

ФАЗОВЫЕ ПРЕВРАЩЕНИЯ

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Martin's Kinetic Mean-Field Model Revisited—Frequency Noise Approach *versus* Monte Carlo

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Development of the non-linear kinetic mean-field model suggested by George Martin in 1990 is discussed. Its steady-state limit is shown to coincide with Khachaturyan's model. It is proved rigorously that Martin's model and its 3D version always provide decrease of free energy and are unable to model any overcoming of free-energy barrier, including nucleation. To enable nucleation processes within the mean-field models, the introduction of noise is necessary. Contrary to common way of noise introduction (noise of concentration), we introduce the noise of jump frequencies as a basic reason of fluctuations. The new method is called as Stochastic Kinetic Mean Field (SKMF). In this paper, we investigate and compare the dispersion and spatial correlations of concentration fluctuations by three methods—direct Monte Carlo simulation, numeric simulation by SKMF method, and analytic approximation within the scope of SKMF. Comparison confirms the correspondence of frequency noise to the averaging over finite number of Monte Carlo runs (over finite number of copies of the canonical ensemble).

Key words: kinetics, mean-field approximation, diffusion, noise, fluctuation, correlation, probability.

Запропоновано розвиток нелінійного кінетичного середньопольового моделю Жоржа Мартана 1990 року. Показано, що у наближенні квазістаціонарності він відповідає Хачатуряновому моделю. Строго доведено, що Мартанів модель та його 3D-версія завжди забезпечують зменшення вільної енергії та не уможливають моделювати подолання бар'єру вільної енергії разом з зародкуванням. Для реалізації процесів зародкування в

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середньо-польових моделях необхідно вводити шум. На відміну від поширеного способу введення шуму (як шуму концентрації), ми вводим шум частоти обмінів місцями через стрибки як основну причину флюктуацій. Нова метода називається SKMF (Stochastic Kinetic Mean Field). У цій роботі досліджуються та порівнюються дисперсія та просторові кореляції флюктуацій концентрації за допомогою трьох методів — прямого моделювання за методом Монте-Карло, чисельного моделювання за методом SKMF й аналітичного наближення в рамках SKMF. Порівняння цих методів підтверджує відповідність певної амплітуди шуму частот усередненню по відповідній скінченній кількості Монте-Карло-запусків (по скінченній кількості копій канонічного ансамблю).

Ключові слова: кінетика, середньопольове наближення, дифузія, шум, коливання, флюктуація, кореляція, ймовірність.

Предложено развитие нелинейной кинетической среднеполевой модели Жоржа Маргана 1990 года. Показано, что в приближении квазистационарности она соответствует модели Хачатуряна. Строго доказано, что модель Маргана и её 3D-версия всегда обеспечивают уменьшение свободной энергии и не позволяют моделировать преодоление барьера свободной энергии вместе с зародышеобразованием. Для реализации процессов зародышеобразования в среднеполевых моделях необходимо вводить шум. В отличие от распространённого способа введения шума (как шума концентрации), мы вводим шум частоты обменов местами посредством скачков как основную причину флюктуаций. Новый метод называется SKMF (Stochastic Kinetic Mean Field). В этой работе исследуются и сравниваются дисперсия и пространственные корреляции флюктуаций концентрации, полученные с помощью трёх методов — прямого моделирования методом Монте-Карло, численного моделирования по методу SKMF, аналитического приближения в рамках SKMF. Сравнение этих методов подтверждает соответствие определённой амплитуды шума частоты усреднению по соответствующему конечному количеству Монте-Карло-запусков (по конечному числу копий канонического ансамбля).

Ключевые слова: кинетика, среднеполевое приближение, диффузия, шум, флюктуація, корреляція, вероґатність.

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1. INTRODUCTION

Mean-field approximation is typically used for simplified analysis of many equilibrium properties of gases, plasma, and condensed matter [1–7]. Its main tricks are Eq. (1a) using unary probability distributions for calculations of the potential energy like

$$U(\mathbf{r})(\mathbf{r}) = \iiint K(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') d^3 r' \quad (1a)$$

and Eq. (1b) simultaneously using Boltzmann distribution for this

unary probability with approximation (1a) for potential energy, making this problem self-consistent one:

$$\rho(\mathbf{r}) = \frac{\exp(-U(\mathbf{r})/kT)}{\iiint \exp(-U(\mathbf{r}')/kT) d^3 r'}. \quad (1b)$$

Interesting quasi-1D modification of the mean-field approach to kinetic problems of atomic transport in solid state was suggested by George Martin in 1990 [8]. In this approach, the master equation for probability C_p of finding atom A at the site belonging to plane number 'p', based on balance of local in- and out-fluxes for any site, self-consistently uses the mean-field approximation for calculation of energy barriers in the jump frequencies:

$$\begin{aligned} \frac{dC_p}{dt} = & -Z_v [C_p(1 - C_{p-1})\Gamma_{p,p-1} - (1 - C_p)C_{p-1}\Gamma_{p-1,p} + \\ & + C_p(1 - C_{p+1})\Gamma_{p,p+1} - (1 - C_p)C_{p+1}\Gamma_{p+1,p}]. \end{aligned} \quad (2a)$$

Here, $Z = Z_i + 2Z_v$ is a total number of nearest neighbours, Z_i is a number of nearest neighbours in the central plane 'p' perpendicular to the concentration gradient, Z_v —number of nearest neighbours in the right 'p + 1' and in the left plane 'p - 1' (Fig. 1):

$$\Gamma_{p,p+1} = v \exp\left(-\frac{E_{p,p+1}}{kT}\right). \quad (2b)$$

$\Gamma_{p,p+1}$ is a frequency (probability per unit time) of exchange between atom A in plane 'p' and atom B in plane 'p + 1'. $E_{p,p+1}$ —the difference between the saddle-point energy E^s and interaction energy of jumping atoms before energy.

In Ref. [9], we generalized Martin's equations to the 3D-case with the following kinetic equations for 'concentration' (probability) at site 'i' surrounded by nearest neighbours (the sites indicated by 'in'):

$$\frac{dC_A[i]}{dt} = \sum_{in=1}^Z (-C_A[i]C_B[in]\Gamma[in(A),in(B)] + C_B[in]C_A[i]\Gamma[in(A),i(B)]). \quad (3)$$

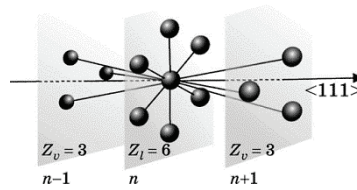


Fig. 1. Quasi-1D model of atomic migration (direction $\langle 111 \rangle$ for f.c.c. lattice).

Here, the jumps are restricted (within the Martin's model) only to the first co-ordination shell (exchanges between nearest neighbours). Exchange frequencies between A and B in the neighbouring sites ' i ' and ' in ' are determined in [8, 9] *via* Arrhenius law like

$$\Gamma[i(A), in(B)] = v_0 \exp\left(-\frac{Q_{i,in}}{kT}\right) = v_0 \exp\left(-\frac{E^s - (E_A[i] + E_B[in])}{kT}\right) \quad (4)$$

with saddle-point assumed the same for all jumps, and with energies before jump calculated taking into account interaction only with Z nearest neighbours (V_{AA} , V_{BB} , V_{AB}) and without any account of correlations—within the mean-field approximation:

$$\begin{aligned} E_A[i] &= \sum_{in=1}^Z (C_A[in]V_{AA} + C_B[in]V_{AB}), \\ E_B[in] &= \sum_{inn=1}^Z (C_A[in]V_{BA} + C_B[in]V_{BB}). \end{aligned} \quad (5)$$

Martin's approach was later applied to strongly non-linear diffusion in nanofilms with sharp gradients of the jump frequencies. Among other effects, this approach predicted a possibility of the sharpening of diffusion profiles (instead of traditional smoothing) and other non-linear effects at the initial stages of interdiffusion [10, 11].

2. STEADY-STATE LIMIT OF 3D-GENERALIZATION OF THE MARTIN'S MODEL

In his original paper [8], G. Martin considers in detail the steady-state case of the kinetic equations in quasi-1D scheme. We will also start (in our general 3D case) from analysis of the steady-state solutions of Eqs. (3)–(5). Obviously, all time derivatives (for all sites ' i ') in Eq. (3) are equal to zero if the detailed balance is satisfied:

$$C_A[i]C_B[in]\Gamma[i(A), in(B)] = C_B[i]C_A[in]\Gamma[in(A), i(B)] \quad (6a)$$

or

$$\frac{C_A[i]}{C_B[i]} \exp\left(\frac{E_A[i] - E_B[i]}{kT}\right) = \frac{C_A[in]}{C_B[in]} \exp\left(\frac{E_A[in] - E_B[in]}{kT}\right). \quad (6b)$$

Equation (6b) is a steady state condition, which can be interpreted as the equalizing of chemical potentials throughout the system. Due to the exchange mechanism of diffusion, it is sufficient to equalize the reduced chemical potential (change of free energy due to substitution of atom B by the atom A):

$$\tilde{\mu}[i] = \tilde{\mu}[in] \equiv \tilde{\mu} = \text{const.} \quad (7)$$

Here,

$$\begin{aligned} \tilde{\mu}[i] &= \mu_A[i] - \mu_B[i] = kT \ln \frac{C_A[i]}{C_B[i]} + E_A[i] - E_B[i] = \\ &= kT \ln \frac{C_A[i]}{C_B[i]} - 2V^{\text{mix}} \sum_{in=1}^Z C_A[in] + Z(V_{AB} - V_{BB}), \end{aligned} \quad (8)$$

$\mu_A[i] = kT \ln C_A[i] + E_A[i] + \text{const}$, $\mu_B[i] = kT \ln C_B[i] + E_B[i] + \text{const}$ are chemical potentials within the mean-field approximation; $V^{\text{mix}} = V_{AB} - (V_{AA} + V_{BB}) / 2$ —mixing energy.

As we know, Martin's kinetic equations always tend to steady state, and steady state in closed system means equilibrium—stable or metastable. Thus, Eq. (8) immediately leads to the self-consistent set of non-linear algebraic equations

$$\frac{C_A[i]}{(1 - C_A[i])} = \exp\left(\frac{2V^{\text{mix}}}{kT} \sum_{in=1}^Z C_A[in]\right) \exp\left(\frac{\tilde{\mu} - Z(V_{AB} - V_{BB})}{kT}\right) (i = 1, \dots, N) \quad (9)$$

with constraint of matter conservation:

$$\sum_{i=1}^N C_A[i] = N\bar{C}_A. \quad (10)$$

Equation equivalent to Eq. (9) was suggested by A. Khachatryan [7] with arguments of Fermi–Dirac-type equation. He used it in his method of concentration waves describing ordered binary structures (see also [12–14]). These equations may be rather effectively applied for the construction of equilibrium phase diagrams of binary and multicomponent alloys, but with important restriction of the universal rigid lattice. Thus, limiting (steady-state) case of Martin's kinetic approach provides self-consistent mean-field thermodynamics. Now let us consider the relaxation processes in Martin's approach.

3. TIME EVOLUTION OF FREE ENERGY IN MARTIN'S MODEL AND ITS 3D GENERALIZATION

To analyse the time evolution of the free energy, we will represent the kinetic equation (3) in terms of individual pairs of sites 'i', 'in' that automatically provides the matter conservation:

$$\frac{dC_A[i]}{dt} = \sum_{in=1}^Z \frac{dC_A^{(i,in)}}{dt},$$

$$\frac{dC_A^{(i,in)}}{dt} = -C_A[i]C_B[in]\Gamma[i(A), in(B)] + C_B[i]C_A[in]\Gamma[in(A), i(B)] \quad (11)$$

Here, $dC_A^{(i,in)}/dt$ can be called the ‘partial’ time derivative showing change of concentration in site ‘ i ’ (and opposite change of concentration in neighbouring site ‘ in ’) due to exchange only between these two sites. Then

$$\begin{aligned} \frac{dF}{dt} &= \sum_{(i,in)}^{NZ/2} (\tilde{\mu}_{AB}[i] - \tilde{\mu}_{AB}[in]) \frac{dC_A^{(i,in)}}{dt} = \\ &= \sum_{(i,in)}^{NZ/2} \left(\left(kT \ln \frac{C_A[i]}{C_B[i]} + E_A[i] - E_B[i] \right) - \left(kT \ln \frac{C_A[in]}{C_B[in]} + E_A[in] - E_B[in] \right) \right) \times \\ &\quad \times (-C_A[i]C_B[in]\Gamma[i(A), in(B)] + C_B[i]C_A[in]\Gamma[in(A), i(B)]) \end{aligned}$$

Further,

$$\begin{aligned} \frac{dF}{dt} &= -v_0 \exp\left(-\frac{E^s}{kT}\right) kT \times \\ &\quad \times \sum_{(i,in)}^{NZ/2} C_B[i]C_B[in] \exp\left(\frac{E_B[i] + E_B[in]}{kT}\right) \times \\ &\quad \times \left(\ln\left(\frac{C_A[i]}{C_B[i]} \exp\left(\frac{E_A[i] - E_B[i]}{kT}\right)\right) - \ln\left(\frac{C_A[in]}{C_B[in]} \exp\left(\frac{E_A[in] - E_B[in]}{kT}\right)\right) \right) \times \\ &\quad \times \left(\frac{C_A[i]}{C_B[i]} \exp\left(\frac{E_A[i] - E_B[i]}{kT}\right) - \frac{C_A[in]}{C_B[in]} \exp\left(\frac{E_A[in] - E_B[in]}{kT}\right) \right). \end{aligned}$$

In notations of the reduced chemical potentials, it gives:

$$\begin{aligned} \frac{dF}{dt} &= -v_0 \exp\left(-\frac{E^s}{kT}\right) \times \\ &\quad \times \sum_{(i,in)}^{NZ/2} C_B[i]C_B[in] \exp\left(\frac{E_B[i] + E_B[in]}{kT}\right) (\tilde{\mu}_{AB}[i] - \tilde{\mu}_{AB}[in]) \times \\ &\quad \times \left(\exp\left(\frac{\tilde{\mu}_{AB}[i]}{kT}\right) - \exp\left(\frac{\tilde{\mu}_{AB}[in]}{kT}\right) \right). \end{aligned} \quad (12)$$

It is evident that the expression $(f1 - f2)(\exp(f1) - \exp(f2))$ is always positive except case $f1 = f2$ when it is equal to zero. Therefore, expression $\left(\frac{\tilde{\mu}_{AB}[i]}{kT} - \frac{\tilde{\mu}_{AB}[in]}{kT}\right) \left(\exp\left(\frac{\tilde{\mu}_{AB}[i]}{kT}\right) - \exp\left(\frac{\tilde{\mu}_{AB}[in]}{kT}\right)\right)$ in Eq. (12) is al-

ways positive except case of equal chemical potentials.

In this product (which differs from typical expressions in the entropy production or the free energy release rate), the first factor (difference of reduced chemical potential between neighbouring sites) is the driving force of exchange, and second factor (difference between exponents of reduced chemical potentials divided by kT) corresponds to general nonlinear expression for the flux of exchanging atom. This is a main reason why Martin's scheme is better adjusted to the early stages of diffusion at very sharp concentration gradients and is able to predict such non-trivial behaviour as the possibility of concentration profile sharpening instead of smoothing [10, 11]. (Exponential form of the driving force was suggested by M. Ivanov *et al.* [15].)

Thus, taking also into account the common 'minus' before the sum in Eq. (12), the time derivative of the free energy is always negative except steady-state (absolute or metastable minima), when it is zero.

So, we just proved that the Martin's equation and its 3D generalization might describe only evolution with minimization of the free energy.

Nucleation process, or any other process related to overcoming the free energy barrier, cannot be described by KMF.

To model the evolution from metastable state to the stable state by overcoming of the nucleation barrier, it is necessary to introduce additional noise—noise of initial conditions [9] or, better, the dynamic noise during the evolution.

4. STOCHASTIC GENERALIZATION OF KMF

As just mentioned, noise should be introduced into the mean-field scheme, to describe the first-order phase transformations. In linear theories of atomic transport, the noise of concentration and of order parameter was introduced into the Onsager scheme following the fluctuation-dissipation theorem, for example, by Khachaturyan *et al.* [16, 17]. Yet, this method had some drawbacks:

- (1) Onsager scheme for atomic local fluxes was linear and not self-consistent, Onsager coefficients and their activation energies were not interrelated with local composition and its energetics (contrary to Martin's approach);
- (2) order parameter fluctuations were introduced independently of concentration fluctuation; on the contrary, in Martin's approach the order is not something independent, instead, it is determined by the oscillations of local concentration (unary probabilities at the sites) between sublattices;
- (3) it seems more natural to introduce the fluctuations of the jump frequencies as a true reason of the noise.

In 2016, we (jointly with Debrecen team) introduced a new simulation method called SKMF (Stochastic Kinetic Mean Field), based on in-

roduction of the jump frequencies noise [18]:

$$\frac{dC_i}{dt} = -\sum_{j=1}^Z \left[C_i(1-C_j)(\Gamma_{i,j} + \delta\Gamma_{i,j}^{\text{Lang}}) - (1-C_i)C_j(\Gamma_{j,i} + \delta\Gamma_{j,i}^{\text{Lang}}) \right], \quad (13)$$

$$\delta\Gamma_{i,k}^{\text{Lang}} = \frac{A_n}{\sqrt{dt}} \sqrt{3}(2\text{random} - 1). \quad (14)$$

In analytical form, Langevin noise of frequencies satisfies the following condition:

$$\langle \delta\Gamma_{i,j}^{\text{Lang}}(t) \delta\Gamma_{k,m}^{\text{Lang}}(t') \rangle = A_n^2 \delta_{ik} \delta_{jm} \delta(t-t'). \quad (15)$$

Among other results, we found simple regularities for modelling fluctuations in an ideal solid solution by SKMF.

a) Composition deviation (mean-squared fluctuation of concentration at one site) is proportional to the frequency noise amplitude A_n :

$$\sqrt{\langle (\delta C)^2 \rangle} = \frac{\bar{C}(1-\bar{C})}{\sqrt{\Gamma_0}} A_n. \quad (16)$$

b) Using of certain frequency noise amplitude in SKMF is equivalent to using of M^{runs} runs of Monte Carlo simulation, with

$$M^{\text{runs}} = \frac{\Gamma_0}{\bar{C}(1-\bar{C})A_n^2}. \quad (17)$$

In other words, M^{runs} is a finite number of copies in the canonical ensemble over which the averaging is done. Zero noise is equivalent to the infinite number of copies in the canonical ensemble, and it is mean-field.

Both equations (16) and (17) were discussed, proven analytically and checked numerically for the case of ideal solution in [18].

Here, we consider in details the fluctuations in non-ideal solutions with positive as well as with negative mixing energies V^{mix} . One should distinguish two cases: (1) homophase fluctuations at ‘high’ temperature and (2) heterophase fluctuations (nucleation) at ‘low’ temperature. For example, under positive mixing energy, ‘high’ temperature

means $T > \frac{2ZV^{\text{mix}}}{k} C(1-C)$, when the regular solution demonstrates

only homophase fluctuations without decomposition. In case 2 of ‘low’ temperature, the system (within certain composition interval) demonstrates decomposition ($V^{\text{mix}} > 0$) or ordering (for example, f.c.c. alloy with $V^{\text{mix}} < 0$, $C = 1/4$ or $C = 1/2$) or ordering with decomposition (for example, f.c.c. alloy with $V^{\text{mix}} < 0$, $C = 1/8$). Below in this paper, all ex-

amples will be calculated for the case of f.c.c. lattice. Case 2 will be considered elsewhere.

5. FLUCTUATIONS OF CONCENTRATION IN F.C.C. SOLID SOLUTION WITH NON-ZERO MIXING ENERGY

Here, we consider a homogeneous (except local fluctuations) binary f.c.c. solid solution with equal average probability (concentration) of A atom being found at any site: $\langle C_i \rangle = \langle C_j \rangle = \bar{C}$. Local (at site 'i') concentration is fluctuating:

$$C_i = \bar{C} + \delta C_i.$$

As before, we are, first of all, interested in concentration dispersion (which is of course positive and the same for each site of globally homogeneous system:

$$x_0 \equiv \langle \delta C_i \delta C_i \rangle = \langle \delta C^2 \rangle. \quad (18)$$

We also will discuss two spatial correlations:

$$x_1 \equiv \langle \delta C_i \delta C_{in} \rangle, \quad x_2 \equiv \langle \delta C_i \delta C_{inn} \rangle. \quad (19)$$

Here, 'in' is any nearest neighbour site of the site 'i'—(site at the first co-ordination shell around 'i'), 'inn' is the next nearest neighbour site of the site 'i'—(site at the second co-ordination shell around 'i'). Despite initial neglect of correlation in the basic equations of SKMF, it is physically evident that in case of positive mixing energy, when the alloy has a tendency to decomposition (which becomes successful at low temperature), the neighbouring sites should demonstrate the tendency to the same sign of fluctuation, so that the spatial correlation $x_1 \equiv \langle \delta C_i \delta C_{in} \rangle$ is expected to be not zero, but positive. On the contrary, in case of negative mixing energy, when the alloy has a tendency to ordering, $x_1 \equiv \langle \delta C_i \delta C_{in} \rangle$ is expected to be not zero, but negative. Immediate reason of correlations is a dependence of jump frequencies on the local concentration fluctuations:

$$\begin{aligned} \Gamma_{i,j}(A(i) \square B(j)) &= v_0 \exp\left(-\frac{Q_{i,j}}{kT}\right) = v_0 \exp\left(-\frac{E^s - (E_A(i) + E_B(j))}{kT}\right) = \\ &= v_0 \exp\left(-\frac{E^s - (\bar{E}_A + \bar{E}_B)}{kT}\right) \exp\left(\frac{\delta E_A(i) + \delta E_B(j)}{kT}\right) \approx \bar{\Gamma} \left(1 + \frac{\delta E_A(i) + \delta E_B(j)}{kT}\right). \end{aligned} \quad (20)$$

Thus, in case of non-ideal alloy, the variations of frequencies are

caused not only directly by Langevin noise of frequencies, but as well by the local variations of concentrations:

$$\delta\Gamma_{i,j} = \delta\Gamma_{i,j}^{\text{Lang}} + \delta\Gamma_{i,j}^{\text{conc}},$$

where $\delta\Gamma_{i,j}^{\text{conc}}$ is a variation of frequency generated by local deviation of composition influencing the activation energy:

$$\begin{aligned}\delta\Gamma_{i,j}^{\text{conc}}(A(i) \square B(j)) &\approx \bar{\Gamma} \frac{\delta E_A(i) + \delta E_B(j)}{kT}, \\ \delta\Gamma_{i,j}^{\text{conc}}(B(i) \square A(j)) &\approx \bar{\Gamma} \frac{\delta E_B(i) + \delta E_A(j)}{kT}.\end{aligned}\quad (21)$$

Thus,

$$\begin{aligned}\frac{d\delta C_i}{dt} &= -Z\bar{\Gamma}\delta C_i + \bar{\Gamma}\sum_{j=1}^Z\delta C_j - \bar{C}(1-\bar{C})\sum_{j=1}^Z[\delta\Gamma_{i,j}^{\text{Lang}} - \delta\Gamma_{j,i}^{\text{Lang}}] - \\ &- \bar{C}(1-\bar{C})\bar{\Gamma}\sum_{j=1}^Z\left[\frac{\delta E_A(i) + \delta E_B(j)}{kT} - \frac{\delta E_B(i) + \delta E_A(j)}{kT}\right].\end{aligned}\quad (22)$$

Variations of basic energies are:

$$\begin{aligned}\delta E_A(i) - \delta E_B(i) &= -2V^{\text{mix}}\sum_{in=1}^Z(\delta C_A(in)), \\ \delta E_B(j) - \delta E_A(j) &= 2V^{\text{mix}}\sum_{jn=1}^Z(\delta C_A(jn)).\end{aligned}\quad (23)$$

Substitution of Eq. (23) into Eq. (22) gives:

$$\begin{aligned}\frac{d\delta C_A(i)}{dt} &= -Z\bar{\Gamma}\delta C_A(i) + \bar{\Gamma}\sum_{j=1}^Z\delta C_A(j) - \bar{C}(1-\bar{C})\sum_{j=1}^Z[\delta\Gamma_{i,j}^{\text{Lang}} - \delta\Gamma_{j,i}^{\text{Lang}}] - \\ &- \bar{C}(1-\bar{C})\bar{\Gamma}\frac{2V^{\text{mix}}}{kT}\sum_{j=1}^Z\left(-\sum_{in=1}^Z(\delta C_A(in)) + \sum_{jn=1}^Z(\delta C_A(jn))\right).\end{aligned}\quad (24)$$

Multiply this equation by δC_i and make an averaging for steady state:

$$\begin{aligned}\langle \delta C_i \frac{d\delta C_i}{dt} \rangle &= \frac{d \langle (\delta C)^2 \rangle}{2dt} = 0 = -Z\bar{\Gamma} \langle (\delta C)^2 \rangle + \bar{\Gamma}\sum_{j=1}^Z \langle \delta C_A(i)\delta C_A(j) \rangle - \\ &- \bar{C}(1-\bar{C})\bar{\Gamma}\frac{2V^{\text{mix}}}{kT}\sum_{j=1}^Z\left(-\sum_{in=1}^Z \langle \delta C_A(i)\delta C_A(in) \rangle + \sum_{jn=1}^Z \langle \delta C_A(i)\delta C_A(jn) \rangle\right) - \\ &- \bar{C}(1-\bar{C})\sum_{j=1}^Z[\langle \delta C_i\delta\Gamma_{i,j}^{\text{Lang}} \rangle - \langle \delta C_i\delta\Gamma_{j,i}^{\text{Lang}} \rangle].\end{aligned}\quad (25)$$

Here, ' j ' correspond to nearest neighbours of i , ' in ' are the neighbours of i , ' jn '—neighbours of j , 4 sites are simultaneously the neighbours for i and j (see Fig. 2).

Here, in 'first approximation', we consider concentrations fluctuations in sites as statistically correlated only for nearest neighbours (neglecting, so far, the correlation in the second co-ordination shell):

$$\langle (\delta C_A(k))(\delta C_A(m)) \rangle = \begin{cases} \langle \delta C^2 \rangle = x_0, & k = m \\ \langle \delta C_A(i)\delta C_A(in) \rangle = x_1, & m \text{ is a neighbour of } k \\ 0, & \text{in all other cases.} \end{cases}$$

(Let us remind that, in 'zeroth approximation', the correlation between nearest neighbours is taken as just zero). Then, in our 'first approximation',

$\sum_{in=1}^Z \langle \delta C_A(i)\delta C_A(in) \rangle = Zx_1$. In the sum $\sum_{jn=1}^Z \langle \delta C_A(i)\delta C_A(jn) \rangle$ over the nearest neighbours of site j , which in turn is a neighbour of site ' i ', one term survives as x_0 , since i is one of the neighbours of j ; also four terms survive as x_1 (one can geometrically check that each of nearest neighbours of ' i ' has other 4 nearest neighbours of ' i ' in its first co-ordination shell—see Fig. 2).

Therefore,

$$\sum_{jn=1}^Z \langle \delta C_A(i)\delta C_A(jn) \rangle = 1x_0 + 4x_1. \tag{26}$$

So,

$$\sum_{j=1}^Z \left(-\sum_{in=1}^Z \langle \delta C_A(i)\delta C_A(in) \rangle + \sum_{jn=1}^Z \langle \delta C_A(i)\delta C_A(jn) \rangle \right) = Z(-Zx_1 + x_0 + 4x_1) = Zx_0 - Z(Z - 4)x_1.$$

Thus, Eq. (25) is reduced to

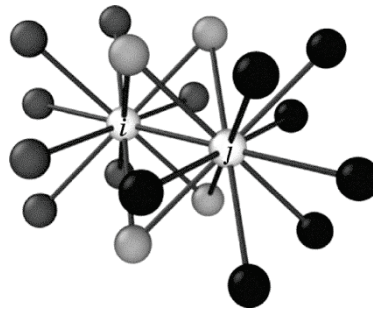


Fig. 2. Neighbouring sites i and j have four common neighbours.

$$\begin{aligned}
Z\bar{\Gamma}x_0\left(1 + \bar{C}(1 - \bar{C})\frac{2V^{\text{mix}}}{kT}\right) - Z\bar{\Gamma}x_1\left(1 + \bar{C}(1 - \bar{C})\frac{2V^{\text{mix}}}{kT}(Z - 4)\right) &= \\
= \bar{C}(1 - \bar{C})\sum_{j=1}^Z\left[\langle \delta C_i \delta \Gamma_{j,i}^{\text{Lang}} \rangle - \langle \delta C_i \delta \Gamma_{i,j}^{\text{Lang}} \rangle\right]. & \quad (27)
\end{aligned}$$

In full analogy with Appendix in [18], one can show that for any i ,

$$\sum_{j=1}^Z\left[\langle \delta C_i \delta \Gamma_{j,i}^{\text{Lang}} \rangle - \langle \delta C_i \delta \Gamma_{i,j}^{\text{Lang}} \rangle\right] = \bar{C}(1 - \bar{C})ZA_n^2. \quad (28)$$

Thus,

$$x_0\left(1 + \bar{C}(1 - \bar{C})\frac{2V^{\text{mix}}}{kT}\right) - x_1\left(1 + \bar{C}(1 - \bar{C})\frac{16V^{\text{mix}}}{kT}\right) = \bar{C}^2(1 - \bar{C})^2 A_n^2 / \bar{\Gamma}. \quad (29)$$

One can prove (using additional long algebra) that the account of non-zero correlations in the second co-ordination shell converts Eq. (29) into the following equation:

$$\begin{aligned}
x_0\left(1 + \frac{\bar{C}(1 - \bar{C})2V^{\text{mix}}}{kT}\right) - x_1\left(1 + \frac{\bar{C}(1 - \bar{C})16V^{\text{mix}}}{kT}\right) + x_2\frac{\bar{C}(1 - \bar{C})4V^{\text{mix}}}{kT} &= \\
= \bar{C}^2(1 - \bar{C})^2 A_n^2 / \bar{\Gamma}. & \quad (30)
\end{aligned}$$

We have now three unknowns— $x_0 = \langle \delta C^2(i) \rangle$, $x_1 = \langle \delta C(i)\delta C(in1) \rangle$, and $x_2 = \langle \delta C(i)\delta C(in2) \rangle$ (' $in1$ ' and ' $in2$ ' correspond to the first and second co-ordination shells, so that we need two more equations. For this, we take once more the kinetic equation (16) and multiply it in other way—first, by the fluctuation of concentration in one of the sites ' $in1$ ', neighbouring to ' i ', and, second, by the fluctuation in the ' $in2$ ' in the second co-ordination shell. At that, due to equivalence of all sites in homogeneous alloy,

$$\begin{aligned}
\langle \delta C_{in1} \frac{d\delta C_i}{dt} \rangle &= \langle \delta C_i \frac{d\delta C_{in1}}{dt} \rangle = \\
= \frac{1}{2}\left(\langle \delta C_{in1} \frac{d\delta C_i}{dt} \rangle + \langle \delta C_i \frac{d\delta C_{in1}}{dt} \rangle\right) &= \frac{d\langle \delta C_{in1}\delta C_i \rangle}{2dt} = 0 \quad (31)
\end{aligned}$$

$$\begin{aligned}
\langle \delta C_{in2} \frac{d\delta C_i}{dt} \rangle &= \langle \delta C_i \frac{d\delta C_{in2}}{dt} \rangle = \\
= \frac{1}{2}\left(\langle \delta C_{in2} \frac{d\delta C_i}{dt} \rangle + \langle \delta C_i \frac{d\delta C_{in2}}{dt} \rangle\right) &= \frac{d\langle \delta C_{in2}\delta C_i \rangle}{2dt} = 0. \quad (32)
\end{aligned}$$

Substituting Eq. (24) for $d\delta C_i/dt$ into Eqs. (31), (32), and making ra-

ther long and tiresome algebra, one gets, together with Eq. (29) with notations

$$\nu \equiv \bar{C}(1 - \bar{C}) \frac{V^{\text{mix}}}{kT}, \quad I \equiv \bar{C}^2(1 - \bar{C})^2 \frac{A_n^2}{\bar{\Gamma}}, \quad (33)$$

the set of three algebraic equations for three unknowns x_0, x_1, x_2 :

$$\begin{aligned} (1 + 2\nu)x_0 + (-1 - 16\nu)x_1 + 4\nu x_2 &= I, \\ (1 + 16\nu)x_0 + (-8 + 6\nu)x_1 + (2 + 24\nu)x_2 &= I, \\ 2\nu x_0 + (-1 + 12\nu)x_1 + (3 + 8\nu)x_2 &= 0. \end{aligned} \quad (34)$$

Solution is following:

$$x_0^{\text{analyt}} = I \frac{19 - 54\nu - 416\nu^2}{19 - 54\nu - 1204\nu^2 - 1136\nu^3} = k_0^{\text{analyt}}(\nu)I, \quad (35a)$$

$$x_1^{\text{analyt}} = I\nu \frac{2(19 + 36\nu)}{19 - 54\nu - 1204\nu^2 - 1136\nu^3} = k_1^{\text{analyt}}(\nu)I, \quad (35b)$$

$$x_2^{\text{analyt}} = I\nu^2 \frac{212}{19 - 54\nu - 1204\nu^2 - 1136\nu^3} = k_2^{\text{analyt}}(\nu)I. \quad (35c)$$

Thus, our analytic approximation of SKMF method predicts proportionality to I (actually, to the squared noise amplitude multiplied by $\bar{C}^2(1 - \bar{C})^2$). To check this prediction, we found x_0, x_1, x_2 by direct numeric simulation of fluctuations according to numeric solution of the Eqs. (13), (14). Results of simulation are shown in Fig. 3. Indeed, all of the above-mentioned three characteristics are proportional to the reduced noise parameter $I \equiv \bar{C}^2(1 - \bar{C})^2 A_n^2 / \bar{\Gamma}$ as predicted: $x_0^{\text{numeric}} = k_0^{\text{numeric}}(\nu)I$, $x_1^{\text{numeric}} = k_1^{\text{numeric}}(\nu)I$, $x_2^{\text{numeric}} = k_2^{\text{numeric}}(\nu)I$.

So far, we calculated dispersion per one site. This is not convenient for comparison with Monte Carlo and phenomenological thermodynamics. Therefore, we also calculated the dispersion for the cluster containing n sites.

In Figure 4, we compare theoretical predictions and numeric results for the dependence of factors k_0, k_1, k_2 on the renormalized mixing energy $\nu \equiv \bar{C}(1 - \bar{C}) V^{\text{mix}} / kT$ for the case when dispersion and correlations are calculated for 'cluster' containing one site. In Figure 4, we can see that the difference between analytic approximation and numeric simulation is not more than few percent; it is almost ideal for zero and negative mixing energies and increases for large positive mixing energies.

To compare with Monte Carlo, we should consider concentrations for cluster containing at least $n = 1 + 12 = 13$ sites. Therefore, we recalculated the results for dispersion for the case of larger clusters. Composition fluctuation in clusters containing central atom and some part of the neighbourhood, can be found for various cluster definitions, but

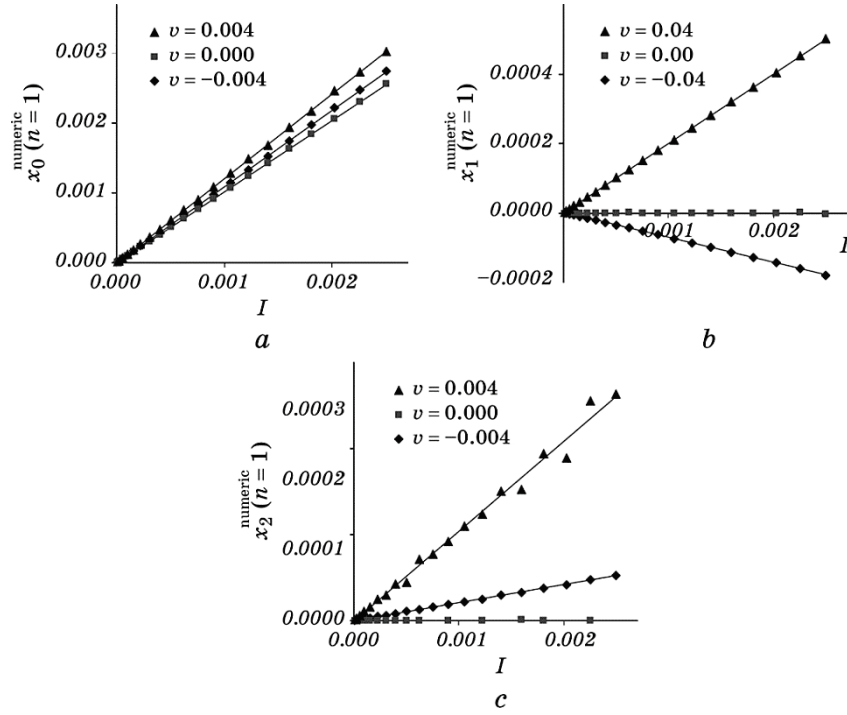


Fig. 3. Dependences of dispersion x_0 (a) and of correlations in the first and second co-ordination shells x_1 (b), x_2 (c) on $I \equiv \bar{C}^2(1-\bar{C})^2 A_n^2/\bar{\Gamma}$ for positive 0.04, negative -0.04 and zero mixing energy $v \equiv \bar{C}(1-\bar{C})V^{\text{mix}}/kT$. So far, all characteristics were calculated for single site ($n = 1$) by numeric SKMF modelling.

we choose a cluster containing 13 equivalent sites with the same ‘weight’ in calculating the average:

$$x_0^{\text{analyt}}(n = 13) = \left\langle \left(\frac{1}{13} \left[\delta C(i) + \sum_{in=1}^{12} \delta C(in) \right] \right)^2 \right\rangle = \frac{13x_0 + 48x_1 + 6x_2}{169}. \quad (36)$$

In Figure 5, we compare analytic approximation and numeric results of SKMF modelling for dispersion $x_0(n = 13)$ calculated for concentrations averaged over cluster of 1 + 12 sites as a function of reduced noise I , and for corresponding coefficient $k_0(n = 13) = x_0(n = 13)/I$ as a function of renormalized mixing energy v .

Now, let us compare SKMF simulation results with Monte Carlo simulation. Standard Metropolis algorithm for exchange mechanism was applied.

Concentration for every site at each step was calculated as an average over cluster containing $13 = 1 + 12$ sites (central atom plus first co-ordination shell of the f.c.c. lattice) and $19 = 1 + 12 + 6$ (central site

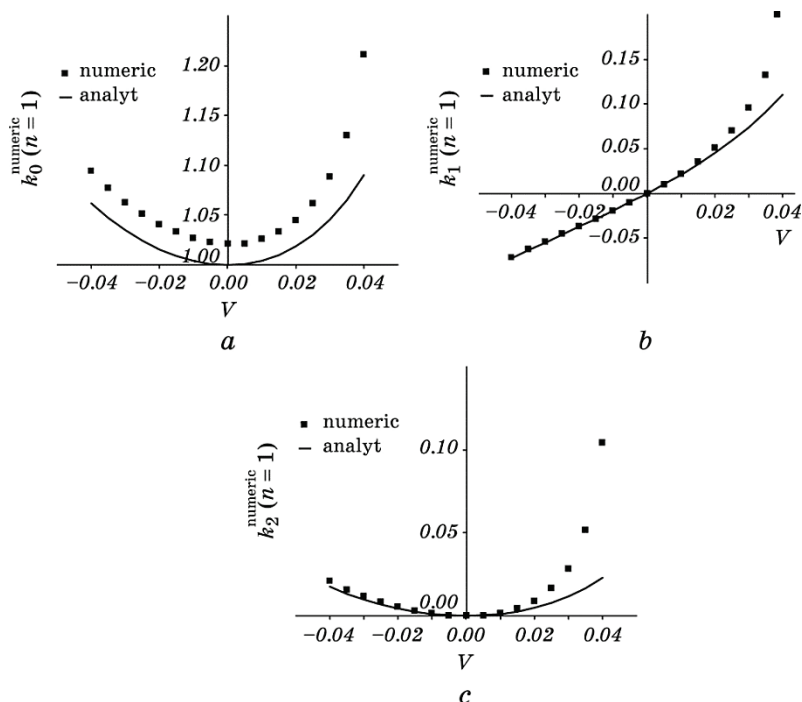


Fig. 4. Dependences of factors k_0 (a), k_1 (b), k_2 (c) on $v \equiv \bar{C}(1 - \bar{C})V^{\text{mix}}/kT$ for analytic SKMF (solid line) approximation and for numeric SKMF (dots) modelling. All calculations made for ‘cluster’ containing one site ($n = 1$).

plus two co-ordination shells). Monte Carlo results for these two choices of averaging clusters are shown in Fig. 6.

To compare the kinetic Monte Carlo (KMC) simulation results with SKMF, it could present some problem, since SKMF model contains noise amplitude A_n . Luckily, as mentioned above, at least for the case of ideal solution we managed to solve this problem [18]. Namely, we relate the noise amplitude to the number of runs of Monte Carlo simulation, in case when the concentration at each site at each moment is calculated as an average over the M^{runs} copies of the system. At that, dispersion of concentration (for an ideal solution) is equal to

$$I \equiv \bar{C}^2(1 - \bar{C})^2 \frac{A_n^2}{\Gamma} \text{ in SKMF approach and to } \frac{\bar{C}(1 - \bar{C})}{M^{\text{runs}}} \text{ in Monte Carlo}$$

approach with averaging over M^{runs} runs. To make these two expressions for dispersion in two approaches coinciding, we got interrelation

$$(17) \text{— } M^{\text{runs}} = \frac{\Gamma_0}{\bar{C}(1 - \bar{C})A_n^2}.$$

Now, we will try to derive the analogue of interrelation for the case

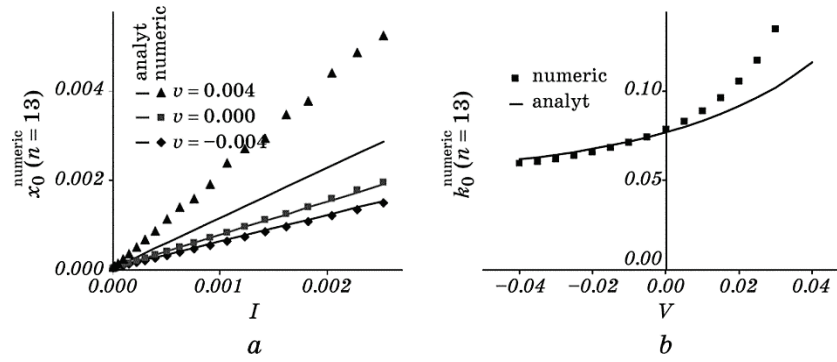


Fig. 5. Comparison between analytic approximation (solid lines) and numerical results of SKMF modelling (dots) for dispersion $x_0(n=13)$ calculated for concentrations averaged over cluster of 1 + 12 sites as a function of reduced noise $I \equiv \bar{C}^2(1-\bar{C})^2 A_n^2/\bar{\Gamma}$ (a) and for corresponding coefficient $k_0(n=13) \equiv x_0(n=13)/I$ as a function of renormalized mixing energy $v \equiv \bar{C}(1-\bar{C})V^{\text{mix}}/kT$ (b).

of regular solid solution.

As for Monte Carlo approach, we made the calculations with averaging over M^{runs} runs (simultaneous copies within canonical ensemble). We specially checked that all above-mentioned characteristics are inversely proportional to M^{runs} (see Fig. 7). For example, at $v \equiv \bar{C}(1-\bar{C})V^{\text{mix}}/kT = 0.02$,

$$x_0^{\text{KMC}}(n=13, v=0.02, M^{\text{runs}}) \propto \frac{0.0251}{M^{\text{runs}}}. \quad (37)$$

As for analytic approximation of the SKMF approach, we passed to

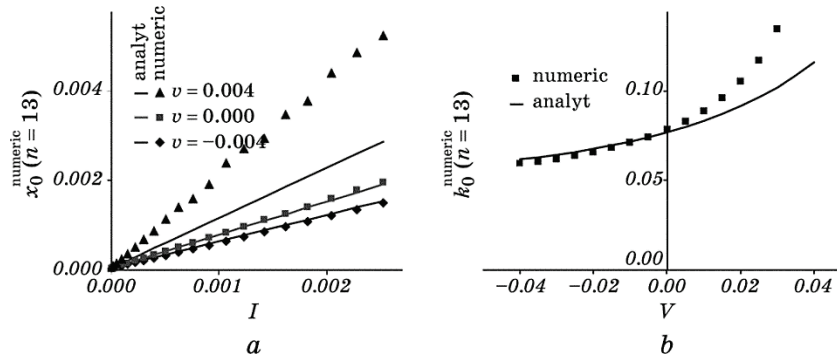


Fig. 6. Dependences of dispersion x_0^{KMC} and of correlations in the first and second co-ordination shells x_1^{KMC} , x_2^{KMC} versus $v \equiv \bar{C}(1-\bar{C})V^{\text{mix}}/kT$ calculated for concentrations averaged over clusters containing $n=13$ (filled dots) and $n=19$ (unfilled dots) by numeric SKMF modelling.

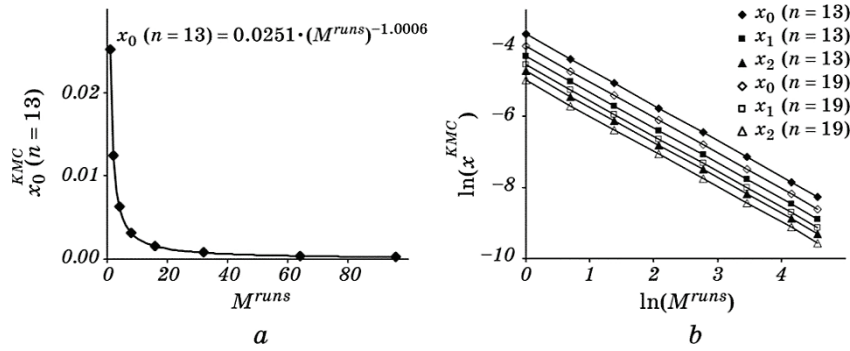


Fig. 7. Dispersion $x_0^{KMC}(n = 13)$ versus M^{runs} (a) and logarithm $x^{KMC}(n, M^{runs})$ for $n = 13$ (filled dots) and $n = 19$ (unfilled dots) versus $\ln M^{runs}$ (b) at $v \equiv \bar{C}(1 - \bar{C})V^{mix}/kT = 0.02$.

the clusters containing many sites, $n \gg 1$. Then, analytic approximation of the short-range order in SKMF model predicts that

$$\left\langle \left(\frac{1}{n} \sum_{i=1}^K \delta C(i) \right)^2 \right\rangle \approx \frac{nx_0 + nZ_1x_1 + nZ_2x_2}{n^2} = \frac{1}{n}(x_0 + Z_1x_1 + Z_2x_2), \quad (38)$$

where co-ordination numbers for the first and second shells of f.c.c. lattice are $Z_1 = 12, Z_2 = 6$.

Taking into account the analytical solution (35), one gets

$$\begin{aligned} \left\langle \left(\frac{1}{n} \sum_{i=1}^n \delta C(i) \right)^2 \right\rangle &\approx \frac{1}{n}(x_0 + 12x_1 + 6x_2) = \\ &= \frac{1}{n} \frac{(19 - 54v - 416v^2) + 12v(38 + 72v) + 1272v^2}{19 - 54v - 1204v^2 - 1136v^3} I. \end{aligned}$$

Further, here, we will limit ourselves by the linear approximation in terms of renormalized mixing energy. It gives

$$\left\langle \left(\frac{1}{n} \sum_{i=1}^n \delta C(i) \right)^2 \right\rangle \approx \frac{(1 + 24v)}{n} I = \frac{\bar{C}^2(1 - \bar{C})^2}{n} \frac{A_n^2}{\Gamma} \left(1 + 24\bar{C}(1 - \bar{C}) \frac{V^{mix}}{kT} \right). \quad (39)$$

On the other hand, according to thermodynamic theory of fluctuation, in regular solutions, the composition fluctuation in the cluster containing n sites, is equal to

$$\langle \delta C^2 \rangle_n = \frac{1}{n} \frac{kT}{\left(\frac{\partial^2 g}{\partial C^2} \right)} = \frac{1}{n} \frac{kT}{\bar{C}(1 - \bar{C}) - 2ZV^{mix}} = \frac{1}{n} \frac{\bar{C}(1 - \bar{C})}{1 - \frac{2ZV^{mix}}{kT} \bar{C}(1 - \bar{C})}.$$

If one averages the results over M^{runs} copies of the canonical ensemble, then the dispersion will be M^{runs} times less:

$$\langle \delta C^2 \rangle_{n, M^{\text{runs}}} = \frac{1}{M^{\text{runs}}} \frac{1}{n} \frac{\bar{C}(1 - \bar{C})}{1 - 2ZV^{\text{mix}}\bar{C}(1 - \bar{C})/(kT)}. \quad (40)$$

In the same approximation of small values of $\upsilon = \bar{C}(1 - \bar{C})V^{\text{mix}}/(kT)$, Eq. (40) transforms into

$$\langle \delta C^2 \rangle_{n, M^{\text{runs}}} \approx \frac{1}{M^{\text{runs}}} \frac{1}{n} \bar{C}(1 - \bar{C}) \left(1 + 24 \frac{V^{\text{mix}}}{kT} \bar{C}(1 - \bar{C}) \right). \quad (41)$$

Equalizing Eqs. (41) and (39) for regular solution within the cluster of N sites gives:

$$\begin{aligned} \frac{1}{n} \bar{C}^2(1 - \bar{C})^2 \frac{A_n^2}{\Gamma} \left(1 + 24 \bar{C}(1 - \bar{C}) \frac{V^{\text{mix}}}{kT} \right) &= \\ = \frac{1}{M^{\text{runs}}} \frac{1}{n} \bar{C}(1 - \bar{C}) \left(1 + 24 \frac{V^{\text{mix}}}{kT} \bar{C}(1 - \bar{C}) \right); & \end{aligned} \quad (42)$$

so, $M^{\text{runs}} = \frac{\Gamma_0}{\bar{C}(1 - \bar{C})A_n^2}$ that totally coincides with Eq. (8) for ideal so-

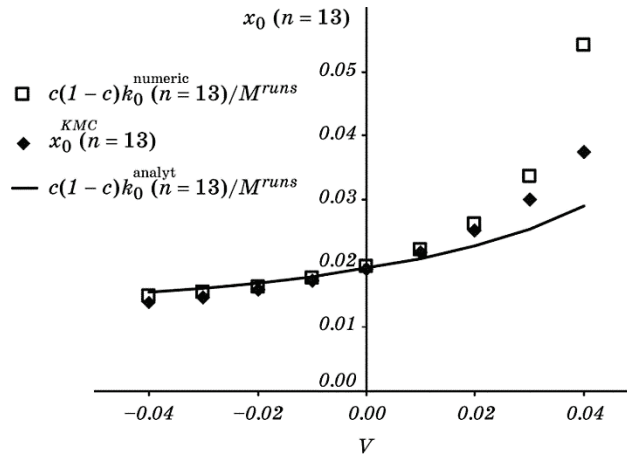


Fig. 8. Comparison of Monte Carlo dispersion under averaging over fixed number of MC runs for the clusters of size $n = 13$ (diamond) $x_0^{\text{KMC}}(n = 13)$ with analytic (solid lines) $\bar{C}(1 - \bar{C})k_0^{\text{analyt}}(n = 13)/M^{\text{runs}}$ and numeric (square) $\bar{C}(1 - \bar{C})k_0^{\text{numeric}}(n = 13)/M^{\text{runs}}$ SKMF results as a function of renormalized mixing energy $\upsilon \equiv \bar{C}(1 - \bar{C})V^{\text{mix}}/kT$. Data are given for $M^{\text{runs}} = 1$, but practically the same is valid for any M^{runs} .

lution and M^{runs} runs of Monte Carlo.

Thus, for the regular solution, at least for linear approximation over renormalized mixing energy, our interpretation of noise amplitude remains the same as for ideal solution—inverse squared noise amplitude is equivalent to averaging over finite number M^{runs} (Eq. (8)) of the copies of canonical ensemble. In other words, we predict that in regular solution

$$\langle \delta C^2 \rangle_{n, M^{\text{runs}}}^{\text{KMC}} \approx \frac{k_0^{\text{SKMF}}(n) \bar{C}(1 - \bar{C})}{M^{\text{runs}}}. \quad (43)$$

To check a validity of this analytic prediction, we compare $x_0^{\text{KMC}}(n = 13, M^{\text{runs}})$ and $\bar{C}(1 - \bar{C})k_0^{\text{SKMF}}(n = 13)/M^{\text{runs}}$. Numeric experiment confirms the above-described analytic theory, at least, for small positive and for any reasonable negative mixing energy (see Fig. 8).

6. CONCLUSIONS

1. G. Martin's approach to kinetic mean-field and its generalization to 3D contain mean-field thermodynamics of Khachaturyan [7] as a steady-state limit.

2. Martin's kinetic is nonlinear in respect to fluxes, and therefore should be more appropriate for simulation of atomic migration and phase transformations in the sharp concentration gradients.

3. 3D-generalization of Martin's KMF equations is proved (for the first time) to provide only negative or zero time derivative. Therefore, KMF cannot provide the first-order transformations with overcoming the nucleation barrier.

4. We introduce frequency noise instead of concentration noise as a basic reason of stochastic behaviour leading to concentration fluctuations and to overcoming the nucleation barriers.

5. Introduction of frequency noise leads to characteristics of fluctuations coinciding with Monte Carlo approach under the following interrelation between noise amplitude and the number of ensemble copies

$$(\text{MC runs}) \text{ over which the averaging is done: } M^{\text{runs}} = \frac{\Gamma_0}{\bar{C}(1 - \bar{C})A_n^2}.$$

6. Dependences of dispersion and correlations on the mixing energies are reasonably well described by analytic approximation (35), especially for negative and for small positive mixing energies.

7. SKMF is much faster than MC and gives analogous results for fluctuations. Therefore, it looks reasonable to use SKMF for modelling of nucleation behaviour, keeping in mind the interrelation (8). It might be a good tool to check and distinguish the alternative theories of nucleation [22–24], especially in the sharp concentration gradients [25, 26].

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REFERENCES

1. J. S. Rowlinson, *Journal of Statistical Physics*, **20**, No. 2: 197 (1979).
2. A. A. Vlasov, *Many-Particle Theory and Its Application to Plasma* (New York: Gordon and Breach: 1961); A. A. Vlasov, *Teoriya Mnogikh Chastits. 2nd Ed.* (Moscow: LIBROKOM: 2012).
3. A. A. Vlasov, *Non-Local Statistical Mechanics* (Moscow: Nauka: 1978) (in Russian).
4. W. Anderson, *Phys. Rev.*, **79**, No. 4: 705 (1950).
5. P. O. Löwdin, *Phys. Rev.*, **97**, No. 6: 1490 (1955).
6. R. H. Fowler and E. A. Guggenheim, *Proc. of the Royal Society of London. Series A, Mathematical and Physical Sciences* (1940), vol. **174**, p. 189.
7. A. Khachaturyan, *Theory of Structural Transformations in Solids* (New York: John Wiley & Sons: 1983).
8. G. Martin, *Phys. Rev. B*, **41**, No. 4: 2279 (1990).
9. N. V. Storozhuk, K. V. Sopiga, and A. M. Gusak, *Philos. Mag.*, **93**, No. 16: 1999 (2013).
10. Z. Erdélyi, I. A. Szaby, and D. L. Beke, *Phys. Rev. Lett.*, **89**, No. 16: 165901-1 (2002).
11. Z. Erdélyi, M. Sladeczek, L. M. Stadler, I. Zizak, G. A. Langer, M. Kis-Varga, D. L. Beke, and B. Sepiol, *Science*, **306**: 1913 (2004).
12. T. M. Radchenko, V. A. Tatarenko, and H. Zapolsky, *Solid State Phenomena*, **138**: 283 (2008).
13. S. M. Bokoch, V. A. Tatarenko, and I. V. Vernyhora, *Uspehi Fiziki Metallov*, **13**: 269 (2012).
14. T. M. Radchenko and V. A. Tatarenko, *Uspehi Fiziki Metallov*, **9**, No. 1: 1 (2008) (in Ukrainian).
15. M. A. Ivanov, M. M. Churakov, and V. I. Glushchenko, *Physics of Metals and Metallography*, **88**, No. 2: 12 (1999) (in Russian).
16. Y. Wang, L. Chen, and A. Khachaturyan, *Solid-to-Solid Phase Transformations (PTM'94, 1994)*, p. 245.
17. Y. Wang, D. Banerjee, C. C. Su, and A. G. Khachaturyan, *Acta Mater.*, **46**, No. 9: 2983 (1998).
18. Z. Erdélyi, M. Pasichnyy, V. Bezpachuk, J. J. Tomán, B. Gajdics, and A. M. Gusak, *Computer Physics Communications*, **204**: 31 (2016).
19. V. M. Bezpachuk, M. O. Pasichnyy, and A. M. Gusak, *Metallofiz. Noveishie Tekhnol.*, **38**, No. 9: 1135 (2016) (in Ukrainian).
20. V. M. Bezpachuk, A. M. Gusak, and R. Kozubski, *Uspehi Fiziki Metallov*, **18**,

- No. 3: 205 (2017).
21. V. M. Bezpachuk, D. S. Ruseiko, and A. M. Gusak, *Metallofiz. Noveishie Tekhnol.*, **39**, No. 7: 865 (2017) (in Ukrainian).
 22. A. S. Abyzov and J. W. Schmelzer, *J. Non-Crystalline Solids*, **384**: 8 (2014).
 23. J. W. Schmelzer, A. S. Abyzov, and J. Möller, *J. Chem. Phys.*, **121**, No. 14: 6900 (2004).
 24. V. Bezpachuk, R. Kozubski, M. Pasichnyy, and A. Gusak, *Defect and Diffusion Forum*, **383**: 59 (2018).
 25. A. M. Gusak, F. Hodaj, and G. Schmitz, *Philos. Mag. Lett.*, **91**, No. 9: 610 (2011).
 26. A. M. Gusak, T. V. Zaporozhets, Y. O. Lyashenko, S. V. Kornienko, M. O. Pasichnyy, and A. S. Shirinyan, *Diffusion-Controlled Solid State Reactions: in Alloys, Thin-Films, and Nanosystems* (New York: John Wiley & Sons: 2010).