest neighbors of only one of these sites, site 0 or site 1, and takes fourteen values: 3, 5, 6, 7, 8, 10, 11, $\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}, \bar{9}$ or $\overline{12}$. Quantity $f_{p\Delta}^\mu$ or f_u^ν in Eq. (42) is the Mayer function which, according to Eq. (21), corresponds to the sum of non-zero contributions of the saddle-point interaction (9) and the kinetic interaction (18):

$$
\begin{aligned}
f_{p\Delta}^\mu &= \exp[\beta(2u_1^\mu - \Delta_p^\mu)] - 1, \\
f_u^\nu &= \exp(\beta u_1^\nu) - 1,
\end{aligned}
\quad (44)
$$

where u_1^ν is the nearest-neighbor kinetic interaction.

The vacancy correlation effects in concentrated alloys will be described using two approximations.

(i) The simplest "Lidiard-Le Claire" approximation which supposes that a vacancy that leaves the first neighbor shell of a solute atom does not return [8]. It corresponds to the nearest-neighbor effective interaction: $h_n = \delta_{n,1} h_1$ [17] and will be called the "nearest-neighbor-jump approximation" (NNJA). For the NNJA, Eqs. (33)–(36) include only terms with $n = 1$ and $m = 1$, and Eqs. (34) and (37) take the form:

$$l_{p,1}^\lambda = \sum_{k=1}^{4} \langle \hat{w}_{01}^p (n_k - n_{k+4} - n_{1,k} + n_{1,k+4})^\lambda \rangle, \quad (45)$$

$$m_{p,1}^q = \sum_{k=1}^{4} \langle (\hat{w}_{0k}^p - \hat{w}_{0,k+4}^p) n_1^q \rangle, \quad (46)$$

$$
t_{p,11}^{q\lambda} =
= \sum_{k=1}^{12} \left\langle \hat{w}_{0k}^p n_1^q \sum_{l=1}^{4} (n_l - n_{l+4} - n_{k,l} + n_{k,l+4})^\lambda \right\rangle. \quad (47)
$$

(ii) The more refined approximation (which for dilute alloys has been suggested by Bocquet [5]) that neglects the probability of return of a vacancy which leaves the second shell of neighbors, to be called "the second-shell-jump" approximation (SSJA). For dilute alloys, it seems to describe vacancy correlation effects with the accuracy of the order of percents [5] sufficient for most of applications. In Eqs. (34)–(36), SSJA corresponds to $n_{max} = 5$, that is, to the presence of five

fields h_n with the following vectors $\mathbf{R}_{n,1}$ in Eq. (36) (in $a_0/2$ units):

$$
\begin{aligned}
\mathbf{R}_{1,1} &= (0,1,1), \quad \mathbf{R}_{2,1} = (0,0,2), \\
\mathbf{R}_{3,1} &= (1,2,1), \quad \mathbf{R}_{4,1} = (1,1,2), \\
\mathbf{R}_{5,1} &= (0,2,2),
\end{aligned}
\quad (48)
$$

while the set l_n^+ of vectors $\mathbf{R}_{l_n^+}$ in Eqs. (34) and (37) for n equal to 1, 2, 3, 4 and 5 includes 6, 1, 8, 4 and 4 vectors $\mathbf{R}_{l_n^+}$, respectively.

Therefore, to find atomic fluxes $J_{0 \to 1}^p$ in Eqs. (33), we should calculate statistical averages of three different types: quantities $\overline{w}_p = \langle \hat{w}_{01}^p \rangle$ in Eq. (42); quantities $l_{p,n}^\lambda$ and $m_{p,n}^q$ in Eqs. (34) and (37) which include "one-site" averages $\langle \hat{w}_{01}^p n_i^\lambda \rangle$; and quantities $t_{p,nm}^{q\lambda}$ in (37) which include "two-site" averages $\langle \hat{w}_{01}^p n_i^q n_j^\lambda \rangle$.

4. CALCULATIONS OF STATISTICAL AVERAGES

4.1. Exact relations

Before to discuss methods of calculations of averages $\overline{w}_p$, $l_{p,n}^\lambda$, $m_{p,n}^q$ and $t_{p,nm}^{q\lambda}$ in Eqs. (33)–(37) we consider some exact relations which follow either from definitions of these averages or from the crystal symmetry.

First, we note that according to definitions (27), (34), (37), each such an average is proportional to the factor $\exp(\beta\lambda_v)$, that is, to the reduced thermodynamic activity coefficient a_v for vacancies defined by Eqs. (65)–(69) below. This factor enters into the coefficient Γ_p in Eqs. (28), and it is determined by the vacancy-solute interactions $v_{v\alpha}$. Therefore, at nonzero solute site fractions c_α, the vacancy-solute interaction has an influence on all diffusion coefficients, contrary to the usual ideas [1–9, 17], and this influence is fully described by the common factor $a_v = \exp(\beta\lambda_v^{int})$ defined by Eqs. (65)–(69) or (104) which enters into each Onsager and diffusion coefficient.

Second, we note two operator identities which are useful for calculations of one-site or two-site averages, i. e., of quantities $l_{p,n}^\lambda$, $m_{p,n}^q$ or $t_{p,nm}^{q\lambda}$ in Eqs. (33)–(36). These identities include the product of the operator n_i^q and one of factors in two last products in Eq. (42):

$$
\begin{aligned}
n_i^q \left(1 + \sum_\lambda n_i^\lambda f_{p\Delta}^\lambda \right) &= n_i^q e_{p\Delta}^q, \\
n_i^q \left(1 + \sum_\lambda n_i^\lambda f_u^\lambda \right) &= n_i^q e_u^q,
\end{aligned}
\quad (49)
$$

where we denote for brevity:

$$e_{p\Delta}^q = \exp[\beta(2u_1^q - \Delta_p^q)], \quad e_u^q = \exp(\beta u_1^q). \quad (50)$$

We note that when index q in Eqs. (49) corresponds to a host atom: $q = h$, factor $e^h_{p\Delta}$ or e^h_u in (49) is unity:

$$e^h_{p\Delta} = e^h_u = 1 \qquad (51)$$

as the product $n^h_i n^\lambda_i$ in (49) is zero. Equations (49) imply, for example, that in Eq. (45) for l^λ_p, the product $\left(1 + \sum_\mu n^\mu_2 f^\mu_{p\Delta}\right) n^\lambda_2$ in the operator $\hat{w}^p_{01} n^\lambda_2$ is reduced to $e^\lambda_{p\Delta} n^\lambda_2$, while the product $\left(1 + \sum_\mu n^\mu_6 f^\mu_u\right) n^\lambda_6$ is reduced to $e^\lambda_u n^\lambda_6$. It simplifies calculations of statistical averages.

Third, we consider the crystal symmetry relations for one-site and two-site averages, to be denoted ν^q_{pi} and $\nu^{q\lambda}_{p,ij}$:

$$\nu^q_{pi} = \langle \hat{w}^p_{01} n^q_i \rangle, \quad \nu^{q\lambda}_{p,ij} = \langle \hat{w}^p_{01} n^q_i n^\lambda_j \rangle. \qquad (52)$$

These relations can be conveniently discussed using Figs. 1 and 2 which illustrate the crystal symmetry of different sites near the bond $(0,1)$ corresponding to an inter-site jump $p \leftrightarrows v$. These sites can be divided into three groups: (i) sites 0 and $1 \equiv \bar{0}$, to be called "sites h" as occupation of these sites is described in Eq. (42) by the operators n^h_0 and n^h_1; (ii) sites 2, 4, 9 and 12 being the nearest neighbors of both sites 0 and site 1, to be called "sites Δ" as the occupation operator n^λ_l for each of these sites enters into Eq. (42) with the factor $f^\lambda_{p\Delta}$; (iii) the rest nearest neighbors of site 0 or site 1, that is, sites 3, 5, 6, 7, 8, 10, 11, and $\bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}, \bar{9}, \overline{12}$, to be called "sites u" as the operator $n^\mu_{m_1}$ or $n^\nu_{m_2}$ for these sites enters into Eq. (42) with the factor f^μ_u or f^ν_u.

The sites u can also be divided into three groups of the different topology illustrated by Fig. 2: (i) the "vertex" sites 3, $\bar{3}$, 5 and $\bar{5}$, to be called "sites v", (ii) the "side" sites 6, 8, 10, 11, $\bar{2}, \bar{4}, \bar{9}$ and $\overline{12}$, to be called "sites s", and (iii) the "central" sites 7 and $\bar{1}$, to be called "sites c". These different types of the site symmetry will be denoted by symbol ξ which takes values Δ and u or, for a more detailed description, Δ, v, s, and c.

The above-discussed symmetry relations can be used to simplify Eq. (45) for $l^\lambda_{p,1}$ which is originally written as

$$l^\lambda_{p,1} = \langle \hat{w}^p_{01}[(n_1 + n_2 + n_3 + n_4 - n_5 - n_6 - n_7 - n_8)^\lambda -$$
$$- (n_{\bar{1}} + n_{\bar{2}} + n_{\bar{3}} + n_{\bar{4}} - n_{\bar{5}} - n_{\bar{6}} - n_{\bar{7}} - n_{\bar{8}})^\lambda]\rangle. \qquad (53)$$

First, three last terms in the second brackets can be rewritten according to Eq. (43). Second, terms with n^λ_0 and n^λ_1 in (53) vanish as the operator $\hat{w}^p_{01}$ (42) includes factors n^h_0 and n^h_1 while $n^h_i n^\lambda_i = 0$. Thus, we obtain:
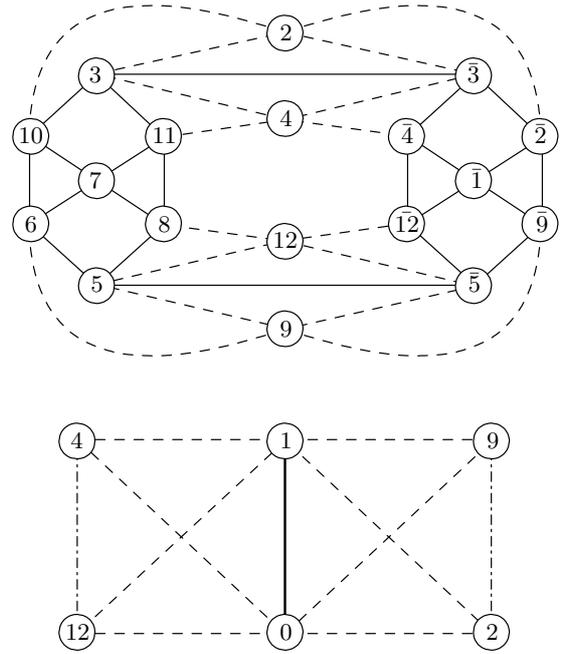

Fig. 2. Schematic representation of bonds of types (h, h), (h, Δ), (Δ, Δ), (Δ, u) and (u, u) described in the text. Seven bonds $(0, k)$ and seven bonds $(1, \bar{k})$ which belong to type (h, u) are not shown for clarity of figure (color online [13])

$$l^\lambda_{p,1} = \langle \hat{w}^p_{01}[(n_2 + n_4 + n_9 + n_{12})^\lambda +$$
$$+ (n_3 - n_5 - n_{\bar{3}} + n_{\bar{5}} - n_6 - n_8 - n_{\bar{2}} - n_{\bar{4}}) - n_7 - n_{\bar{1}})^\lambda]\rangle. \qquad (54)$$

Figures 1 and 2 show that the four Δ-sites, 2, 4, 9, 12, are equivalent to each other, as well as four v-sites 3, 5, $\bar{3}$, $\bar{5}$, eight s-sites 6, 8, 10, 11, $\bar{2}, \bar{4}, \bar{9}, \overline{12}$, and two c-sites, 7 and $\bar{1}$. Therefore, Eq. (54) includes only three different terms:

$$l^\lambda_{p,1} = (4\nu^\lambda_{p\Delta} - 4\nu^\lambda_{ps} - 2\nu^\lambda_{pc}), \qquad (55)$$

where $\nu^\lambda_{p\xi}$ means the one-site average ν^λ_{pi} (52) for a site i of the symmetry ξ:

$$\nu^\lambda_{p\Delta} = \langle \hat{w}^p_{01} n^\lambda_2 \rangle, \quad \nu^\lambda_{ps} = \langle \hat{w}^p_{01} n^\lambda_6 \rangle,$$
$$\nu^\lambda_{pc} = \langle \hat{w}^p_{01} n^\lambda_7 \rangle. \qquad (56)$$

Expressions (46) and (47) for $m^q_{p,1}$ and $t^{q\lambda}_{p,11}$ include operators $\hat{w}^p_{0k}$ which describe atomic jumps along bonds $(0, k)$ rather than along the bond $(0,1)$ considered above. To use the above-discussed symmetry relations, we can employ the rotation of the FCC lattice which transforms the bond $(0, k)$ into the $(0,1)$ one. Table 1 shows changes of positions of different sites under such rotations.

Table 1.   Changes of positions of lattice sites under rotations of the FCC lattice which transform bonds $(0,k)$ into bond (0,1)

k	Components of vector $\mathbf{R}$	Position of sites											
1	(x,y,z)	1	2	3	4	5	6	7	8	9	10	11	12
2	$(-y,x,z)$	4	1	2	3	8	5	6	7	12	9	10	11
3	$(-x,-y,z)$	3	4	1	2	7	8	5	6	11	12	9	10
4	$(y,-x,z)$	2	3	4	1	6	7	8	5	10	11	12	9
5	$(x,-z,y)$	3	10	7	11	1	9	5	12	2	6	8	4
6	$(-y,-z,x)$	11	3	10	7	12	1	9	5	4	2	6	8
7	$(x,-y,-z)$	7	6	5	8	3	2	1	4	10	9	12	11
8	$(y,-z,-x)$	10	7	11	3	9	5	12	1	6	8	4	2
9	$(-z,y,x)$	12	4	11	8	9	2	10	6	1	3	7	5
10	$(-z,x,-y)$	8	12	4	11	6	9	2	10	5	1	3	7
11	$(z,-x,-y)$	6	10	2	9	8	11	4	12	7	3	1	5
12	$(z,y,-x)$	9	6	10	2	12	8	11	4	5	7	3	1

Using Table 1, we can write $m_{p,1}^q$ in (46) as

$$m_{p,1}^q = \langle \hat{w}_{01}^p (n_4+n_3+n_2-n_3-n_{11}-n_7-n_{10})^q \rangle =$$
$$= (2\nu_{p\Delta}^q - 2\nu_{ps}^q - \nu_{pc}^q). \quad (57)$$

It implies

$$l_{p,1}^q = 2\, m_{p,1}^q, \quad (58)$$

where we use the same considerations and notation as in (53)–(56), while index q corresponds to either λ or h.

The similar methods can be used to explicitly write the average $t_{p,11}^{q\lambda}$ in (47). It can be written as the sum of two terms, "one-site" and "two-site" ones:

$$t_{p,11}^{q\lambda} = t_{1p}^{q\lambda} + t_{2p}^{q\lambda}. \quad (59)$$

The one-site term $t_{1p}^{q\lambda}$ has the form similar to (55):

$$t_{1p}^{q\lambda} = \delta_{q\lambda} \left(2\nu_{p\Delta}^\lambda + 2\nu_{pv}^\lambda + 4\nu_{ps}^\lambda + \nu_{pc}^\lambda \right), \quad (60)$$

where ν_{pv}^λ is $\langle \hat{w}_{01}^p n_3^\lambda \rangle$.

The two-site term $t_{2p}^{q\lambda}$ in (59) includes 21 non-equivalent averages $\nu_{p,ij}^{q\lambda}$ which can be grouped into terms $t_{p,\xi\xi'}^{q\lambda}$ corresponding to symmetries ξ and ξ' of sites i and j:

$$t_{2p}^{q\lambda} = \sum_{\xi,\xi'} t_{p,\xi\xi'}^{q\lambda}, \quad (61)$$

where both ξ and ξ' takes the value Δ, v, s or c. The non-zero terms $t_{p,\xi\xi'}^{q\lambda}$ in (61) can be written as follows:

$$
\begin{aligned}
t_{p,\Delta\Delta}^{q\lambda} &= (4\nu_{2,4} + 2\nu_{2,9})_p^{q\lambda}, \\
t_{p,\Delta s}^{q\lambda} &= -2(\nu_{2,6} + \nu_{2,8} + \nu_{2,10} + \nu_{2,11})_p^{q\lambda}, \\
t_{p,\Delta c}^{q\lambda} &= -4(\nu_{2,7})_p^{q\lambda}, \\
t_{p,vv}^{q\lambda} &= 2(\nu_{3,\bar{5}} - \nu_{3,5} - \nu_{3,\bar{3}})_p^{q\lambda}, \\
t_{p,vs}^{q\lambda} &= 2(\nu_{3,10} - \nu_{3,6} - \nu_{3,\bar{2}} + \nu_{3,\bar{9}})_p^{q\lambda}, \\
t_{p,ss}^{q\lambda} &= 2(\nu_{6,10} - \nu_{6,11} + \nu_{6,\bar{2}} + \nu_{6,\bar{4}})_p^{q\lambda}, \\
t_{p,sc}^{q\lambda} &= 2(\nu_{6,7} + \nu_{6,\bar{1}})_p^{q\lambda}, \quad t_{p,cc}^{q\lambda} = (\nu_{7,\bar{1}})_p^{q\lambda}.
\end{aligned} \quad (62)
$$

Here the lower index p and the upper indices $q\lambda$ at brackets mean that they should be put at each term within brackets, while the notation $\nu_{i,j}$ (used for clarity) means the same as ν_{ij} in (52). Quantities $t_{\xi'\xi}^{q\lambda}$ with $\xi' \neq \xi$ not presented in Eqs. (62) can be obtained from those given in (62) by interchanging indices q and λ: $t_{\xi'\xi}^{q\lambda} = t_{\xi\xi'}^{\lambda q}$.

The above-discussed relations of symmetry are useful for statistical calculations using the methods more refined than the simple kinetic mean-field approximation described in Sec. 4.2, such as the pair-cluster approximation discussed in Sec. 5. These symmetry relations can also be used to calculate quantities $l_{p,n}^\lambda$, $m_{p,n}^q$ and $t_{p,nm}^{q\lambda}$ in Eqs. (34)–(37) with $n, m > 1$ employed in the SSJA.

4.2. Kinetic mean-field calculations

In this section, we describe calculations of averages $\langle \hat{w}_{01}^p \rangle$, $l_{p,n}^\lambda$, $m_{p,n}^q$ and $t_{p,nm}^{q\lambda}$ in Eqs. (42), (34), (37) using the simplest of our approximations which neglects fluctuations of occupation numbers n_i^p in these averages: each n_i^p is replaced by its mean value $\langle n_i^p \rangle = c_p$. At the same time, thermodynamic quantities, in particular, chemical potentials λ_ρ in Eqs. (28), will be found using the more exact, pair-cluster approximation – PCA (which is fully equivalent to the so-called "pair cluster variation method — pair CVM" but uses more simple calculations and is more convenient for generalizations [24–26]). It can significantly raise the accuracy of calculations with respect to usual, simplest versions of the mean-field approximation (MFA), particularly for dilute alloys where the PCA becomes exact [25, 26]. To differ this our approach from the usual MFA, we call it "the kinetic mean-field approximation" (KMFA).

Let us first find the KMFA expression for the mean frequency ω_p in Eq. (29). Replacing each n_i^p in Eqs. (27), (28), and (42) by site fraction c_p, we obtain:

$$\omega_p^{\mathrm{KMFA}} \equiv \omega_p^0 = (\Gamma_p/c_p)c_h^2 S_{p\Delta}^4 S_u^{14}. \qquad (63)$$

The upper index "0" at averages w_p, ν_p, m_p, l_p and t_p will mean "KMFA", and we denote for brevity:

$$S_{p\Delta} = \left(1 + \sum_\lambda c_\lambda f_{p\Delta}^\lambda\right),$$
$$S_u = \left(1 + \sum_\mu c_\mu f_u^\mu\right). \qquad (64)$$

The factor Γ_p in (63), according to (28), can be expressed via the activation frequency γ_p and the chemical potentials λ_ρ of vacancies or solute atoms with respect to host atoms. Each λ_ρ is the sum of the ideal solution term $\lambda_\rho^{id} = T\ln(c_\rho/c_h)$ and the interaction term λ_ρ^{int}:

$$\beta\lambda_v = \ln(c_v/c_h) + \beta\lambda_v^{int},$$
$$\beta\lambda_\alpha = \ln(c_\alpha/c_h) + \beta\lambda_\alpha^{int}. \qquad (65)$$

In a dilute alloy, the interaction term λ_ρ^{int} is linear in solute site fractions c_α. We will describe these terms by the PCA expressions which for dilute alloys become exact [26]. For a binary alloy, these expressions are given below by Eqs. (104), while for a multi-component dilute alloy these terms can be obtained from Eqs. (26)–(31) in [26]:

$$\beta\lambda_v^{int} = -\sum_\gamma \sum_{n=1} z_n f_n^{v\gamma} c_\gamma,$$
$$\beta\lambda_\alpha^{int} = -\sum_\gamma \sum_{n=1} z_n f_n^{\alpha\gamma} c_\gamma. \qquad (66)$$

Here, z_n is the coordination number for the n-th shell in the crystal, and $f_n^{\rho\gamma}$ is the Mayer function for the configurational interaction $v_n^{\rho\gamma}$ (5) in this shell:

$$f_n^{\rho\gamma} = [\exp(\beta\, v_n^{\rho\gamma}) - 1]. \qquad (67)$$

Using Eqs. (28), (29), (65), we can write the KMFA expressions (63) for mean frequencies ω_p as

$$\omega_\alpha^0 = \omega_{\alpha 0} c_v a_v a_\alpha S_{\alpha\Delta}^4 S_u^{14},$$
$$\omega_h^0 = \omega_{h0} c_v a_v S_{h\Delta}^4 S_u^{14}. \qquad (68)$$

Here the factor a_v or a_α defined by the relation

$$a_v = \exp(\beta\lambda_v^{int}), \quad a_\alpha = \exp(\beta\lambda_\alpha^{int}) \qquad (69)$$

can be called "the reduced activity coefficient" for a vacancy or a solute atom. For a binary alloy AB, the relation between a_α in (69) and conventional activity coefficients γ_B and γ_A (used, e. g., in [8]) is given by Eq. (108) below.

Factors ω_{p0} in Eqs. (68) are related to the vacancy site fraction c_v and to activation frequencies γ_p in (16) as follows:

$$\omega_{\alpha 0} = c_v \gamma_{\alpha v}, \quad \omega_{h0} = c_v \gamma_{hv}. \qquad (70)$$

When $c_\alpha \to 0$, factors a_v, a_α, $S_{p\Delta}$, S_u in (64) and (69) tend to unity. Hence ω_{p0} has the meaning of the mean frequency of $p \rightleftharpoons v$ jumps for a p-species atom at $c_\alpha \to 0$, and the KMFA results (68) for ω_p become exact in this limit. For a concentrated alloy, ω_p^0 in (68) is the value of this mean frequency found in the KMFA. We note that the mean frequency $\omega_{\alpha 0}$ in (70) differs from the "solute jump frequency" w_α used in the standard five-frequency model [1–9] which is related to our $\omega_{\alpha 0}$ as

$$w_\alpha = \omega_{\alpha 0} e_1^{v\alpha}, \quad e_1^{v\alpha} = \exp(\beta v_1^{v\alpha}), \qquad (71)$$

where $v_1^{v\alpha}$ is the nearest-neighbor vacancy-solute interaction. Factor $e_1^{v\alpha}$ in (71) corresponds to the factor $\exp(\beta \hat{E}_{pi,vj}^{in})$ in (7), and it is canceled in the mean frequency $\omega_{\alpha 0}$ due to the presence of statistical averaging in Eqs. (15).

Discussing calculations of one-site averages $\nu_{p\xi}^q$ in Eqs. (55), (58) and (60), we first note that differences between averages which include occupation operators of sites of a different symmetry v, s or c arise only

due to the inter-site correlations. As in the KMFA, these correlatios are neglected, each of indices v, s, c in Eqs. (56)–(60) can be replaced by the common index u mentioned above. Second, identities (49) show that the average $\nu_{p\xi}^q = \langle \hat{w}_{01}^p n_\xi^q \rangle$ differs from the average $\langle \hat{w}_{01}^p \rangle = w_p^0$ only by replacing one of factors $S_{p\xi}$ in Eq. (63) (with $S_{pu} \equiv S_u$) to the factor $c_q e_{p\xi}^q$ with $e_{p\xi}^q$ from Eqs. (50). It yields the following relations:

$$\nu_{p\Delta}^{q0} = c_p c_q \omega_p^0 \eta_{p\Delta}^q, \quad \nu_{pu}^{q0} = c_p c_q \omega_p^0 \eta_u^q, \tag{72}$$

where we denote for brevity

$$\eta_{p\Delta}^q = e_{p\Delta}^q / S_{p\Delta}, \quad \eta_u^q = e_u^q / S_u. \tag{73}$$

The same methods can be used for the KMFA calculations of two-site averages $\nu_{p,ij}^{q\lambda}$ in (62). Hence the KMFA expressions for one-site and two-site averages are similar:

$$\nu_{pi}^{q0} = c_p c_q \omega_p^0 \eta_{p\xi}^q, \quad \nu_{p,ij}^{q\lambda,0} = c_p c_q c_\lambda \omega_p^0 \eta_{p\xi}^q \eta_{p\xi'}^\lambda. \tag{74}$$

Here indices ξ and ξ' equal to Δ or u indicate the above-mentioned symmetry of site i and site j, respectively, and relations $\eta_{pu}^q \equiv \eta_u^q$, $\eta_{pu}^\lambda \equiv \eta_u^\lambda$ are implied.

The resulting KMFA expressions for quantities $m_{p,1}^q$, $t_{1p}^{q\lambda}$ and $t_{2p}^{q\lambda}$ in Eqs. (58) and (59) can be written as follows

$$
\begin{aligned}
m_{p,1}^{q0} &= c_p c_q \omega_p^0 (2\eta_{p\Delta}^q - 3\eta_u^q), \\
t_{1p}^{q\lambda,0} &= \delta_{q\lambda} c_p c_\lambda \omega_p^0 (2\eta_{p\Delta}^q + 7\eta_u^q), \\
t_{2p}^{q\lambda,0} &= c_p c_q c_\lambda \omega_p^0 \times \\
&\times \left[6\eta_{p\Delta}^q \eta_{p\Delta}^\lambda - 12(\eta_{p\Delta}^q \eta_u^\lambda + \eta_{p\Delta}^\lambda \eta_u^q) + 11\eta_u^q \eta_u^\lambda \right].
\end{aligned}
\tag{75}
$$

Calculations of averages $l_{p,n}^\lambda$, $m_{p,n}^q$ and $t_{p,nm}^{q\lambda}$ in Eqs. (34) and (37) for values $n, m > 1$ used in the SSJA can be made similarly to those for the NNJA described above, though the description of rotations of vectors $\mathbf{R}_{l_n^+}$ and $\mathbf{R}_{l_n^-}$ in (37) (analogous to those given by Table 1 for vectors $\mathbf{R}_{1k}$) should be made for each n and m separately. The results can be written in terms of "reduced" quantities $\tilde{l}_{p,n}^\lambda$ and $\tilde{m}_{p,n}^q$ defined by the following relations:

$$l_{p,n}^{\lambda 0} = c_\lambda c_p \omega_p^0 \tilde{l}_{p,n}^\lambda, \quad m_{p,n}^{q0} = c_q c_p \omega_p^0 \tilde{m}_{p,n}^q, \tag{76}$$

where ω_p^0 is the same as in (68). Expressions for quantities $\tilde{l}_{p,n}^\lambda$ and $\tilde{m}_{p,n}^q$ in (76) via $\eta_{p\Delta}^q$ and η_u^q in (73) and the factor

$$\xi_u^q = (\eta_u^q - 1) \tag{77}$$

Table 2. Reduced values $\tilde{l}_{p,n}^\lambda$ and $\tilde{m}_{p,n}^q$ in Eqs. (76)

n	1	2	3	4	5
$\tilde{l}_{p,n}^\lambda$	$(4\eta_{p\Delta}^\lambda - 6\eta_u^\lambda)$	$2\xi_u^\lambda$	$4\xi_u^\lambda$	$4\xi_u^\lambda$	$2\xi_u^\lambda$
$\tilde{m}_{p,n}^q$	$(2\eta_{p\Delta}^q - 3\eta_u^q)$	$4\xi_u^q$	ξ_u^q	$2\xi_u^q$	ξ_u^q

are given in Table 2. Similarly, matrices $t_{p,nm}^{q\lambda}$ which enter into Eqs. (37) can be expressed via "reduced" matrices $\tilde{t}_{p,nm}^\lambda$ and $\tilde{t}_{p,nm}^{q\lambda}$:

$$t_{p,nm}^{q\lambda,0} = c_q c_p \omega_p^0 \left(\delta_{q\lambda} \tilde{t}_{1p,nm}^\lambda + c_\lambda \tilde{t}_{2p,nm}^{q\lambda} \right). \tag{78}$$

Here the matrix $\tilde{t}_{1p,nm}^\lambda$ has a relatively simple form

$$
\begin{pmatrix}
2\eta_{p\Delta}^\lambda + 7\eta_u^\lambda & -\eta_u^\lambda & -2\eta_u^\lambda & -2\eta_u^\lambda & -\eta_u^\lambda \\
-4\eta_u^\lambda & 4\eta_u^\lambda + 8 & 0 & -4 & 0 \\
-\eta_u^\lambda & 0 & 2\eta_u^\lambda + 9 & -1 & -1 \\
-2\eta_u^\lambda & -1 & -2 & 2\eta_u^\lambda + 10 & -2 \\
-\eta_u^\lambda & 0 & -2 & -2 & \eta_u^\lambda + 11
\end{pmatrix}
$$

while the matrix $\tilde{t}_{2p,nm}^{q\lambda}$ can be written as follows:

$$
\begin{pmatrix}
\tilde{t}_{2p,11}^{q\lambda} & \chi_p^{q\lambda} & 2\chi_p^{q\lambda} & 2\chi_p^{q\lambda} & \chi_p^{q\lambda} \\
4\chi_p^{\lambda q} & \tilde{t}_{2,22}^{q\lambda} & 8\varepsilon^{q\lambda} & 8\varepsilon^{q\lambda} + 4 & 4\varepsilon^{q\lambda} \\
\chi_p^{\lambda q} & \varepsilon^{q\lambda} & \tilde{t}_{2,33}^{\lambda q} & 2\varepsilon^{q\lambda} + 1 & \varepsilon^{q\lambda} + 1 \\
2\chi_p^{\lambda q} & 2\varepsilon^{q\lambda} + 1 & 4\varepsilon^{q\lambda} + 2 & \tilde{t}_{2,44}^{q\lambda} & 2\varepsilon^{q\lambda} + 2 \\
\chi_p^{\lambda q} & \varepsilon^{q\lambda} & 2\varepsilon^{q\lambda} + 2 & 2\varepsilon^{q\lambda} + 2 & \tilde{t}_{2,55}^{q\lambda}
\end{pmatrix},
$$

where the diagonal elements $\tilde{t}_{2p,nn}^{q\lambda}$ are

$$
\begin{aligned}
\tilde{t}_{2p,11}^{q\lambda} &= 6\eta_{p\Delta}^q \eta_{p\Delta}^\lambda - 12 \left(\eta_{p\Delta}^q \eta_u^\lambda + \eta_u^q \eta_{p\Delta}^\lambda \right) + \\
&\quad\quad + 11\eta_u^q \eta_u^\lambda, \\
\tilde{t}_{2,22}^{q\lambda} &= 4 \left(\eta_u^q \eta_u^\lambda - 2\eta_u^q - 2\eta_u^\lambda \right), \\
\tilde{t}_{2,33}^{q\lambda} &= \left(2\eta_u^q \eta_u^\lambda - 4\eta_u^q - 4\eta_u^\lambda - 5 \right), \\
\tilde{t}_{2,44}^{q\lambda} &= 2 \left(3\eta_u^q \eta_u^\lambda - 4\eta_u^q - 4\eta_u^\lambda - 1 \right), \\
\tilde{t}_{2,55}^{q\lambda} &= \left(\eta_u^q \eta_u^\lambda - 2\eta_u^q - 2\eta_u^\lambda - 9 \right).
\end{aligned}
\tag{79}
$$

The non-diagonal elements are expressed via only two quantities, $\chi_p^{q\lambda}$ and $\varepsilon^{q\lambda}$:

$$
\begin{aligned}
\chi_p^{q\lambda} &= \left(4\eta_{p\Delta}^q \eta_u^\lambda - 5\eta_u^q \eta_u^\lambda - 4\eta_{p\Delta}^q + 6\eta_u^q \right), \\
\varepsilon^{q\lambda} &= 2\xi_u^q \xi_u^\lambda = 2(\eta_u^q - 1)(\eta_u^\lambda - 1).
\end{aligned}
\tag{80}
$$

5. CALCULATIONS OF FLUCTUATIVE TERMS USING THE PAIR-CLUSTER APPROXIMATION

Kinetic mean-field calculations described in Sec. 4.2 neglect fluctuations of occupations of sites n_i^α in statistical averages. These fluctuations can be taken into account using more refined statistical methods or Monte Carlo simulations. In this section, we describe methods of calculations of contributions of these fluctuations to statistical averages (to be called "fluctuative terms") using the pair-cluster approximation — PCA mentioned in Sec. 4.2.

KMFA replaces each occupation operator n_i^q in statistical averages by its mean value c_q. To describe fluctuations, we write each n_i^q as the sum of c_q and the fluctuation $\Delta n_i^q = (n_i^q - c_q)$:

$$n_i^q = (c_q + \Delta n_i^q) = c_q(1 + \Delta n_i^q/c_q). \quad (81)$$

Then the fluctuative term (to be denoted by the lower index "f") for each quantity can be characterized by the relative difference between its exact value and that given by the KMFA expressions (68), (74) or (75). For example, for the mean frequency ω_p in Eqs. (27) and (29), the fluctuative term ω_{pf} is related to the KMFA value ω_p^0 as follows:

$$\omega_p = \omega_p^0(1 + \omega_{pf}). \quad (82)$$

This fluctuative term can be written as the statistical average of the appropriate fluctuation operator $\hat\omega_{p,f}$ which, according to Eqs. (42) and (82), has the form of product of four factors describing fluctuations in the first, second, third and fourth factor in (42), respectively:

$$(1 + \omega_{pf}) = \langle 1 + \hat\omega_{p,f}\rangle = \Big\langle \left(1 + \Delta n_0^h/c_h\right) \times$$
$$\times \left(1 + \Delta n_1^h/c_h\right) \prod_l \left(1 + \sum_\mu \Delta n_l^\mu f_{p\Delta}^\mu/S_{p\Delta}\right) \times$$
$$\times \prod_m \left(1 + \sum_\nu \Delta n_m^\nu f_u^\nu/S_u\right) \Big\rangle. \quad (83)$$

Here $S_{p\Delta}$ and S_u are the same as in (64), while l and m take the same 4 and 14 values, respectively, as in Eq. (42).

For one-site and two-site averages (52), the fluctuative terms $\nu_{pi,f}^q$ or $\nu_{p,ij,f}^{q\lambda}$ can be defined similarly to Eq. (82):

$$\nu_{pi}^q = \nu_{pi}^{q0}(1 + \nu_{pi,f}^q), \quad \nu_{p,ij}^{q\lambda} = \nu_{p,ij}^{q\lambda,0}(1 + \nu_{p,ij,f}^{q\lambda}), \quad (84)$$

where ν_{pi}^{q0} or $\nu_{p,ij}^{q\lambda,0}$ is the KMFA expression given by Eq. (74). Each of these fluctuative terms is the average of the appropriate fluctuation operator $\hat\nu_{pi,f}^q$ or $\hat\nu_{p,ij,f}^{q\lambda}$. According to Eqs. (52) and (49), the operator $\hat\nu_{pi}^q$ corresponds to replacing factor $(1 + \sum_\lambda n_i^\lambda f_{p\Delta}^\lambda)$ or $(1 + \sum_\lambda n_i^\lambda f_u^\lambda)$ in the expression (42) for $\hat w_{01}^p$ by the operator $n_i^q e_{p\Delta}^q$ or $n_i^q e_u^q$. Hence the fluctuation operator $\hat\nu_{pi,f}^q$ corresponds to replacing one of factors in the third or the fourth product in Eq. (83) by a more simple factor $(1 + \Delta n_i^q/c_q)$. For example, for site $i = 2$ which has symmetry Δ, fluctuative term $\nu_{p2,f}^q = \nu_{p\Delta,f}^q$ is defined by the following relation:

$$\left(1 + \nu_{p\Delta,f}^q\right) = \Big\langle \left(1 + \Delta n_0^h/c_h\right)\left(1 + \Delta n_1^h/c_h\right) \times$$
$$\times \left(1 + \Delta n_2^q/c_q\right) \prod_{l\neq 2} \left(1 + \sum_\mu \Delta n_l^\mu f_{p\Delta}^\mu/S_{p\Delta}\right) \times$$
$$\times \prod_m \left(1 + \sum_\nu \Delta n_m^\nu f_u^\nu/S_u\right) \Big\rangle, \quad (85)$$

where index l in the second line, unlike Eq. (83), takes only three values: 4, 9 and 12, but not $l = 2$.

Similarly, for a two-site average $\nu_{p,ij}^{q\lambda}$ in (84), the fluctuation operator $\hat\nu_{p,ij,f}^{q\lambda}$ is obtained by replacing in two last products in Eq. (83) the two factors which include fluctuations Δn_i and Δn_j by the factor $(1 + \Delta n_i^q/c_q)(1 + \Delta n_i^\lambda/c_\lambda)$. For example, for site $i = 2$ of symmetry Δ and site $j = 6$ of symmetry s, we have:

$$\left(1 + \nu_{p,26,f}^{q\lambda}\right) = \Big\langle \left(1 + \Delta n_0^h/c_h\right)\left(1 + \Delta n_1^h/c_h\right) \times$$
$$\times \left(1 + \Delta n_2^q/c_q\right) \prod_{l\neq 2} \left(1 + \sum_\mu \Delta n_l^\mu f_{p\Delta}^\mu \Big/ S_{p\Delta}\right) \times$$
$$\times \left(1 + \Delta n_6^\lambda/c_\lambda\right) \prod_{m\neq 6} \left(1 + \sum_\nu \Delta n_m^\nu f_u^\nu/S_u\right) \Big\rangle. \quad (86)$$

For simplicity, below we calculate fluctuative terms only for averages $\overline{w}_p$, m_{p1}^q and $t_{p,11}^{q\lambda}$ in Eqs. (27), (46), (47) which are used in the NNJA, and suppose the solute-solute configurational interactions $v_n^{\rho\gamma}$ in (67) to be significant only for the nearest-neighbors: $v_1^{\rho\gamma} \gtrsim T$, $v_{n>1}^{\rho\gamma} \ll T$. Then correlations of fluctuations Δn_i^λ and Δn_j^μ for the not-nearest sites i and j can be neglected, many-site correlations can be decoupled into the pairwise ones [24], and calculations of fluctuation terms (83)–(86) can be made using the simple "diagram technics" described below.

Let us first consider the term $\omega_{pf} = \langle\hat\omega_{p,f}\rangle$ in Eq. (83) which is the sum of various fluctuation prod-

ucts $\langle \Delta n_i^q \ldots \Delta n_j^r \ldots \rangle$ with some coefficients. As mentioned, each of these products can be decoupled into the sum of products of all possible pair terms which include the pair correlators of fluctuations, K_{qr}^{ij}, for neighboring sites i and j:

$$K_{qr}^{ij} = \langle \Delta n_i^q \Delta n_j^r \rangle. \tag{87}$$

These sites i and j are some of 20 sites k and $\bar{k}$ shown in Fig. 2, while various correlators K_{qr}^{ij} correspond to different bonds (i, j) in this figure, or to the bonds $(0, k)$ or $(1, \bar{k})$ not shown in this figure. As was discussed in Sec. 4.1, these 20 sites can be divided into three groups of sites having the different crystal symmetry ξ with respect to bond $(0,1)$: sites 0 and 1 with $\xi = h$; sites 2, 4, 9, 12 with $\xi = \Delta$, and the rest 14 sites k and $\bar{k}$ with $\xi = u$. Depending on symmetries ξ and ξ' of sites i and j, terms with the correlator K_{qr}^{ij} make different contributions $X_{\xi\xi'}$ into averages $\langle \Delta n_i^q \ldots \Delta n_j^r \ldots \rangle$ which enter in Eq. (83):

$$X_{hh} = \frac{1}{c_h^2} K_{hh}, \quad X_{h\Delta} = \frac{1}{c_h S_{p\Delta}} \sum_\mu K_{h\mu} f_{p\Delta}^\mu,$$

$$X_{hu} = \frac{1}{c_h S_u} \sum_\nu K_{h\mu} f_u^\mu,$$

$$X_{uu} = \frac{1}{S_u^2} \sum_{\mu\nu} K_{\mu\nu} f_u^\mu f_u^\nu, \tag{88}$$

$$X_{\Delta u} = \frac{1}{S_{p\Delta} S_u} \sum_{\mu\nu} K_{\mu\nu} f_{p\Delta}^\mu f_u^\nu,$$

$$X_{\Delta\Delta} = \frac{1}{S_{p\Delta}^2} \sum_{\mu\nu} K_{\mu\nu} f_{p\Delta}^\mu f_{p\Delta}^\nu.$$

These different contributions $X_{\xi\xi'}$ into the average ω_{pf} in Eq. (83) are illustrated by different lines in Fig. 2. Terms X_{hh} are drawn by a thick line; terms $X_{h\Delta}$, by dotted lines; terms $X_{\Delta\Delta}$, by chain lines; terms $X_{\Delta u}$, by dashed lines; and terms X_{uu}, by thin lines. Terms X_{hu} are not shown in Fig. 2.

Therefore, the PCA calculation of the average ω_{pf} in Eq. (83) yields the sum of various powers of quantities $X_{\xi\xi'}$ presented in Eq. (88) with some combinatorial coefficients. If we denote for brevity:

$$X_{hh} = X_1, \quad X_{h\Delta} = X_2, \quad X_{hu} = X_3,$$
$$X_{\Delta\Delta} = X_4, \quad X_{\Delta u} = X_5, \quad X_{uu} = X_6, \tag{89}$$

this ω_{pf} has the form of some polynomial in X_i:

$$\omega_{pf} = \sum_{n_1,n_2,\ldots n_6} C_{n_1,n_2,\ldots,n_6} X_1^{n_1} X_2^{n_2} \ldots X_6^{n_6}. \tag{90}$$

Here, $n_i \geq 0$ are integers obeying evident inequalities:

$$1 \leq \sum_{i=1}^6 n_i \leq 10, \tag{91}$$

while coefficient $C_{n_1,n_2,\ldots n_6}$ is the total number of possible sets of bonds which include n_1 bonds of type X_1, n_2 bonds of type X_2, ... and n_6 bonds of type X_6. As explained above, each site in these sets of bonds belongs either to a single bond or to no bond at all, while the bonds are chosen among 49 bonds shown in Fig. 2 and 14 bonds $(0, k)$ and $(1\bar{k})$ not shown in this figure.

In terms of the graph theory [30], $C_{n_1,n_2,\ldots,n_6}$ is the number of sets of edges which contain no adjacent edges and include n_1 edges of type X_1, n_2 edges of type X_2,... and n_6 edges of type X_6. Such sets of edges are called the independent edge sets, or "matchings", and various problems related to matchings are often met in the graph theory [30]. Thus the problem of finding of coefficients $C_{n_1,n_2,\ldots,n_6}$ in (90) can be formulated as follows: we need to find all matchings in the graph, and each of these matchings contributes unity to the coefficient $C_{n_1,n_2,\ldots,n_6}$ which corresponds to the presence of n_i edges (bonds) of type i in the matching. Inequalities (91) state that each matching can include up to 10 vertices. The empty matching should not be considered as it corresponds to the first term, unity, in brackets in (82) and hence makes no contribution to ω_{pf}. Since each graph corresponding to Fig. 2 includes not too much vertices and edges, the problem can be solved by a simple explicit recursive algorithm. We implemented such algorithm as a program in the Python programming language.

For one-site or two-site averages ν_{pi}^q or $\nu_{p,ij}^{q\lambda}$ defined by Eqs. (52), the PCA calculations of fluctuative terms $\nu_{pi,f}^q$ or $\nu_{p,ij,f}^{q\lambda}$ in Eq. (84) can be made similarly. Expression for the one-site term $\nu_{pi,f}^q$ differs from that for ω_{pf} by replacing the factor $\left(1 + \sum_\mu \Delta n_i^\mu f_{p\Delta}^\mu / S_{p\Delta}\right)$ in (83) by the factor $(1 + \Delta_i^q / c_q)$, while the two-site term $\nu_{p,ij,f}^{q\lambda}$ differs from $\nu_{pi,f}^q$ by one more replacing, that of the $\left(1 + \sum_\mu \Delta n_j^\mu f_{p\Delta}^\mu / S_{p\Delta}\right)$ or $\left(1 + \sum_\nu \Delta n_j^\nu f_u^\nu / S_u\right)$ in (83) by $(1 + \Delta n_j^\lambda / c_\lambda)$, as illustrated by Eqs. (85) and (86). Hence the above-discussed fluctuation products for the term $\nu_{pi,f}^q$ can include the appropriate factor $X_{i\xi}^q$ related to the correlator K_{qr}^{ij} between site i and the site j of the symmetry ξ, and this $X_{i\xi}^q$ is defined analogously to $X_{\xi\xi'}$ in (88). Similarly, the fluctuation products for two-site term $\nu_{p,ij,f}^{q\lambda}$ can include factors $X_{i\xi}^q$, $X_{j\xi}^\lambda$, and also factor $X_{ij}^{q\lambda}$ with the correlator of fluctuations of sites i and j (if they are the nearest neighbors):

$$X_{ih}^q = \frac{1}{c_q c_h} K_{qh}, \quad X_{i\Delta}^q = \frac{1}{c_q S_{p\Delta}} \sum_\mu K_{q\mu} f_{p\Delta}^\mu,$$

$$X_{iu}^q = \frac{1}{c_q S_u} \sum_\nu K_{q\mu} f_u^\mu, \quad X_{ij}^{q\lambda} = \frac{K_{q\lambda}}{c_q c_\lambda}. \tag{92}$$

If we denote factors $X_{i\xi}^q$, $X_{j\xi}^\lambda$ and $X_{ij}^{q\lambda}$ in (92) similarly to $X_{\xi\xi'}$ in (89),

$$\begin{aligned}
X_{ih}^q &= X_7, \quad X_{i\Delta}^q = X_8, \quad X_{iu}^q = X_9, \\
X_{jh}^\lambda &= X_{10}, \quad X_{j\Delta}^\lambda = X_{11}, \quad X_{ju}^\lambda = X_{12}, \\
X_{ij}^{q\lambda} &= X_{13},
\end{aligned} \tag{93}$$

then fluctuative terms $\nu_{pi,f}^q$ or $\nu_{p,ij,f}^{q\lambda}$ can be written similarly to the term ω_{pf} in Eq. (90):

$$\begin{aligned}
\nu_{pi,f}^q &= \sum_{n_1,\dots,n_9} C_{n_1,\dots,n_9}^q X_1^{n_1} X_2^{n_2} \dots X_9^{n_9}, \\
\nu_{p,ij,f}^{q\lambda} &= \sum_{n_1,\dots,n_{13}} C_{n_1,\dots,n_{13}}^{q\lambda} X_1^{n_1} X_2^{n_2} \dots X_{13}^{n_{13}},
\end{aligned} \tag{94}$$

while integers n_i in these sums obey inequalities analogous to (91)

$$1 \le \sum_{i=1}^9 n_i \le 10, \quad 1 \le \sum_{i=1}^{13} n_i \le 10. \tag{95}$$

Coefficients $C_{n_1,\dots,n_9}^q$ and $C_{n_1,\dots,n_{13}}^{q\lambda}$ in Eqs. (94) can be found analogously to $C_{n_1,n_2,\dots,n_6}$ in (90) by considering each matching as a term in one of sums (94). One vertex (or two vertices) in the graph in Fig. 2 now should be marked by index i (or i and j), and each edge adjacent to this vertex (these vertices) contributes an appropriate factor X_7, $X_8, \dots$ or X_{13} from (93) (rather than X_1, $X_2, \dots$ or X_6 from (89)) to the corresponding product of all $X_m^{n_m}$ in (94). The resulting form of expansions (90) and (94) for ω_{pf}, $\nu_{pi,f}^q$ and $\nu_{p,ij,f}^q$ is illustrated in Appendix A and in [13].

The correlators $K_{qr} = K_{qr}^{ij}$ which enter into the fluctuation factors X_n in Eqs. (88)–(90) and (92)–(94) can be found using the PCA equations for multicomponent alloys presented in [26]. When both indices $q = \alpha$ and $r = \gamma$ correspond to solute atoms, this correlator is expressed via the PCA parameters y_α and Z defined in [26] as follows:

$$K_{\alpha\gamma} = \frac{y_\alpha y_\gamma}{Z} - c_\alpha c_\gamma. \tag{96}$$

Dependencies of parameters y_α and Z on concentra-

Table 3. Estimates of Mayer functions $f_1^{BB} = [\exp(-\beta v_1^{BB}) - 1]$ from data about thermodynamic factors Φ presented in Ref. [10]

Alloy	CuNi	CuPd	CuAu	AuNi	AuAg	FeNi
T, K	1220	1334	1016	1173	1173	1373
f_1^{BB}	0.22	−0.31	−0.29	0.27	−0.17	−0.14

tions c_α for an m-component alloy are determined by the following system of $(m-1)$ algebraic equations:

$$\begin{aligned}
c_\alpha &= \frac{y_\alpha}{Z}\left(1 + \sum_\gamma e_{\alpha\gamma} y_\gamma\right), \\
Z &= 1 + 2\sum_\gamma y_\gamma + \sum_{\alpha,\gamma} e_{\alpha\gamma} y_\alpha y_\gamma,
\end{aligned} \tag{97}$$

where $e_{\alpha\gamma}$ is $\exp(-\beta v_1^{\alpha\gamma})$, and $v_1^{\alpha\gamma}$ is the configurational interaction for neighboring α and γ atoms.

If one or both indices q and r in the correlator K_{qr} correspond to a host atom h, this K_{qr} can be expressed via the correlators $K_{\alpha\beta}$ for solute atoms using the identity $n_i^h = 1 - \sum_\alpha n_i^\alpha$; for example, $K_{h\alpha} = -\sum_\beta K_{\alpha\beta}$.

For a binary alloy AB, Eqs. (97) can be solved analytically, and the correlator K_{BB} is expressed via the solute site fraction $c_B = c$ and the Mayer function $f_1^{BB} = [\exp(-\beta v_1^{BB}) - 1]$ as follows:

$$K_{BB} = 4c^2(1-c)^2 f_1^{BB}/(R_1 + 1)^2, \tag{98}$$

where R_1 is $[1 + 4c(1-c)f_1^{BB}]^{1/2}$. For a dilute multicomponent alloy, Eqs. (97) can be analytically solved, too, and then correlator $K_{\alpha\gamma}$ has the form

$$K_{\alpha\gamma} = f_1^{\alpha\gamma} c_\alpha c_\gamma. \tag{99}$$

The binary alloy result (98) can be used to estimate the order of magnitude of correlators $K_{\alpha\gamma}$ and factors X_i in Eqs. (88)–(96) for real alloys. The Mayer function f_1^{BB} can be estimated using experimental data about the thermodynamic factor Φ which in the PCA is described by Eq. (113) below. In Table 3, we show such estimates for six FCC alloys with unlimited solubility using the thermodynamic data about Φ presented in Ref. [10]. For simplicity, in these estimates, we use the model of nearest-neighbor solute-solute interactions, the PCA expression (113) for Φ, and the equiatomic composition $c = 0.5$. We see that the f_1^{BB} values estimated lie between about (-0.3) and 0.3, which is close to the thermodynamic stability limits for disordered FCC alloys with respect to the ordering and the decomposition, respectively.

These estimates seem to imply that the maximum values of $|K_{BB}|$ in (98) reached at $c \sim 0.5$ are about 0.02. Supposing factors X_i in Eqs. (88)–(96) to have the same order of magnitude as K_{BB} in (98), we can expect that expansions in powers of X_i in Eqs. (90) and (94) usually rapidly converge. It is illustrated by the estimates of terms ω_{pi}, $\nu_{p\xi,f}^{\lambda}$ and $\nu_{p,ij,f}^{\lambda\mu}$ presented in Appendix A and in [13]. Equations (98) and (99) also show that for dilute alloys, the fluctuative correction ω_{pf} in (90) has the second order in solute concentrations c_{α}. Hence for the mean frequencies ω_p in dilute alloys, the KMFA results (68) are exact up to the second order in c_{α}.

For one-site average ν_{pi}^{λ} in dilute alloys, fluctuative corrections $\nu_{pi,f}^{\lambda}$ in Eqs. (92)–(94) include terms $\nu_{pi,f}^{\lambda,lin}$ linear in c_{α}. These terms can be found considering Fig. 2 and using Eq. (85) (or its analogues for other symmetries ξ):

$$\nu_{p\Delta,f}^{\lambda,lin} = \sum_{\mu} f_1^{\lambda\mu} c_{\mu} (f_{p\Delta}^{\mu} + 4f_u^{\mu} - 2),$$

$$\nu_{pv,f}^{\lambda,lin} = \sum_{\mu} f_1^{\lambda\mu} c_{\mu} (2f_{p\Delta}^{\mu} + 3f_u^{\mu} - 1),$$

$$\nu_{ps,f}^{\lambda,lin} = \sum_{\mu} f_1^{\lambda\mu} c_{\mu} (f_{p\Delta}^{\mu} + 3f_u^{\mu} - 1), \tag{100}$$

$$\nu_{pc,f}^{\lambda,lin} = \sum_{\mu} f_1^{\lambda\mu} c_{\mu} (4f_u^{\mu} - 1).$$

Similarly, for a two-site average $\nu_{p,ij}^{\lambda\mu}$ with neighboring sites i and j in dilute alloys, the fluctuative term $\nu_{p,ij,f}^{\lambda\mu}$ in Eqs. (92)–(94) includes the constant term $\nu_{p,ij,f}^{\lambda\mu,0}$ independent of c_{α}:

$$\nu_{p,ij,f}^{\lambda\mu,0} = f_1^{\lambda\mu}. \tag{101}$$

Both terms $\nu_{p\xi,f}^{\lambda,lin}$ in (100) and $\nu_{p,ij,f}^{\lambda\mu,0}$ in (101) make linear in c_{α} contributions to the diffusion coefficients. Hence they make finite contributions to the enhancement factors b_p for dilute alloys. At the same time, the contributions to these b_p of terms $\nu_{p\xi,f}^{h}$ and $\nu_{p,ij,f}^{h\mu}$ (which correspond to replacing a solute atom λ by a host atom h in the averages considered) are negligible: Eqs. (84)–(86) show that such terms include a small factor c_{λ}/c_h with respect to terms $\nu_{p\xi,f}^{\lambda}$ and $\nu_{p,ij,f}^{\lambda\mu}$.

Estimates of fluctuative contributions to diffusion coefficients for some real alloys will be discussed elsewhere.

6. DIFFUSION IN BINARY ALLOYS

6.1. Expressions for intrinsic diffusion coefficients via mean frequencies and correlation factors

The intrinsic diffusion coefficients D_p are defined by the Fick's first law [8]:

$$\mathbf{J}_A = -D_A \nabla n_A, \quad \mathbf{J}_B = -D_B \nabla n_B, \tag{102}$$

where $\mathbf{J}_p$ is the atomic flux density, and n_p is the number density for p-species atoms (related to their site fraction c_p and mean volume $\bar{v}$ per atom as $n_p = c_p/\bar{v}$), while Eq. (22) relates the flux $\mathbf{J}_p$ density to the gradients of partial chemical potentials, μ_A and μ_B. These chemical potentials are related to our $\lambda_{\alpha} = \lambda_B$ in Eqs. (24) and to the grand canonical potential per atom, to be denoted Ω, by the following relations [26]:

$$\mu_B = \lambda_B + \Omega, \quad \mu_A = \Omega. \tag{103}$$

The PCA expressions for λ_B and Ω in (103), as well as for the chemical potential λ_v of vacancies relative to host atoms in (65), are presented in Ref. [15, 26]. They can be written as sums of the ideal solution and the interaction terms marked by indices "id" and "int", respectively:

$$\lambda_B = \lambda_B^{id} + \lambda_B^{int}, \quad \Omega = \Omega^{id} + \Omega^{int},$$

$$\lambda_v = \lambda_v^{id} + \lambda_v^{int}, \quad \lambda_B^{id} = T \ln \frac{c}{c_A},$$

$$\Omega^{id} = T \ln c_A, \quad \lambda_v^{id} = T \ln \frac{c_v}{c_A},$$

$$\lambda_B^{int} = -T \sum_{n=1} z_n \ln \left(1 + 2\frac{c f_n^{BB}}{R_n + 1}\right), \tag{104}$$

$$\Omega^{int} = -\frac{T}{2} \sum_{n=1} z_n \ln \left(1 - 2\frac{c^2 f_n^{BB}}{R_n + 1 + 2c f_n^{BB}}\right),$$

$$\lambda_v^{int} = -T \sum_{n=1} z_n \ln \left(1 + 2\frac{c f_n^{vB}}{R_n + 1}\right).$$

Here and below, we omit index B at c_B for brevity: $c = c_B$; z_n, f_n^{BB} and f_n^{BB} are the same as in (66), in particular:

$$f_n^{vB} = \left[\exp(-\beta v_n^{vB}) - 1\right],$$
$$f_n^{BB} = \left[\exp(-\beta v_n^{BB}) - 1\right], \tag{105}$$

R_n is expressed via f_n^{BB} as

$$R_n = (1 + 4c c_A f_n^{BB})^{1/2}, \tag{106}$$

while PCA expressions for the "reduced activity coefficients", a_v and a_B defined in Sec. 4.2, are obtained by

substitution of expressions for λ_B^{int} and λ_v^{int} from (104) in Eqs. (69). The relation between a_B or λ_B^{int} and conventional activity coefficients γ_B and γ_A defined by the thermodynamic equations [8]

$$
\begin{aligned}
\mu_B(c) &= \mu^0 + T \ln(c\gamma_B), \\
\mu_A(c_A) &= \mu^0 + T \ln(c_A \gamma_A)
\end{aligned}
\tag{107}
$$

(where μ^0 is a constant independent of c) can be obtained by comparison of Eqs. (103) and (104) with (107). It yields

$$
a_B = \exp(\beta\lambda_B^{int}) = (\gamma_B/\gamma_A).
\tag{108}
$$

To write explicit expressions for D_A and D_B in (102) via the Onsager coefficients L_{pq} in (22), we can use the Gibbs–Duhem relation [8]:

$$
c_A d\mu_A + c_B d\mu_B = c_A \, d\Omega + c \, d\mu_B = 0
\tag{109}
$$

(which for the PCA expressions (103)–(106) can also be checked by a direct calculation). Using Eqs. (22), (102) and (109) and supposing the mean atomic volume $\bar{v}$ to obey the Vegard's law

$$
\bar{v} \equiv 1/n = \overline{v}_A c_A + \overline{v}_B c_B,
\tag{110}
$$

where $\overline{v}_p$ is the atomic volume of a p-component in an alloy, we can write the intrinsic diffusion coefficients as follows

$$
\begin{aligned}
D_A &= \frac{T}{n^2 \overline{v}_B} \left(\frac{L_{AA}}{c_A} - \frac{L_{AB}}{c} \right) \Phi, \\
D_B &= \frac{T}{n^2 \overline{v}_A} \left(\frac{L_{BB}}{c} - \frac{L_{BA}}{c_A} \right) \Phi.
\end{aligned}
\tag{111}
$$

Here the "thermodynamic factor" Φ is related to the interaction term λ_B^{int} in (108) and to γ_B in (107) as

$$
\Phi = 1 + cc_A \frac{d(\beta\lambda_B^{int})}{dc} = 1 + \frac{d\ln\gamma_B}{d\ln c}
\tag{112}
$$

(due to the Gibbs-Duhem relation (109), the last term in (112) can also be written as $d\ln\gamma_A/d\ln c_A$). The PCA expression for Φ can be obtained if we use for λ_B^{int} in (112) the PCA expression from (104):

$$
\Phi = 1 - cc_A \times
$$
$$
\times \sum_{n=1} z_n 2 f_n^{BB} \frac{R_n + 1 - 4c(1-2c)f_n^{BB}}{(R_n + 1)(R_n + 1 + 2cf_n^{BB})}.
\tag{113}
$$

To discuss influence of various physical factors which affect diffusion in an alloy, it is also convenient to express each Onsager coefficient L_{AB} in (111) via the mean frequency ω_p and the "correlative" coefficients

L_{pq}^c which describe vacancy correlation effects and are defined by the following relations:

$$
\begin{aligned}
\frac{T}{na_0^2} L_{AA} &= \omega_A c_A (1 - cL_{AA}^c), \\
\frac{T}{na_0^2} L_{AB} &= \omega_B cc_A L_{AB}^c, \\
\frac{T}{na_0^2} L_{BA} &= \omega_B cc_A L_{BA}^c, \\
\frac{T}{na_0^2} L_{BB} &= \omega_B c(1 - c_A L_{BB}^c).
\end{aligned}
\tag{114}
$$

We note that non-diagonal Onsager coefficients L_{AB} and L_{BA} in (111), as well as L_{AB}^c and L_{BA}^c in (114), should actually be equal to each other [8], and the presence of this symmetry relation (discussed below in Secs. 6.2, 7.2, and 8) can characterize the consistency or the accuracy of the theory.

In the notation (114), the intrinsic diffusion coefficients D_p in (111) can be concisely written as

$$
D_p = (a_0^2/n\overline{v}_{\tilde{p}})\omega_p f_p \Phi,
\tag{115}
$$

$$
\begin{aligned}
f_A &= 1 - \left(\frac{\omega_B}{\omega_A} c_A L_{AB}^c + cL_{AA}^c \right), \\
f_B &= 1 - (c_A L_{BB}^c + cL_{AB}^c),
\end{aligned}
\tag{116}
$$

where symbol $\tilde{p}$ (used for brevity) means $\tilde{A} \equiv B$, $\tilde{B} \equiv A$, and correlation factors f_A and f_B in these equations have evidently the meaning of a correlation factor for a concentrated alloy.

Equations (111) and (116) show that each intrinsic diffusion coefficient is proportional to several factors of different nature: the mean frequency ω_p, the correlation factor f_p, and the thermodynamic factor Φ. Equation (115) is analogous to that commonly used for dilute alloys (for which $\Phi = 1$) [8], but in a concentrated alloy, each of factors ω_p, f_p and Φ varies with the solute site fraction c. Explicit expressions for correlative coefficients L_{pq}^c in (114) are discussed below in Secs. 7 and 8.

6.2. General statistical expressions for Onsager coefficients in a binary alloy

For a binary alloy AB with $h = A$ and $\alpha = B$, fields $h_n^{\alpha\alpha}$ in Eqs. (33) and (36) are zero due to the antisymmetry property (25). Hence Eqs. (36) with $p = A$ take the form of a system of n_{max} equations for n_{max} different fields $h_n^{\alpha v} = h_n^{Bv}$:

$$
\begin{aligned}
\sum_{m=1}^{n_{max}} A_{nm} h_m^{Bv} &= (m_{B,n}^A \delta\mu_B - m_{A,n}^B \delta\mu_A), \\
A_{nm} &= \left(t_{A,nm}^{BB} - t_{B,nm}^{AB} - 2m_{B,n}^A \delta_{m1} \right),
\end{aligned}
\tag{117}
$$

where δ_{m1} is unity when $m = 1$ and zero otherwise.

In the NNJA, Eqs. (117) include only one field h_1^{Bv} which is simply expressed via quantities $m_{p,1}^q$ and $t_{p,11}^{q\lambda}$ in Eqs. (57)–(59):

$$h_1^{Bv} = (m_{B,1}^A \delta\mu_B - m_{A,1}^B \delta\mu_A)/A_{11},$$
$$A_{11} = \left(t_{A,11}^{BB} - t_{B,11}^{AB} - 2m_{B,1}^A\right). \tag{118}$$

Substituting this h_1^{Bv} in Eq. (33) with $n_{max} = 1$ and using also Eq. (58), we obtain the following relations between fluxes $J_{0\to1}^p$ and differences $\delta\mu_q$:

$$J_{0\to1}^B =$$
$$= -\beta\delta\mu_B \left[\overline{w}_B + 2m_{B,1}^A(\overline{w}_B + m_{B,1}^B)/A_{11}\right] +$$
$$+ \beta\delta\mu_A 2m_{A,1}^B(\overline{w}_B + m_{B,1}^B)/A_{11},$$
$$J_{0\to1}^A = -\beta\delta\mu_{Bv} 2m_{A,1}^B m_{B,1}^A/A_{11} -$$
$$- \beta\delta\mu_A \left[\overline{w}_A - 2(m_{A,1}^B)^2/A_{11}\right], \tag{119}$$

which determine Onsager coefficients L_{pq} in (41).

We note that the Onsager symmetry relation,

$$L_{BA} = L_{AB}, \tag{120}$$

in our approach is obeyed identically. According to Eq. (119), Eq. (120) implies

$$m_{B,1}^B + m_{A,1}^A = -\overline{w}_B. \tag{121}$$

Using Eqs. (55)–(58), we can re-write (121) as

$$\langle \hat{w}_B [2(n_2^B + n_2^A) - 2(n_6^B + n_6^A) -$$
$$- (n_7^B + n_7^A)]\rangle = -\langle \hat{w}_B\rangle, \quad (122)$$

which holds identically as $(n_i^B + n_i^A) \equiv 1$. In Sec. 7.2 we show that relation (120) holds also for the SSJA, and probably also for any value n_{max} in Eqs. (117) (which we checked analytically for the value $m_{max} = 2$). Presence of this symmetry relation irrespectively of concentrations and approximations considered illustrates the theoretical consistency of the master equation approach used.

7. EXPLICIT EXPRESSIONS FOR INTRINSIC DIFFUSION COEFFICIENTS IN A BINARY ALLOY

7.1. Onsager and diffusion coefficients in the NNJA-KMFA

Using Eqs. (119), (120), and (29), we can write the general NNJA expressions for Onsager coefficients in a concentrated binary alloy as follows:

$$\frac{T}{na_0^2}L_{AA} = \left[c_A\omega_A - \frac{2(m_{A,1}^B)^2}{A_{11}}\right],$$
$$\frac{T}{na_0^2}L_{AB} = \frac{2m_{A,1}^B m_{B,1}^A}{A_{11}}, \tag{123}$$
$$\frac{T}{na_0^2}L_{BB} = \left[c_B\omega_B - \frac{2(m_{A,1}^A)^2}{A_{11}}\right],$$

where A_{11} is given in (118), while statistical averages $m_{p,1}^q$ and $t_{p,11}^{q\lambda}$ are defined by general relations (57)–(62).

In this section, we use for these averages and for mean frequencies ω_p in (123) the KMFA expressions (68), (76) and (78). We also omit index $\alpha = B$ of the only kind of solute atoms in site fraction $c_\alpha = c_B$ and in quantities $\eta_{p\Delta}^\alpha$, $e_{p\Delta}^\alpha$, η_u^α, e_u^α defined by Eqs. (73), and employ in Eqs. (123) the "reduced" denominator D_{nn} rather than quantity A_{11} from (118), as well as the frequency ratio $z = \omega_B^0/\omega_A^0$ rather than frequency ω_B^0 from (68):

$$c_B = c, \quad \eta_{A\Delta}^B = \eta_{A\Delta}, \quad e_{A\Delta}^B = e_{A\Delta},$$
$$\eta_u^B = \eta_u, \quad e_u^B = e_u, \quad A_{11} = cc_A\omega_A^0 D_{nn}, \tag{124}$$
$$z = \omega_B^0/\omega_A^0 = (\omega_{B0}/\omega_{A0})a_B S_{B\Delta}^4/S_{A\Delta}^4.$$

Then expressions (123) for Onsager coefficients in the NNJA-KMFA take the following form:

$$\frac{T}{na_0^2}L_{AA} = \omega_A^0 c_A \left[1 - \frac{2c(3\eta_u - 2\eta_{A\Delta})^2}{D_{nn}}\right],$$
$$\frac{T}{na_0^2}L_{AB} = \omega_B^0 cc_A 2(3\eta_u - 2\eta_{A\Delta})\frac{3\eta_u^A - 2\eta_{B\Delta}^A}{D_{nn}}, \quad (125)$$
$$\frac{T}{na_0^2}L_{BB} = \omega_B^0 c \left[1 - \frac{2c_A z(3\eta_u^A - 2\eta_{B\Delta}^A)^2}{D_{nn}}\right].$$

The denominator D_{nn} in (125) can be conveniently written as the sum of two terms: that with no common factor of site fraction c and that including this factor:

$$D_{nn} = (A_{1,11} + cA_{2,11}). \tag{126}$$

Here quantities $A_{1,11}$ and $A_{2,11}$ are expressed via the reduced parameters $\tilde{m}_{p,1}^q$, $\tilde{t}_{1p,11}^{q\lambda}$, and $\tilde{t}_{2p,11}^{q\lambda}$ in (76) and (78) in accordance with Eqs. (118) and (124):

$$A_{1,11} = (\tilde{t}_{1A,11}^B - 2\tilde{m}_{B,1}^A),$$
$$A_{2,11} = (\tilde{t}_{2A,11}^{BB} - z\tilde{t}_{2B,11}^{AB}) \tag{127}$$

or, explicitly:

$$A_{1,11} = (2\eta_{A\Delta} + 7\eta_u) + 2z(3\eta_u^A - 2\eta_{B\Delta}^A), \tag{128}$$

$$A_{2,11} = \left(6\eta_{A\Delta}^2 - 24\eta_{A\Delta}\eta_u + 11\eta_u^2\right) -$$
$$- z\left[6\eta_{B\Delta}^A\eta_{B\Delta} - 12(\eta_{B\Delta}^A\eta_u + \eta_{B\Delta}\eta_u^A) + 11\eta_u^A\eta_u\right]. \quad (129)$$

In Eqs. (124)–(127), quantities $\eta_{B\Delta}^A$, η_u^A, $\eta_{A\Delta}$ and η_u are defined by Eqs. (73) and (51):

$$\eta_{B\Delta}^A = 1/S_{B\Delta}, \quad \eta_u^A = 1/S_u,$$

$$\eta_{A\Delta} = e_{A\Delta}/S_{A\Delta},$$

$$\eta_u = e_u/S_u, \quad \eta_{B\Delta} = e_{B\Delta}/S_{B\Delta},$$

$$S_{A\Delta} = 1 + cf_{A\Delta}, \quad S_{B\Delta} = 1 + cf_{B\Delta}, \quad (130)$$

$$S_u = 1 + cf_u, \quad f_{A\Delta} = e_{A\Delta} - 1,$$

$$f_{B\Delta} = e_{B\Delta} - 1, \quad f_u = e_u - 1,$$

while factors $e_{A\Delta}$ and e_u in (130) are defined by Eqs. (124), (50) and (44).

The correlative coefficients L_{pq}^c in (116) for NNJA-KMFA can be found comparing Eqs. (114) and (125):

$$L_{AA}^c = 2(3\eta_u - 2\eta_{A\Delta})^2/D_{nn},$$

$$L_{AB}^c = 2(3\eta_u - 2\eta_{A\Delta})(3\eta_u^A - 2\eta_{B\Delta}^A)/D_{nn}, \quad (131)$$

$$L_{BB}^c = 2z(3\eta_u^A - 2\eta_{A\Delta}^A)^2/D_{nn}.$$

The NNJA-KMFA expression for the diffusion coefficient D_p is given by the general relations (115) and (116) with the KMFA expression ω_p^0 (68) for ω_p, expressions (131) for L_{pq}^c, and Eq. (113) for Φ.

7.2. Onsager and diffusion coefficients in the SSJA-KMFA

When vacancy-solute correlations are described in the SSJA, Eqs. (37) include averages $m_{p,n}^q$ and $t_{p,nm}^{q\lambda}$ for values $n, m > 1$. These averages can be calculated similarly to those for the NNJA, and results can be written in terms of "reduced" quantities $\tilde{l}_{p,n}^\lambda$, $\tilde{m}_{p,n}^q$, $\tilde{t}_{p,nm}^\lambda$ and $\tilde{t}_{p,nm}^{q\lambda}$ defined analogously to those in (75):

$$l_{p,n}^{\lambda 0} = c_\lambda c_p \omega_p^0 \tilde{l}_{p,n}^\lambda, \quad m_{p,n}^{q0} = c_q c_p \omega_p^0 \tilde{m}_{p,n}^q,$$

$$t_{p,nm}^{q\lambda,0} = c_q c_p \omega_p^0 \left(\delta_{q\lambda}\tilde{t}_{1p,nm}^\lambda + c_\lambda \tilde{t}_{2p,nm}^{q\lambda}\right), \quad (132)$$

where ω_p^0 is the same as in (68). Explicit expressions for quantities $\tilde{l}_{p,n}^\lambda$, $\tilde{m}_{p,n}^q$, $\tilde{t}_{p,nm}^\lambda$ and $\tilde{t}_{p,nm}^{q\lambda}$ are given by Table 2 and Eqs. (78)–(80).

In this section, we present the SSJA-KMFA expressions for Onsager coefficients in a concentrated binary alloy. In the SSJA, we should solve the system of five linear equations (117) for effective fields $h_m^{\alpha v}$ and then find Onsager coefficients using Eqs. (33), (38), and (41). To this end, we first write the matrix A_{nm} in (117) in terms of "reduced" matrices A_{nm}^r, $A_{1,nm}$ and $A_{2,nm}$ defined analogously to D_{nn}, $A_{1,11}$ and $A_{2,11}$ in Eqs. (126)–(129):

$$A_{nm} = cc_A\omega_A^0 A_{nm}^r,$$

$$A_{nm}^r = (A_{1,nm} + cA_{2,nm}),$$

$$A_{1,nm} = (\tilde{t}_{1A,nm}^B - 2z\tilde{m}_{B,n}^A\delta_{m1}), \quad (133)$$

$$A_{2,nm} = (\tilde{t}_{2A,nm}^{BB} - z\tilde{t}_{2B,nm}^{AB}),$$

where z is the same as in (124) and $\tilde{m}_{B,n}^A$ is the same as in Table 2.

It will be also convenient to use the shortened notation for quantities $\eta_{p\Delta}^q$, η_p^q and $\tilde{m}_{p,1}^{q0}$ in Eqs. (73) and (75):

$$\eta_{A\Delta} = x, \quad \eta_{A\Delta}^A = \bar{x}, \quad \eta_{B\Delta} = y,$$

$$\eta_{B\Delta}^A = \bar{y}, \quad \eta_u = v, \quad \eta_u^A = \bar{v}, \quad (134)$$

$$\tilde{m}_{B,1}^{A0} = (2\bar{y} - 3\bar{v}), \quad \tilde{m}_{A,1}^{B0} = (2x - 3v).$$

This notation enables us, in particular, to more concisely write the NNJA-KMFA expressions for quantities L_{pq}^c, $A_{1,11}$ and $A_{2,11}$ in Eqs. (126)–(131):

$$L_{AA}^c = 2(3v - 2x)^2/D_{nn},$$

$$L_{AB}^c = 2(3v - 2x)(3\bar{v} - 2\bar{y})/D_{nn},$$

$$L_{BB}^c = 2z(3\bar{v} - 2\bar{y})^2/D_{nn},$$

$$\quad (135)$$

$$A_{1,11} = (2x + 7v) + 2z(3\bar{v} - 2\bar{y}),$$

$$A_{2,11} = (6x^2 - 24xv + 11v^2) -$$

$$- z[6y\bar{y} - 12(\bar{y}v + y\bar{v}) + 11v\bar{v}].$$

Matrix $A_{1,nm}$ in (133) is the difference of matrix $\tilde{\mathbf{t}}_{1A}^B$ in (78) and the simple one-column matrix:

$$\mathbf{A}_1 = \tilde{\mathbf{t}}_{1A}^B - 2z \begin{pmatrix} \tilde{m}_{B,1}^{A0} & 0 & 0 & 0 & 0 \\ 4\xi_u^A & 0 & 0 & 0 & 0 \\ \xi_u^A & 0 & 0 & 0 & 0 \\ 2\xi_u^A & 0 & 0 & 0 & 0 \\ \xi_u^A & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$
\tilde{\mathbf{t}}_{1A}^{B} =
$$

$$
= \begin{pmatrix}
2x+7v & -v & -2v & -2v & -v \\
-4v & 4v+8 & 0 & -4 & 0 \\
-v & 0 & 2v+9 & -1 & -1 \\
-2v & -1 & -2 & 2v+10 & -2 \\
-v & 0 & -2 & -2 & v+11
\end{pmatrix}, \quad (136)
$$

where x, y, v, $\bar{v}$ and $\tilde{m}_{B,1}^{A0}$ are the same as in Eqs. (134), while ξ_u^A is $(\eta_u^A - 1) = (\bar{v} - 1)$.

Similarly, matrix $\mathbf{A}_2$ in (133) is an analogue of matrix $\tilde{\mathbf{t}}_{2p}^{q\lambda}$ in Eq. (78) which can be concisely written as the sum of two more simple matrices:

$$
\tilde{\mathbf{A}}_2 = \begin{pmatrix}
A_{2,11} & \tilde{\chi}_{AB} & 2\tilde{\chi}_{AB} & 2\tilde{\chi}_{AB} & \tilde{\chi}_{AB} \\
4\tilde{\chi}_{BA} & \tilde{t}_{AB,22} & 8\tilde{\varepsilon}_{AB} & 8\tilde{\varepsilon}_{AB} & 4\tilde{\varepsilon}_{AB} \\
\tilde{\chi}_{BA} & \tilde{\varepsilon}_{AB} & \tilde{t}_{AB,33} & 2\tilde{\varepsilon}_{AB} & \tilde{\varepsilon}_{AB} \\
2\tilde{\chi}_{BA} & 2\tilde{\varepsilon}_{AB} & 4\tilde{\varepsilon}_{AB} & \tilde{t}_{AB,44} & 2\tilde{\varepsilon}_{AB} \\
\tilde{\chi}_{BA} & \tilde{\varepsilon}_{AB} & 2\tilde{\varepsilon}_{AB} & 2\tilde{\varepsilon}_{AB} & \tilde{t}_{AB,55}
\end{pmatrix},
$$

$$
\mathbf{A}_2 = \tilde{\mathbf{A}}_2 + \delta_z \times \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 4 & 0 \\
0 & 0 & 0 & 1 & 1 \\
0 & 1 & 2 & 0 & 2 \\
0 & 0 & 2 & 2 & 0
\end{pmatrix}. \quad (137)
$$

Here $A_{2,11}$ is the same as in Eq. (135), while parameters $\tilde{\chi}_{AB}$, $\tilde{\varepsilon}_{AB}$, $\tilde{t}_{AB,nn}$ and δ_z are expressed via quantities $\chi_p^{q\lambda}$, $\chi_p^{\lambda q}$, $\varepsilon^{q\lambda}$, $\tilde{t}_{2p,nn}^{q\lambda}$ in Eqs. (78)–(80) and the frequency ratio $z = \omega_B^0 / \omega_A^0$ as follows:

$$
\begin{aligned}
\tilde{\chi}_{AB} &= (\chi_A^{BB} - z\chi_B^{AB}), \\
\tilde{\chi}_{BA} &= (\chi_A^{BB} - z\chi_B^{BA}), \\
\tilde{\varepsilon}_{AB} &= (\varepsilon^{BB} - z\varepsilon^{AB}), \\
\tilde{t}_{AB,nn} &= (\tilde{t}_{2,nn}^{BB} - z\tilde{t}_{2,nn}^{AB}), \quad \delta_z = (1-z).
\end{aligned} \quad (138)
$$

Here $\chi_p^{q\lambda}$, $\chi_p^{\lambda q}$, $\varepsilon^{q\lambda}$ and $\tilde{t}_{2p,nn}^{q\lambda}$ in the notation (134) can be written as follows:

$$
\begin{aligned}
\chi_A^{BB} &= (4xv - 5v^2 - 4x + 6v), \quad \varepsilon^{BB} = 2\xi_u^2, \\
\chi_B^{AB} &= (4\bar{y}v - 5v\bar{v} - 4\bar{y} + 6\bar{v}), \quad \varepsilon^{AB} = 2\xi_u^A \xi_u, \\
\chi_B^{BA} &= (4y\bar{v} - 5v\bar{v} - 4y + 6v), \\
\xi_u &= (v-1), \quad \xi_u^A = (\bar{v}-1);
\end{aligned} \quad (139)
$$

$$
\begin{aligned}
\tilde{t}_{2,22}^{BB} &= 4v(v-4), \quad \tilde{t}_{2,22}^{AB} = 4(v\bar{v} - 2\bar{v} - 2v), \\
\tilde{t}_{2,33}^{BB} &= (2v^2 - 8v - 5), \\
\tilde{t}_{2,33}^{AB} &= (2v\bar{v} - 4v - 4\bar{v} - 5), \\
\tilde{t}_{2,44}^{BB} &= 2(3v^2 - 8v - 1), \\
\tilde{t}_{2,44}^{AB} &= 2(3v\bar{v} - 4v - 4\bar{v} - 1), \\
\tilde{t}_{2,55}^{BB} &= (v^2 - 4v - 9), \\
\tilde{t}_{2,55}^{AB} &= (v\bar{v} - 2v - 2\bar{v} - 9).
\end{aligned} \quad (140)
$$

KMFA expressions for coefficients $l_{p,n}^{\lambda}$ in Eqs. (33) are given by Eqs. (58), (132) and by Table 2, with taking into account identity (121). Solving Eqs. (117) for $h_m^{\alpha v}$ by standard methods of linear algebra and using Eqs. (33), (38), (41), we obtain the correlative Onsager coefficients L_{pq}^c in (114). These coefficients are expressed via the determinant D of matrix A_{nm}^r in (133) and the functions D_{ss} and ρ_i with i equal to c, l or r which are the following combinations of minors M_{mn} of this determinant:

$$
\begin{aligned}
D &= Det \, \|A_{nm}^r\|, \quad D_{ss} = D/M_{11}, \\
\rho_i &= N_i/M_{11}, \\
N_c &= (-4M_{21} + M_{31} - 2M_{41} + M_{51}),
\end{aligned}
$$

$$N_l = (-M_{12} + 2M_{13} - 2M_{14} + M_{15}),$$

$$N_r = [(4M_{22} - M_{32} + 2M_{42} - M_{52}) -$$

$$- 2(4M_{23} - M_{33} + 2M_{43} - M_{53}) + \qquad (141)$$

$$+ 2(4M_{24} - M_{34} + 2M_{44} - M_{54}) -$$

$$- (4M_{25} - M_{35} + 2M_{45} - M_{55})].$$

Our numerical calculations have shown that quantities N_l and N_c in (141) are identically equal to each other (through we did not prove it analytically). This equality leads also to the fulfilment of Onsager symmetry relation (120): $L_{AB} = L_{BA}$. Taking it into account, we can write the SSJA expressions for coefficients L^c_{pq} (114) in the form analogous to that for the NNJA in Eqs. (131):

$$L^c_{AA} = \frac{2}{D_{ss}} \left[(\tilde{m}^{B0}_{A,1})^2 + 2\tilde{m}^{B0}_{A,1} \xi_u \rho_c + \xi^2_u \rho_l \right],$$

$$L^c_{AB} = \frac{2}{D_{ss}} \left[\tilde{m}^{B0}_{A,1} \tilde{m}^{A0}_{B,1} + \right.$$

$$\left. + (\tilde{m}^{B0}_{A,1} \xi^A_u + \tilde{m}^{B0}_{A,1} \xi_u) \rho_c + \xi^A_u \xi_u \rho_r \right], \qquad (142)$$

$$L^c_{BB} = z \frac{2}{D_{ss}} \times$$

$$\times \left[(\tilde{m}^{A0}_{B,1})^2 + 2\tilde{m}^{A0}_{B,1} \xi^A_u \rho_c + (\xi^A_u)^2 \rho_r \right].$$

Here ξ^A_u and ξ_u are the same as in (139), $\tilde{m}^{B0}_{A,1}$ and $\tilde{m}^{A0}_{B,1}$ are the same as in (134), and D_{ss}, ρ_c and ρ_r are the same as in (141).

The intrinsic diffusion coefficients D_p are related to the coefficients L^c_{pq} in (142) by the general relations (115) and (116), with ω_p equal to ω^0_p (68) and Φ given by Eq. (113). We note that the NNJA-KMFA results (131) for L^c_{pq} correspond to putting in the SSJA-KMFA expressions (142): $\rho_i = 0$, $D_{ss} = D_{nn}$.

7.3. Onsager and diffusion coefficients in a dilute binary alloy

In the dilute alloy limit $c \to 0$, frequencies ω_p tend to ω_{p0} in (70), while parameters z, $\eta^A_{B\Delta}$, $\eta_{A\Delta}$, η^A_u and η_u in (125)–(129), according to Eqs. (124) and (130), take the following values:

$$z_0 = \omega_{B0}/\omega_{A0}, \quad (\eta^A_{B\Delta})_0 = (\eta^A_u)_0 = 1,$$

$$(\eta_{A\Delta})_0 = e_{A\Delta}, \quad \eta_{u0} = e_u. \qquad (143)$$

Here and below, the lower index "0" at each quantity indicates its value at $c \to 0$.

To relate our notation to that commonly used for five-frequency model [1–9], we note that the jump rates ("frequencies") w_n of that model in our notation are

$$w_0 = \omega_{A0}, \quad w_1 = \omega_{A0} e_{A\Delta} e^{vB}_1,$$

$$w_2 = \omega_{B0} e^{vB}_1, \quad w_3 = \omega_{A0} e^{vB}_1 e_u, \qquad (144)$$

$$w_4 = \omega_{A0} e_u,$$

where e^{vB}_1 is the same as in (71). At the same time, exponential factors e_u and $e_{A\Delta}$ in (144) are directly related to the kinetic and saddle-point interactions, u^B_1 and Δ^B_A, and have a more clear physical meaning than frequencies w_n. Equations (126)–(130) include also factor $e_{B\Delta}$ analogous to $e_{A\Delta}$ which describes influence on the $Bi \leftrightarrows vj$ jump probability of a solute atom B near the bond (ij). Therefore, to simplify formulas below, we use not frequencies w_n but quantities x_n and y_1 defined by the relations

$$x_1 = e_{A\Delta}, \quad x_2 = \omega_{B0}/\omega_{A0}, \quad x_4 = e_u,$$

$$y_1 = e_{B\Delta} = \exp[\beta(2u^B_1 - \Delta^B_B)] \qquad (145)$$

with x_2 equal to z_0 in (143). In this notation, Mayer functions $f_{p\Delta}$ and f_u and the low-c values of factors ξ_u and ξ^A_u in Eqs. (130) take the following form:

$$f_{A\Delta} = (x_1 - 1), \quad f_{B\Delta} = (y_1 - 1),$$

$$f_u = (x_4 - 1), \quad \xi_u = f_u = (x_4 - 1), \qquad (146)$$

$$\xi^A_u(c \ll 1) = (-cf_u) = -c(x_4 - 1).$$

Below we present the low-c expansions for mean frequencies ω_p and Onsager coefficients L_{pq} up to the first order in c, and the zero-order terms in c for correlative Onsager coefficients L^c_{pq} and correlation factors f_p in Eqs. (114)–(116). The fluctuative corrections mentioned in the end of Sec. 5 make no contribution to these terms, hence we can use the KMFA expressions (131) and (142).

Let us first consider the mean frequency ω_p and define its enhancement factor b^ω_p by the usual relation

$$\omega_p(c) = \omega_{p0}(1 + c\, b^\omega_p). \qquad (147)$$

Using Eqs. (68) for ω^0_p and the PCA expressions (104) for λ^{int}_B and λ^{int}_v in activity coefficients a_v and a_B (69), we find

$$b^\omega_A = 4f_{A\Delta} + 14f_u + b_{vB},$$

$$b^\omega_B = 4f_{B\Delta} + 14f_u + b_{vB} + b_{BB}. \qquad (148)$$

Here $f_{p\Delta}$ and f_u are given in (146), while b_{vB} and b_{BB} are contributions to b^ω_p of the activity coefficients, a_v and a_B:

$$b_{vB} = -\sum_{n=1} z_n f^{vB}_n = -12f^{vB}_1 - 6f^{vB}_2 - \dots, \quad (149)$$

$$b_{BB} = -\sum_{n=1} z_n f^{BB}_n = -12f^{BB}_1 - 6f^{BB}_2 - \dots \quad (150)$$

Discussing the low-c expressions for correlative terms L_{pq}^c and correlation factors f_p in (116), we first consider the more simple approximation NNJA. Using Eqs. (131)–(146), we obtain for the L_{pq}^c and f_p at $c = 0$, to be denoted as L_{pq}^{c0} and f_{p0}, the following expressions:

$$L_{AA}^{c0} = 2(3x_4 - 2x_1)^2/D_0,$$
$$L_{AB}^{c0} = 2(3x_4 - 2x_1)/D_0, \tag{151}$$
$$L_{BB}^{c0} = 2x_2/D_0, \quad D_0 = (2x_1 + 2x_2 + 7x_4),$$

$$f_{A0} = 1 - x_2 L_{AB}^{c0}, \quad f_{B0} = 1 - L_{BB}^{c0}, \tag{152}$$

where D_0 is the value of the reduced denominator D_{nn} in (126) at $c = 0$.

For the SSJA, expressions for Onsager correlative coefficients at $c = 0$ can be obtained as $c \to 0$ limits of general SSJA equations (142) in which values $\rho_c(c = 0) = \rho_0$, $\rho_r(c = 0) = \rho_{r0}$, and $D_{ss}(c = 0) = D_{ss}^0$ are related to the so-called "vacancy escape function" $F = F(x_4)$ used in the five-frequency model (8) as follows:

$$\rho_0 = 7(1 - F) = P_N/P_D, \quad \rho_{r0} = \rho_0 D_0/x_4,$$
$$D_{ss}^0 = D_0 - x_4\rho_0 = (2x_1 + 2x_2 + 7x_0 F) \tag{153}$$

where polynomials $P_N = P_N(x_4)$ and $P_D = P_D(x_4)$ have the following form:

$$P_N(x) = A_1 x + A_2 x^2 + A_3 x^3 + 10x^4,$$
$$P_D(x) = B_0 + B_1 x + B_2 x^2 + B_3 x^3 + 2x^4. \tag{154}$$

For the correlative Onsager coefficients L_{pq}^{c0}. Eqs. (142) and (153) yield in the SSJA:

$$L_{AA}^{c0} = 2\left[(3x_4 - 2x_1)^2 - 2(3x_4 - 2x_1)f_u\rho_0 + \right.$$
$$\left. + f_u^2\rho_0 D_0/x_4\right]/D_{ss}^0,$$
$$L_{AB}^{c0} = 2(3x_4 - 2x_1 - f_u\rho_0)/D_{ss}^0, \tag{155}$$
$$L_{BB}^{c0} = 2x_2/D_{ss}^0,$$

where $f_u = (x_4 - 1)$, while the SSJA expressions for correlation factors f_p in (116) at $c \to 0$ take the form

$$f_{A0} = 1 - 2x_2(3x_4 - 2x_1 - f_u\rho_0)/D_{ss}^0,$$
$$f_{B0} = 1 - 2x_2/D_{ss}^0. \tag{156}$$

As discussed in [8], relations (153)–(156) are true not only for the SSJA, but also for more accurate approximations, such as that of Manning [3], but coefficients A_n and B_n in (154) for other approximations differ

Table 4. Coefficients A_n and B_n in (154) for the SSJA [5] and for Manning's model [3]

Model	A_1	A_2	A_3	B_0	B_1	B_2	B_3
SSJA [5]	1594.5	1031	190	855.5	930.5	328	45
Manning [3]	1341	927	180.5	436	597	254	140.2

from those for the SSJA. In Table 4 we present these coefficients for the SSJA (first obtained by Bocquet [5]) and for the Manning model [3].

Using Eqs. (114) and (147), we can also write the low-c expressions for Onsager coefficients including all terms linear in c:

$$\frac{T}{na_0^2}L_{AA} = \omega_{A0}\left[1 + c(b_A^\omega - 1 - L_{AA}^{c0})\right],$$
$$\frac{T}{na_0^2}L_{AB} = \omega_{B0}\, cL_{AB}^{c0}, \tag{157}$$
$$\frac{T}{na_0^2}L_{BB} = \omega_{B0}\, c\,(1 - L_{BB}^{c0}).$$

For the case of a very low vacancy concentration under consideration ($c_v \ll c_B$), our L_{pq} in Eqs. (157) with the values of b_A^ω and $L_{pq,0}^c$ given by Eqs. (148)–(155) coincide with those found in the traditional theory [8].

Finally, we make remarks on the differences between our results and those of Nastar et al. [16–19] mentioned in Sec. 1. First, basic equations given in [17] are cumbersome and implicit, thus it is difficult to use them. Second, the "Bragg-Williams approximation" employed in papers [16] and [18] corresponds to replacing the correlation operator $\hat{b}_{ij}^p$ in Eq. (28) by a constant, that is, to neglecting both the kinetic interactions u_{il}^α and the saddle-point interactions $\Delta_{p,ij}^{\alpha l}$ which are actually very important for solute diffusion, as both the traditional theories [1–9] and our results in [13, 14] show. Hence the reliability of this "Bragg-Williams approximation" is unclear. Third, the expression for L_{AA} obtained by Nastar [17] corresponds to missing the vacancy-solute interaction term b_{vB} [given by Eq. (149)] in the frequency enhancement factor b_A^ω in (157), which also disagrees with the traditional theory [8]. As discussed in [13, 14, 21], the analogous missing of vacancy-solute interaction was made in the calculations of tracer self-diffusion enhancement factor b_{A*} in [17] (as well as in all other calculations of this enhancement factor [2, 4, 7]). Let us also note that the expressions for Onsager coefficients given by Eqs. (5)–(12) of paper [19] and derived using the NNJA and the pair cluster variation method (pair CVM) are very similar to

our NNJA-KMFA expressions (125)–(129). Most probably, the NNJA-pair CVM and the NNJA-KMFA expressions for Onsager coefficients should coincide with each other, as the thermodynamic results of PCA (used in KMFA) coincide with those of the pair CVM [20]. At the same time, the direct comparison of our explicit expressions (125)–(129) with implicit equations (5)–(12) in [19] is not simple and needs efforts.

8. EFFECT OF NON-PAIRWISE VACANCY CORRELATIONS ON DIFFUSION

The effective hamiltonian $\hat{h}_{eff}$ (11) describes changes in the distribution of vacancies with respect to solute atoms (these changes are commonly called "vacancy correlations") due to the presence of a steady-state diffusion fluxes in an alloy. The first term in (11) describes pairwise correlations, while the second and further terms in (11) describe the non-pairwise correlations which can be significant for a concentrated alloy. In this section, we discuss influence of these non-pairwise correlations on diffusion. For simplicity, we consider the model for which triple fields h_{ijk}^{vBB} in the second term of Eq. (11) act only between nearest neighbors, that is, only between sites which form equilateral triangles in the FCC lattice. Earlier influence of such triple fields on diffusion was discussed in Ref. [18] using the "Bragg-Wiiliams approximation" mentioned above. However, neglecting kinetic and saddle-point interactions in this oversimplified approximation does not allow to compare our microscopic results (formulated in terms of these interactions) with those presented in [18].

Note that the simple model used taking into account triple effective interactions only within triangles of nearest-neighbor sites can not be considered as quantitative and realistic. It is evident, in particular, that the number of triple effective interactions within triangles of next-nearest-neighbor sites of the type (0,1,3), (1,3,4), etc in Fig. 1 (having similar inter-site distances) per alloy atom much exceeds that for thr nearest-neighbor sites, and their influence on diffusion can be significantly stronger. However, in this section we aim to study mainly methodical problems. First, we illustrate the methods of treatment of non-pairwise vacancy-solute correlations in the master equation approach. Second, the results of this section enable us to estimate the scale of manifestations of these non-pairwise correlations in diffision for real alloys.

Considering general expressions (115) for diffusion coefficients, we note that both the mean frequency ω_p

defined by Eqs. (27) and (29) and the thermodynamic factor Φ defined by Eq. (112) do not depend on the effective hamiltonian $\hat{h}_{eff}$ which describes vacancy correlations. Hence various treatments of $\hat{h}_{eff}$ affect only correlation factors f_p determined by the correlative coefficients L_{pq}^c in (116), and below we calculate only these L_{pq}^c.

Using general methods of derivation of equations for time derivatives dc_ρ/dt and fluxes $J_{0\to1}^p$ described in Secs. 2, 3 and Ref. [20], including Eq. (22) in [20], we can generalize Eq. (26) for $J_{0\to1}^p$ to the case of presence of triple fields in (11) as follows:

$$J_{0\to1}^p =$$
$$= -\beta\left\langle \hat{w}_{01}^p(\delta\mu_p + \hat{h}_{01}^{pv} - \hat{h}_{10}^{pv} - \hat{h}_1^p + \hat{h}_0^p + \hat{h}_1^v - \hat{h}_0^v)\right\rangle. \quad (158)$$

At $p = h$, operators $\hat{h}_{is}^{pv}$ and $\hat{h}_i^p$ in this equation are zero, just as operators $\hat{h}_{ij}^{p\lambda}$ in Eq. (24), while at $p = \alpha$ these operators correspond to the appropriate variational derivatives of the effective hamiltonian $\hat{h}_{eff}$ (11):

$$\hat{h}_{is}^{\alpha v} = \frac{\partial^2 \hat{h}_{eff}}{\partial n_i^\alpha \partial n_i} = h_{is}^{\alpha v} + \sum_{j,\sigma} h_{isj}^{\alpha v\sigma} n_j^\sigma,$$

$$\hat{h}_i^\alpha = \frac{\partial \hat{h}_{eff}}{\partial n_i^\alpha} = \sum_{j,\sigma} h_{ij}^{\alpha\sigma} n_j^\sigma + \frac{1}{2}\sum_{j,\sigma,k,\rho} h_{ijk}^{\alpha\sigma\rho} n_j^\sigma n_k^\rho, \qquad (159)$$

while operator $\hat{h}_i^v$ corresponds to replacing index α in the last equation by index v.

Relations of symmetry for fields $h_{i...k}^{\rho...\sigma}$ which generalize Eqs. (25) follow from the antisymmetry of fluxes $J_{0\to1}^p$ (158) with respect to reflections $z \to (-z)$ and $\delta\mu_p \to (-\delta\mu_p)$:

$$h_{ij}^{p\rho} = -h_{\tilde{i}\tilde{j}}^{p\rho}, \quad h_{ijk}^{pq\rho} = -h_{\tilde{i}\tilde{j}\tilde{k}}^{pq\rho}, \qquad (160)$$

where sites $\tilde{i}$, $\tilde{j}$ and $\tilde{k}$ correspond to a mirror reflection of sites i, j and k with respect to any crystal plane xy normal to the direction z of fluxes.

Equations of evolution for two-site and three-site averages generalizing Eq. (24) for dc_i^p/dt have the following form:

$$\frac{d}{dt}\langle n_i^p n_j^q \rangle = \sum_{s(i)} \Big\langle \hat{w}_{is}^p n_j^q (\delta\mu_{si}^{pv} + \hat{h}_{is}^{pv} - \hat{h}_{si}^{pv} - \hat{h}_s^p +$$

$$+ \hat{h}_i^p + \hat{h}_s^v - \hat{h}_i^v)\Big\rangle + \sum_{s(j)} \Big\langle \hat{w}_{js}^q n_i^p (\delta\mu_{sj}^{qv} +$$

$$+ \hat{h}_{js}^{qv} - \hat{h}_{sj}^{qv} - \hat{h}_s^q + \hat{h}_j^q + \hat{h}_s^v - \hat{h}_j^v)\Big\rangle,$$

$$\frac{d}{dt}\langle n_i^p n_j^q n_k^r \rangle =$$

$$= \sum_{s(i)} \Big\langle \hat{w}_{is}^p n_j^q n_k^r \delta\mu_{si}^{pv} + \hat{h}_{is}^{pv} - \hat{h}_{si}^{pv} - \hat{h}_s^p + \qquad (161)$$

$$+ \hat{h}_i^p + \hat{h}_s^v - \hat{h}_i^v)\Big\rangle + \sum_{s(j)} \Big\langle \hat{w}_{js}^q n_i^p n_k^r (\delta\mu_{sj}^{qv} + \hat{h}_{js}^{qv} -$$

$$- \hat{h}_{sj}^{qv} - \hat{h}_s^q + \hat{h}_j^q + \hat{h}_s^v - \hat{h}_j^v)\Big\rangle +$$

$$+ \sum_{s(k)} \Big\langle \hat{w}_{ks}^r n_i^p n_j^q (\delta\mu_{sk}^{rv} +$$

$$+ \hat{h}_{ks}^{rv} - \hat{h}_{sk}^{rv} - \hat{h}_s^r + \hat{h}_k^r + \hat{h}_s^v - \hat{h}_k^v)\Big\rangle.$$

For the steady-state diffusion, the right-hand side of Eqs. (161) should vanish. It is convenient to write these stationarity conditions using the antisymmetric combinations of occupation operators:

$$\frac{d}{dt}\langle n_i^p n_j^q - n_j^p n_i^q \rangle = 0,$$
$$\frac{d}{dt}\langle n_i^p n_j^q n_k^r - n_{\bar{i}}^p n_{\bar{j}}^q n_k^r \rangle = 0, \qquad (162)$$

and to consider in these equations sites $(i, j, k) = (0, 1, 2)$ (in the notation of Fig. 1). Then equations for fluxes and fields which generalize relations (26) and (37) to the case of presence of triple fields $h_{ijk}^{\rho\sigma\tau}$ take the following form:

$$TJ_{0\to1}^p = \overline{w}_p(-\delta\mu_p + 2h_{01}^{vp}) + \sum_{j,\sigma} m_{p,01}^{\sigma j}(h_{01j}^{vp\sigma} - h_{01j}^{pv\sigma} -$$

$$- 2h_{0j}^{p\sigma} + 2h_{0j}^{v\sigma}) + \sum_{j\sigma k\rho} t_{p,01}^{\sigma j,\rho k}(-h_{0jk}^{p\sigma\rho} + h_{0jk}^{v\sigma\rho}), \quad (163)$$

$$\sum_{s\neq1}\Bigg[m_{p,0s}^{q1}(\delta\mu_p - 2h_{0s}^{vp}) +$$

$$+ \sum_{j,\sigma} t_{p,0s}^{q1,\sigma j}(h_{0sj}^{pv\sigma} - h_{0sj}^{vp\sigma} -$$

$$- h_{sj}^{p\sigma} + h_{0j}^{p\sigma} + h_{sj}^{v\sigma} - h_{0j}^{v\sigma}) +$$

$$+ \frac{1}{2}\sum_{j\sigma k\rho} r_{p,0s}^{q1,\sigma j,\rho k}(-h_{sjk}^{p\sigma\rho} +$$

$$+ h_{0jk}^{p\sigma\rho} + h_{sjk}^{v\sigma\rho} - h_{0jk}^{v\sigma\rho})\Bigg] -$$

$$- \sum_{s\neq1}\Bigg[m_{q,0s}^{p1}(\delta\mu_q - 2h_{0s}^{vq}) +$$

$$+ \sum_{j,\sigma} t_{q,0s}^{p1,\sigma j}(h_{0sj}^{qv\sigma} - h_{0sj}^{vq\sigma} - h_{sj}^{q\sigma} +$$

$$+ h_{0j}^{q\sigma} + h_{sj}^{v\sigma} - h_{0j}^{v\sigma}) + \frac{1}{2} +$$

$$+ \sum_{j\sigma k\rho} r_{q,0s}^{p1,\sigma j,\rho k}(-h_{sjk}^{q\sigma\rho} + h_{0jk}^{q\sigma\rho} + h_{sjk}^{v\sigma\rho} -$$

$$- h_{0jk}^{v\sigma\rho})\Bigg] = 0,$$

$$\sum_{s\neq1,2}\Bigg[t_{p,0s}^{q1,r2}(\delta\mu_p - 2h_{0s}^{vp}) +$$

$$+ \sum_{j,\sigma} r_{p,0s}^{q1,r2,\sigma j}(h_{0sj}^{pv\sigma} - h_{0sj}^{vp\sigma} -$$

$$- h_{sj}^{p\sigma} + h_{0j}^{p\sigma} + h_{sj}^{v\sigma} - h_{0j}^{v\sigma}) +$$

$$+ \frac{1}{2}\sum_{j\sigma k\rho} s_{p,0s}^{q1,r2,\sigma j,\rho k}(-h_{sjk}^{p\sigma\rho} +$$

$$+ h_{0jk}^{p\sigma\rho} + h_{sjk}^{v\sigma\rho} - h_{0jk}^{v\sigma\rho})\Bigg] - \qquad (164)$$

$$- \sum_{s\neq1,9}\Bigg[t_{q,0s}^{p1,r9}(\delta\mu_q - 2h_{0s}^{vq}) +$$

$$+ \sum_{j,\sigma} r_{q,0s}^{p1,r9,\sigma j}(h_{0sj}^{qv\sigma} - h_{0sj}^{vq\sigma} - h_{sj}^{q\sigma} +$$

$$+ h_{0j}^{q\sigma} + h_{sj}^{v\sigma} - h_{0j}^{v\sigma}) +$$

$$+ \frac{1}{2}\sum_{j\sigma k\rho} s_{q,0s}^{p1,r9,\sigma j,\rho k} \times$$

$$\times (-h_{sjk}^{q\sigma\rho} + h_{0jk}^{q\sigma\rho} + h_{sjk}^{v\sigma\rho} - h_{0jk}^{v\sigma\rho})\Bigg] -$$

$$- \sum_{s\neq1,9}\Bigg[t_{r,0s}^{p1,q9}(\delta\mu_r - 2h_{0s}^{vr}) +$$

$$+ \sum_{j,\sigma} r_{r,0s}^{p1,q9,\sigma j}(h_{0sj}^{rv\sigma} - h_{0sj}^{vr\sigma} -$$

$$- h_{sj}^{r\sigma} + h_{0j}^{r\sigma} + h_{sj}^{v\sigma} - h_{0j}^{v\sigma}) +$$

$$+ \frac{1}{2}\sum_{j\sigma k\rho} s_{r,0s}^{p1,q9,\sigma j,\rho k}(-h_{sjk}^{r\sigma\rho} +$$

$$+ h_{0jk}^{r\sigma\rho} + h_{sjk}^{v\sigma\rho} - h_{0jk}^{v\sigma\rho})\Bigg] = 0.$$

In Eqs. (164), site "9" is the nearest neighbor of sites

0, 1 and 2, as shown in Fig. 1, and quantities $r_{p,is}^{qj,rk,tl}$ and $s_{p,is}^{qj,rk,tl,um}$ are defined analogously to $t_{p,is}^{qj,rk}$ in (31):

$$r_{p,is}^{qj,rk,tl} = \langle \hat{w}_{is}^p n_j^q n_k^r n_l^t \rangle,$$
$$s_{p,is}^{qj,rk,tl,um} = \langle \hat{w}_{is}^p n_j^q n_k^r n_l^t n_m^u \rangle. \tag{165}$$

For simplicity, below we use the NNJA supposing both pairwise and triple effective interactions to act only between nearest-neighbors. Then symmetry relations (160) imply that for the given sets of species (p, ρ) or (p, q, ρ), only one pairwise field $h_{01}^{p\rho}$ or one triple field $h_{012}^{pq\rho}$ is independent and nonzero, while all other fields can be expressed via these $h_{01}^{p\rho}$ or $h_{012}^{pq\rho}$. The statistical averages in Eqs. (165) have the form

$$\nu_{p,is,i_1 i_2 \ldots i_n}^{q_1, q_2 \ldots q_n} = \langle \hat{w}_{01}^p n_{i_1}^{q_1} n_{i_2}^{q_2} \ldots n_{i_n}^{q_n} \rangle \tag{166}$$

analogous to ν_{pi}^q and $\nu_{p,ij}^{q\lambda}$ in (52), and they will be calculated using the KMFA, just as those in Sec. 4.2. It yields the relations similar to (74):

$$\nu_{p,\xi_1 \ldots \xi_n}^{q_1, \ldots q_n} = c_p c_{q_1} \ldots c_{q_n} \omega_p^0 \eta_{p\xi_1}^{q_1} \ldots \eta_{p\xi_n}^{q_n}, \tag{167}$$

where ξ_m is the symmetry of site i_m, being Δ or u, and the expressions for $\eta_{p\xi}^q$ are given by Eqs. (73). Note that averages in Eqs. (164) include operators $\hat{w}_{0s}^p$ describing a $p \rightleftharpoons v$ jump along bond $(0s)$ rather than that along bond $(0,1)$, as in Eq. (166). Hence these averages should be transformed into those given by Eq. (166), using rotations of crystal lattice discussed in Sec. 4.1.

For the case of a binary alloy AB considered below, Eqs. (164) include only three different fields: the pairwise one, h_{01}^{vB}, and two triple ones, h_{012}^{vBB} and $h_{012}^{BvB} = h_{012}^{BBv}$. For brevity, these fields will be denoted as

$$h_{01}^{vB} = h_1, \quad h_{012}^{vBB} = h_2, \quad h_{012}^{BvB} = h_3, \tag{168}$$

and equations for these h_n can be obtained if we put in the first and the second Eqs. (164): $(p,q) = (B,A)$, $(p,q,r) = (B,A,A)$, and $(p,q,r) = (A,B,A)$, respectively. To calculate Onsager coefficients, it is convenient to write these equations in the following form:

$$\sum_{l=1}^{3} a_{kl} h_l = b_k^A \delta \mu_A + b_k^B z \delta \mu_B, \tag{169}$$

where $z = \omega_B^0 / \omega_A^0$ is the same as in (124). Coefficients a_{kl} in (169) are calculated using Eqs. (164), and these calculations are rather tedious. The resulting coefficient a_{11} coincides with D_{nn} in Eq. (126), while the rest a_{kl} and b_k^p in (169) are presented in Appendix B.

The NNJA-KMFA expressions for atomic fluxes (163) in the notation (134) take the following form:

$$J_{0\to 1}^B = -\beta \omega_B^0 c \Big\{ \delta \mu_B + 2c_A(3\bar{v} - 2\bar{y})h_1 +$$
$$+ 4c_A[(2\bar{y} - 3\bar{v}) + c_A \bar{v}(2\bar{v} - \bar{y})]h_2 +$$
$$+ 4c_A[(3\bar{v} - 2\bar{y}) + c_A(\bar{y}^2 - \bar{y}\bar{v} - \bar{v}^2)]h_3 \Big\}, \tag{170}$$
$$J_{0\to 1}^A = -\beta \omega_A^0 c_A \left[\delta \mu_A + 2c(2x - 3v)h_1 +$$
$$+ 4c^2 v(2v - x)h_2 + 4c^2(x^2 - xv - v^2)h_3 \right].$$

Each solution h_n of linear equations (169) is the sum of two terms proportional to $\delta \mu_A$ and to $z\delta \mu_B$:

$$h_n = h_n^A \delta \mu_A + h_n^B z \delta \mu_B. \tag{171}$$

Substituting these solutions into Eqs. (170) and comparing the resulting relations with Eqs. (38), (41), and (114), we can express the correlative Onsager coefficients L_{pq}^c in (114) via fields h_n^A and h_n^B in (171) as follows:

$$L_{AA}^c = 2(3v - 2x)h_1^A + 4cv(x - 2v)h_2^A -$$
$$- 4c(x^2 - xv - v^2)h_3^A,$$
$$L_{AB}^c = 2(2x - 3v)h_1^B - 4cv(x - 2v)h_2^B +$$
$$+ 4c(x^2 - xv - v^2)h_3^B,$$
$$L_{BA}^c = \Big\{ 2(3\bar{v} - 2\bar{y})h_1^A - 4[(3\bar{v} - 2\bar{y}) +$$
$$+ c_A(\bar{y}\bar{v} - 2\bar{v}^2)]h_2^A + \tag{172}$$
$$+ 4[(3\bar{v} - 2\bar{y}) + c_A(\bar{y}^2 - \bar{y}\bar{v} - \bar{v}^2)]h_3^A \Big\},$$
$$L_{BB}^c = z\Big\{ 2(2\bar{y} - 3\bar{v})h_1^B + 4[(3\bar{v} - 2\bar{y}) +$$
$$+ c_A(\bar{y}\bar{v} - 2\bar{v}^2)]h_2^B -$$
$$- 4[(3\bar{v} - 2\bar{y}) + c_A(\bar{y}^2 - \bar{y}\bar{v} - \bar{v}^2)]h_3^B \Big\},$$

where $\tilde{m}_{A,1}^{B0} = (2x - 3v)$ is the same as in (134). We note that the Onsager symmetry relation (120) here takes the form:

$$c_A[(2x-3v)h_1^B - 2cv(x-2v)h_2^B + 2c(x^2-xv-v^2)h_3^B] =$$
$$= c_A(3\bar{v} - 2\bar{y})h_1^A - 2cy(h_2^A - h_3^A). \tag{173}$$

In the absence of triple fields, this relation was proved in Sec. 6.2 for any concentration c. When the triple fields are present, proof of Eq. (173) at any c is cumbersome, but we have proved it for the case of low c discussed below. The presence of this symmetry relation can be viewed as the evidence of correctness of results of tedious calculations mentioned above and given by Eqs. (185)–(188).

Linear equations (169) for fields h_n^p with the coefficients given by Eqs. (184)–(186) are simply solved using standard computer codes, while Eqs. (172) expresses coefficients L_{pq}^c in Eqs. (116) and hence correlation factors f_p in Eqs. (115) via these h_n^p. Thus, Eqs. (169) and (172) enable to calculate the effect of triple vacancy correlations on diffusion coefficients D_p at any concentration c.

Below we discuss the case of dilute alloys when Eqs. (169) are greatly simplified. For this case, each field h_1^p in (171) can be conveniently written as a sum of the zero-order term h_{10}^p and the linear in c term $c h_{11}^p$ where h_{10}^p corresponds to the solution of Eqs. (169) at $c = 0$:

$$h_1^p = h_{10}^p + c h_{11}^p,$$
$$h_{10}^A = \frac{3x_4 - 2x_1}{D_0}, \quad h_{10}^B = -\frac{1}{D_0}, \quad (174)$$

and x_n and D_0 are the same as in (145) and (152). Then two systems of equations for fields h_{11}^p, h_2^p and h_3^p with $p = A$ and $p = B$ can be concisely written as

$$D_0 h_{11}^p + A_{12} h_2^p + A_{13} h_3^p = B_{1p} - B_{11} h_{10}^p,$$
$$D_0 h_{11}^p + A_{22} h_2^p + A_{23} h_3^p = B_{2p} - B_{21} h_{10}^p, \quad (175)$$
$$D_0 h_{11}^p + A_{32} h_2^p + A_{33} h_3^p = B_{3p} - B_{31} h_{10}^p,$$

where coefficients A_{mn}, B_{mp} and B_{m1} are given in Appendix C.

Let us write the correlative coefficients L_{pq}^c in (172) and the correlation factors f_p in (116) at low c as follows:

$$L_{pq}^c = L_{pq}^{c0} + c L_{pq}^{c1}, \quad f_p = f_{p0}(1 + b_p^c), \quad (176)$$

where L_{pq}^{c0} and f_{p0} are the same as in (152), and b_p^c is the correlation enhancement factor. Then Eqs. (116) show that these enhancement factors are expressed via L_{pq}^{c0} and L_{pq}^{c1} in (176) as follows:

$$b_A^c = \frac{1}{f_{A0}} \left[x_2 L_{AB}^{c0}(1 - l_z') - L_{AA}^{c0} - x_2 L_{AB}^{c1} \right],$$
$$b_B^c = \frac{1}{f_{B0}} \left(L_{BB}^{c0} - L_{AB}^{c0} - L_{BB}^{c1} \right), \quad (177)$$

where l_z' is the logarithmic derivative of the frequency ratio $z = \omega_B^0 / \omega_A^0$ with respect to c at $c = 0$ which, according to Eqs. (124), can be written as

$$l_z' = (d \ln z / dc)_{c=0} = 4y_1 - 4x_1 + b_{BB}. \quad (178)$$

To find terms L_{pq}^{c1} in (176), we can use the following evident relations for the derivatives $\psi' = (d\psi/dc)_{c=0}$ of various functions ψ in (134):

$$x' = -x_1 f_{A\Delta}, \quad \bar{x}' = -f_{A\Delta}, \quad y' = -y_1 f_{B\Delta},$$
$$\bar{y}' = -f_{B\Delta}, \quad v' = -x_4 f_u, \quad \bar{v}' = -f_u, \quad (179)$$
$$f_{A\Delta} = x_1 - 1, \quad f_{B\Delta} = y_1 - 1, \quad f_u = x_4 - 1.$$

Considering the linear in c terms in Eqs. (172), we find that terms L_{pq}^{c1} which enter Eqs. (177) are expressed via fields h_{11}^B, h_2^B, and h_3^B in (175) as follows:

$$L_{AB}^{c1} = 2[2x_1 f_{A\Delta} - 3x_4 f_u)/D_0 + (2x_1 - 3x_4)h_{11}^B +$$
$$+ 2x_4(2x_4 - x_1)h_2^B + 2(x_1^2 - x_1 x_4 - x_4^2)h_3^B)],$$
$$L_{BB}^{c1} = 2x_2[(l_z' + 2f_{B\Delta} - 3f_u)/D_0 - h_{11}^B + \quad (180)$$
$$+ 2y_1(h_2^B - h_3^B)].$$

We note that taking into account only pairwise vacancy correlations (made in Secs. 3–7) corresponds to putting in Eqs. (175) $h_2^p = h_3^p = 0$, while the field h_{11}^p for this case is

$$h_{11,\text{PVC}}^p = (B_{1p} - B_{11} h_{10}^p)/D_0. \quad (181)$$

Applications of results of this section for estimates of influence of non-pairwise vacancy-solute correlations on diffusion in real alloys.

9. CONCLUSIONS

We summarize the main results of this work. We develop the statistical theory of steady-state diffusion in concentrated substitution alloys basing on the master equation approach. To be definite, we consider the nearesr-neighbor pairwise interaction model of FCC alloys as an example. We explicitly write all basic equations of the theory with fully taking into account the vacancy-solute interactions. General expressions for Onsager coefficients in terms of microscopic interatomic interactions and some statistical averages are presented. We discuss methods of calculations of these averages using two statistical approximations: the kinetic mean-field approximation (KMFA) which neglects statistical fluctuations in these averages, while chemical potentials are calculated using the more accurate, pair-cluster approximation (PCA) [24–26], and the full PCA which also takes into account these statistical fluctuations. To describe vacancy-solute correlations, we use the nearest-neighbor-jump approximation which takes into account these correlations only for nearest neighbors, and the second-shell-jump approximation which takes them into account up to the fourth neighbors in the FCC lattice. We also discuss effects of non-pairwise vacancy correlations using the triple vacancy-solute correlation model. For each of these approximations and methods, we derive expressions for Onsager coefficients at any composition of an

alloy. For binary alloys, we also present explicit expressions for diffusion coefficients. Applications of methods developed to statistical calculations of diffusion coefficients in real alloys and to estimates of interatomic interactions important for diffusion from experimental data are described in other papers [13, 14].

APPENDIX A

Fluctuative term ω_{pf} in Eq. (90)

To illustrate the form of expansions of correlative terms ω_{pf}, $\nu^q_{p\xi,f}$ and $\nu^{q\lambda}_{p,ij,f}$ in powers of correlators X_i in Eqs. (90) and (94), below we present the first terms of this expansion for ω_{pf}. For terms $\nu^q_{p\xi,f}$ and $\nu^{q\lambda}_{p,ij,f}$, the analogous "shortened" expansions are presented in Ref. [13]. To make formulas not too lengthy and keeping in mind the estimate $|X_i| \lesssim 0.02$ obtained in Sec. 5, we include in this shortened expression ω^{sh}_{pf}, in addition to all terms linear and quadratic in X_i, only those terms with the higher powers of X_i which at $|X_i| = 0.02$ exceed 10^{-3}. For brevity, each term $X_1^{n_1} X_2^{n_2} \ldots$ is denoted as X with n_1 lower indices 1, n_2 lower indices 2 etc, for example

$$X_1 X_2 X_5 = X_{1,2,5}, \quad X_2 X_6^2 = X_{2,6,6}. \tag{182}$$

Then, denoting this shortened version of the fluctuative term by the upper index "sh", we have

$$\omega^{sh}_{pf} = (X_1 + 8X_2 + 14X_3 + 2X_4 + 16X_5 + 22X_6) +$$
$$+ (2X_{1,4} + 16X_{1,5} + 22X_{1,6} + 12X_{2,2} + 56X_{2,3} +$$
$$+ 8X_{2,4} + 96X_{2,5} + 176X_{2,6} + 49X_{3,3} + 28X_{3,4} +$$
$$+ 208X_{3,5} + 264X_{3,6} + X_{4,4} + 16X_{4,5} + 44X_{4,6} +$$
$$+ 92X_{5,5} + 304X_{5,6} + 183X_{6,6}) + (304X_{1,5,6} +$$
$$+ 183X_{1,6,6} + 264X_{2,2,6} + 624X_{2,3,5} + 1056X_{2,3,6} +$$
$$+ 176X_{2,4,6} + 368X_{2,5,5} + 1824X_{2,5,6} + 1464X_{2,6,6} +$$
$$+ 672X_{3,3,5} + 772X_{3,3,6} + 208X_{3,4,5} + 528X_{3,4,6} +$$
$$+ 1104X_{3,5,5} + 3344X_{3,5,6} + 1830X_{3,6,6} + 304X_{4,5,6} +$$
$$+ 366X_{4,6,6} + 224X_{5,5,5} + 1488X_{5,5,6} + 2120X_{5,5,6} +$$
$$+ 720X_{6,6,6}) + (10032X_{2,3,5,6} + 7320X_{2,3,6,6} +$$
$$+ 12720X_{2,5,6,6} + 8880X_{3,3,5,6} + 14880X_{3,5,5,6} +$$
$$+ 19080X_{3,5,6,6} + 8528X_{5,5,6,6} + 6688X_{5,6,6,6}). \tag{183}$$

At $X_i = 0.02$, Eq. (183) yields $\omega^{sh}_{pf} = 2.081$, while the total ω_{pf} in (90) is 2.064. Similarly, at $X_i = -0.02$

we have $\omega^{sh}_{pf} = -0.775$, $\omega_{pf} = -0.771$. Therefore, the shortened version (183) seems to describe the total ω_{pf} in (90) within about one percent. For terms $\nu^q_{p\xi,f}$ and $\nu^{q\lambda}_{p,ij,f}$, similar results are presented in [13]

APPENDIX B

Coefficients a_{kl} and b^p_k in Eqs. (169)

Coefficients a_{kl} in Eqs. (169) are some polynomials in the solute site fraction $c_B = c$:

$$a_{kl} = \sum_{m=0}^{2} a^{(m)}_{kl} c^m. \tag{184}$$

In the notation (134), the nonzero $a^{(m)}_{kl}$ in (184) are

$$a^{(0)}_{21} = [2z\bar{v}(2\bar{v} - \bar{y}) + x(\bar{x} + \bar{v}) + v(2\bar{x} + 5\bar{v})],$$
$$a^{(1)}_{21} = [z\bar{v}(8y\bar{v} - 3y\bar{y} + 8v\bar{y} - 7v\bar{v}) +$$
$$+ x^2(2\bar{x} + 3\bar{v}) - 2xv(6\bar{x} + 5\bar{v}) + v^2(10\bar{x} + \bar{v})],$$
$$a^{(0)}_{31} = [2z(\bar{v}^2 - \bar{y}^2 + \bar{v}\bar{y}) + x(3\bar{v} - \bar{x}) + v(2\bar{x} + 5\bar{v})],$$
$$a^{(1)}_{31} =$$
$$= \left\{ z \left[y\bar{y}(3\bar{v} - 2\bar{y}) + v\bar{y}(6\bar{y} - 4\bar{v}) + \bar{v}^2(4y - v) \right] +$$
$$+ x^2(9\bar{v} - 2\bar{x}) + 6xv(\bar{x} - 5\bar{v}) + v^2(13\bar{v} - 2\bar{x}) \right\},$$
$$a^{(1)}_{12} = 6zy(\bar{y} - 2\bar{v}) - 6xv - 10v^2,$$
$$a^{(2)}_{12} = v \left[z(6y\bar{y} - 16v\bar{y} - 16y\bar{v} + 14v\bar{v}) -$$
$$- 6x^2 + 32xv - 14v^2 \right],$$
$$a^{(1)}_{22} = zy\bar{v}(3\bar{y} - 8\bar{v}) - x\bar{x}v - 5xv\bar{v} - 4\bar{x}v^2 - 6v^2\bar{v},$$
$$a^{(2)}_{22} =$$
$$= [zv\bar{v}(4y\bar{y} - 18y\bar{v} - 18v\bar{y} + 19v\bar{v}) + v(28x\bar{x}v -$$
$$- 4x^2\bar{x} - 24\bar{x}v^2 - 6x^2\bar{v} + 32xv\bar{v} - 4v^2\bar{v})],$$
$$a^{(1)}_{32} = zy(2\bar{y}^2 - 3\bar{y}\bar{v} - 4\bar{v}^2) - 2xv\bar{v} - \bar{x}v^2 - 4v^2\bar{v},$$
$$a^{(2)}_{32} = [zv(4y\bar{y}^2 - 16\bar{y}^2 v - 6y\bar{y}\bar{v} + 8v\bar{y}\bar{v} - 16y\bar{v}^2 +$$
$$+ 4v\bar{v}^2) + v(4x^2\bar{x} - 14x\bar{x}v - 16x^2\bar{v} +$$
$$+ 62xv\bar{v} + 2\bar{x}v^2 - 34v^2\bar{v})],$$
$$a^{(1)}_{13} = -6zy(\bar{y} - 2\bar{v}) + 4x^2 + 2xv + 10v^2,$$
$$a^{(2)}_{13} = z(6y\bar{y}v - 4y^2\bar{y} + 8v^2\bar{y} + 12y^2\bar{v} - 8yv\bar{v} -$$
$$- 2v^2\bar{v}) + 4x^3 - 18x^2v + 2v^3,$$
$$a^{(1)}_{23} = zy\bar{v}(8\bar{v} - 3\bar{y}) + 2x^2\bar{v} - 2xv\bar{v} + 4v^2\bar{v} + v^2\bar{x},$$
$$a^{(2)}_{23} = [z\bar{v}(6y\bar{y}v - 4y^2\bar{y} + 16y^2\bar{v} + 16\bar{y}v^2 -$$
$$- 8yv\bar{v} - 4v^2\bar{v}) + 4x^3\bar{x} - 12x^2\bar{x}v + 2x\bar{x}v^2 + 4x^3\bar{v} -$$
$$- 12x^2v\bar{v} + 2xv^2\bar{v} + 14\bar{x}v^3 - 2v^3\bar{v}],$$

$$a_{33}^{(1)} = \left[zy(3\bar{y}\bar{v} - 2\bar{y}^2 + 4\bar{v}^2) + 6x^2\bar{v} + \right.$$
$$\left. + 2x\bar{x}v + 4xv\bar{v} + 5v^2\bar{x} + 10v^2\bar{v} \right],$$

$$a_{33}^{(2)} = \left[z(4y^2\bar{y}\bar{v} + 4y\bar{y}^2v - 4y^2\bar{y}^2 + 8y^2\bar{v}^2 - \right. \quad (185)$$
$$- 6y\bar{y}v\bar{v} + 8\bar{y}^2v^2 - 8yv\bar{v}^2 - 8\bar{y}v^2\bar{v} + 2v^2\bar{v}^2) -$$
$$- 4x^3\bar{x} + 4x^2\bar{x}v + 12x^3\bar{v} + 6x\bar{x}v^2 - 40x^2v\bar{v} -$$
$$\left. - 10\bar{x}v^3 - 22xv^2\bar{v} + 10v^3\bar{v} \right],$$

while terms b_k^p in the right-hand side of Eq. (169) are

$$b_1^A = (3v - 2x), \quad b_2^A = [v(2\bar{x} + \bar{v}) - x(\bar{x} + \bar{v})],$$
$$b_3^A = (x\bar{x} - 3x\bar{v} + 3v\bar{v}), \quad b_1^B = (2\bar{y} - 3\bar{v}), \quad (186)$$
$$b_2^B = \bar{v}(\bar{y} - 2\bar{v}), \quad b_3^B = (\bar{y}^2 - \bar{y}\bar{v} - \bar{v}^2).$$

APPENDIX C

Coefficients A_{mn}, B_{np}, and B_{m1} in Eqs. (175)

Coefficients A_{mn}, B_{np}, and B_{m1} in Eqs. (175) are expressed via x_n and y_1 in (145) and b_{BB} in (150) as follows:

$$A_{12} = -(6x_2y_1 + 6x_1x_4 + 10x_4^2),$$
$$A_{13} = (6x_2y_1 + 4x_1^2 + 2x_1x_4 + 10x_4^2),$$
$$A_{22} = -(5x_2y_1 + 6x_1x_4 + 10x_4^2),$$
$$A_{23} = (5x_2y_1 + 2x_1^2 - 2x_1x_4 + 5x_4^2),$$
$$A_{32} = -(5x_2y_1 + 2x_1x_4 + 5x_4^2),$$
$$A_{33} = (5x_2y_1 + 6x_1^2 + 6x_1x_4 + 15x_4^2), \quad (187)$$
$$B_{1A} = (2x_1^2 - 2x_1 - 3x_4^2 + 3x_4),$$
$$B_{2A} = (3x_1^2 - x_1x_4 - 4x_4^2) + (6x_4 - 4x_1),$$
$$B_{3A} = (x_1^2 + 3x_1x_4 - 6x_4^2) + (6x_4 - 4x_1),$$
$$B_{1B} = (3x_4 - 2y_1 - 1),$$
$$B_{2B} = B_{3B} = (3x_4 - y_1 - 2),$$
$$B_{11} = D'_{nn} = x_2(18y_1 - 8x_1 - 5x_4 + 2b_{BB}) +$$
$$+ 4(x_1^2 - 6x_1x_4 + x_4^2) + D_0,$$
$$B_{21} = x_2(15y_1 - 8x_1 - 5x_4 + 2b_{BB}) +$$
$$+ (2x_1^2 - 25x_1x_4 - x_4^2) + 2D_0, \quad (188)$$
$$B_{31} = x_2(15y_1 - 8x_1 - 5x_4 + 2b_{BB}) +$$
$$+ (6x_1^2 - 29x_1x_4 - x_4^2) + 2D_0,$$

where D'_{nn} is $(\partial D_{nn}/\partial c)_{c=0}$ with D_{nn} from (126), and D_0 is the same as in (151).

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