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A Colloidal Self-Organization of Impurities in a Liquid by Density Fluctuations

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Abstract

The two-parametric functional for weakly interacting fluctuations of liquid density and composition is studied within the theory based on Landau potential for these fluctuations in the kind of ensemble of phonons and compound clusters. Using the standard diagram technique, the task for weak-interacting phonons and clusters is reduced to solving the equations of proper-energetic functions of quasi-particle interaction by Neumann iterations of Feynman diagrams in "bootstrapping" of Fourier images (propagators) for correlation of the composition of liquid and its topological structure. It is shown that composition fluctuations as clusters are induced by phonons when impurity atoms being initially outside the dense part of liquid (introduction solution) become inherent constituents of the dense part (addition solution). By renormalizing parameters of the model, we have transformed weakly interacting fluctuations to free "dressed" phonons and clusters whose autocorrelation functions are characterized by various behaviors in small and large scales in comparison with the atomic spacing. In the first case, density fluctuations of liquid do not feel impurities. In the intermediate scale, the liquid matrix is inhomogeneous in the form of colloids, which is not observed at the large scales. Dynamics of such liquid is characterized by diffusion modes of solvent and oscillations of impurities.

Keywords: liquid, density and composition fluctuations, Feynman diagram, bootstrap, phonon, cluster, renormalization

1. Introduction

It is known that any liquid is characterized by a random chaotic packing of atoms. They are easily rearranged by little thermal fluctuations in contrast to a crystal whose topological structure is stable under any thermal fluctuations below the melting point [1].

At the same time, the topological structure of instantaneous dense part of any condensed matter (liquid, crystal, and amorphous) is represented as configurations of closely packed

particles in Delaunay simplexes (dense triangular pyramids with particles in their vertices) that are connected by faces into ramified short-living tetrahedral clusters of density fluctuations [2, 3]. Using the topological criterion [3] in *molecular-dynamic* (MD) simulation of deterministic nonlinear system of many particles, one can exactly select these simplexes by defining a maximal length of their edges over the maximal number of obtained simplex clusters in the MD cell. The statistics of these clusters is gotten for any condensed matter [4] as their *two-dimensional* (2D) discrete distribution on *cardinality* (number of simplexes in the cluster) and on *connectivity* (number of their vertexes belonging also to other clusters).

For any crystal, these clusters consist of one and only one simplex, that is, their cardinality is equal to 1, but their connectivity is distributed normally in the interval of 7–23 (15 on average). In contrast to the crystal heated, the cluster cardinality of amorphous dense part achieves 10, and the connectivity of such clusters is more than 3 but less than 20 (11 on average). It means that the solid state (crystal and amorphous) is characterized by percolation of tetrahedral dense-part clusters of structural fluctuations.

The topological features of a liquid: (1) the cardinality of liquid dense-part clusters reaches 37, that is, almost four times more than the solid ones, and (2) there are almost 5% of dense-part clusters with zero connectivity sufficient for breaking off the percolation of solid dense-part clusters, providing a fluidity of liquid and forming long chains of liquid dense part. These clusters as dense configurations of particles are dynamically changed but statistically preserve the multifractal structure [3].

The existence in liquid metal of such chains with the fractal gyration radius of ~100 nm is confirmed by the experiments [5] on small-angle-scattering of neutrons. These data are obtained on the contrast of liquid-dense and nondense parts, which amount to 10–15% from the contrast of liquid boundary in vacuum.

Thus, a liquid is characterized by existence of dense-part clusters with zero connectivity in contrast to crystal and amorphous solid which have not such clusters. Moreover, the cardinality of dense-part clusters in any crystal is equal to 1, while amorphous solid occupies the intermediate position between crystal and liquid on the discrete 2D distribution of dense-part clusters [4]. At the same time, the tetrahedral clusters of dense-part open for impurity in principle two topologically differing positions in liquid and amorphous solid: (1) outside the dense-part simplexes and (2) in their clusters as compound constituents [6, 7]. The induced by density-fluctuations polymorphic transition of impurity between these positions is the subject of given theoretical consideration.

Revealing a mechanism of such self-organization of impurities in liquids will allow to have found an approach to their structural modification over chosen attributes by impurities.

2. The method of Green function

The method of Green function used in physics of phase transitions allows so to have formulated and disposed questions of theory that one can obtain topologically exact answers without

knowing an explicit kind of the state equation [8]. This method bases on Landau potential [9] which usually is represented by a functional of generalized variables expressing parameters of the local order. Then, structural and phase changes are described by calculus variations of these parameters [8]. They mean by topological and compound (chemical) order. The first is understood as ordering of atoms regardless of the particles nature. The second is characterized by spatial correlation of different atoms and is responsible for the microstratification and clustering of the particles.

Besides the *compound parameter of order* (CPO), the two-parametrical fluctuation model of liquid alloy includes the *topological parameter of order* (TPO) which can induce by density fluctuations the clustering of impurity atoms far off from the phase change [10].

We consider the double system, $A_{1-x}B_x$, where $x = \overline{n_2/(n_1 + n_2)}$ is the average concentration of impurity component, B; n_i is the density of i-particles number (i = 1, 2) for representing Landau potential, ΔF, of this system by the functional of two parameters (n_1, n_2) [10]:

$$\Delta F = \int_V f\left(\Delta_i, \ \vec{\nabla}\Delta_i, n, x\right)d^3r + \Delta F_0(n, x) \tag{1}$$

Here, d^3r is the differential of 3D space, f is the density of Helmholtz free energy, $\Delta_i = n_i - \overline{n}_i$ is the density fluctuation of i-particles number, $\vec{\nabla}$ is the gradient, n is the average density of particles, $\Delta F_0 = \Delta F(\Delta_i = 0)$ is the free energy of homogeneous system, and V is its volume.

The $\Delta_i(\vec{r})$ fluctuations are averaged in the neighborhood of point, $\vec{r}$, in a small volume which however contains sufficiently great number of particles as well as a distance, where $\Delta_i(\vec{r})$ function changes is appreciably more than the interatomic spacing, r_0 [8]. In this case, the other degrees of freedom (electronic, vibration et al) require a time far less than the configuration field, $\Delta_i(\vec{r})$, for reaching equilibrium. Therefore, one can apply the adiabatic approximation for describing the fluctuations fields of CPO and TPO in double system.

Then, one can limit Taylor expansion of $f(\Delta_i)$ as a function of small parameter, Δ_i, by the members of third-order infinitesimal: Δ_1^3, $\Delta_1^2\Delta_2$, and $\Delta_1\Delta_2^2$, which correct the second and third approximation of perturbation theory for F_0. One can also neglect the members of fourth-order infinitesimal: $\{\Delta_i\}^4$, because the coefficients of Δ_i^2 in Taylor expansion of $f(\Delta_i)$ are positive, and the Δ_i proportional members of Taylor series are equal to zero in (1) owing to the constant number of particles in the system.

Further for the isotropic liquid, the first derivatives, $\vec{\nabla} \Delta_i$, can come into Taylor expansion of $f(\Delta_i, \vec{\nabla} \Delta_i)$ only in the scalar combination $(\vec{\nabla} \Delta_i \cdot \vec{\nabla} \Delta_k)$, and the second ones can be as products: *const* $\vec{\nabla}^2 \Delta_i$ and $\Delta_i\vec{\nabla}^2 \Delta_k$. The first of them gives the insignificant addition into the integral (1.1), which for the second is transformed into integral of $(\vec{\nabla} \Delta_i \cdot \vec{\nabla} \Delta_k)$ [11].

Thus, without limiting a task generality for liquid, one can present f as [10]

$$\circ\circ f = \frac{1}{2}\left(\frac{\partial\mu_1}{\partial n_1}\Delta_1^2 + 2\frac{\partial\mu_1}{\partial n_2}\Delta_1\Delta_2 + \frac{\partial\mu_2}{\partial n_2}\Delta_2^2\right) + \frac{1}{6}\left(\frac{\partial^2\mu_1}{\partial n_1^2}\Delta_1^3 + 3\frac{\partial^2\mu_1}{\partial n_1\partial n_2}\Delta_1^2\Delta_2 + 3\frac{\partial^2\mu_1}{\partial n_2^2}\Delta_1\Delta_2^2\right)$$
$$+ \frac{K_{11}}{2n}(\vec{\nabla}\Delta_1)^2 + \frac{K_{12}}{n}(\vec{\nabla}\Delta_1\cdot\vec{\nabla}\Delta_2) + \frac{K_{22}}{2n}(\vec{\nabla}\Delta_2)^2 \qquad (2)$$

Here, μ_i $(n, x, T) \equiv (\partial f/\partial n_i)_{TV}$ is the chemical potential of i-component, T is Kelvin temperature, $K_{ik} = 2|U_{ik}(r_0)|r_0^2 z$, $U_{ik}(r_0)$ is the pair-interaction potential of nearest particles of kind: i and k, and z is the average coordination number. Considering the homogeneous liquid of double system by the model of ideal solution, one can present the chemical potential, μ_i $(i = 1, 2)$, in the form

$$\begin{aligned}\mu_1 &= \mu_{10}(T,n) + T\ln(1-x)\\ \mu_2 &= \mu_{20}(T,n) + T\ln x\end{aligned} \qquad (3)$$

which, obviously, satisfies to Gibbs-Duhem relation

$$(1-x)\frac{\partial\mu_1}{\partial x} + x\frac{\partial\mu_2}{\partial x} = 0 \qquad (4)$$

Then, we will obtain [7]

$$\begin{aligned}\frac{\partial\mu_{10}}{\partial n} &\equiv \frac{\partial\mu_{20}}{\partial n} = \frac{1}{n}\left(\frac{dP}{dn}\right)_T\\[4pt]\frac{\partial\mu_1}{\partial n_1} &= \frac{T}{n}\left(\beta + \frac{x}{1-x}\right)\\[4pt]\frac{\partial\mu_1}{\partial n_2} &= \frac{T}{n}(\beta - 1)\\[4pt]\frac{\partial\mu_2}{\partial n_2} &= \frac{T}{n}\left(\beta + \frac{1-x}{x}\right)\\[4pt]\frac{\partial^2\mu_1}{\partial n_1^2} &= \frac{T}{n^2}\left(\beta' - \frac{x(2-x)}{(1-x)^2}\right)\\[4pt]\frac{\partial^2\mu_1}{\partial n_2^2} &= \frac{\partial^2\mu_1}{\partial n_1\partial n_2} = \frac{T}{n^2}(\beta' + 1)\end{aligned} \qquad (5)$$

at the condition that the first bracket in (2) is the quadratic form positively defined. Here, $\beta = (n/T)(\partial\mu_{10}/\partial n)$, $\beta' = (n^2/T)(\partial^2\mu_{10}/\partial n^2)$, and P is the static pressure.

For simple liquids, $\beta \gg 1$ and $(\partial P/\partial n)_T$ weakly depends on the number density, n, of particles. Therefore, one can accept $\beta' \sim -\beta$ [7].

Transforming the quadratic forms in (2) to diagonal ones, one can present Landau potential as a sum of free-field Hamiltonians and the weak-interaction potential. Then, we will have the almost ideal Bose gas of two components [8].

Using relations (3)–(5), one can do (2) by diagonal square form by means of linear transformation

$$\left.\begin{aligned}\Delta_1 &= n(a_{11}\varphi + a_{12}\chi)\\\Delta_2 &= n(a_{21}\varphi + a_{22}\chi)\end{aligned}\right|$$

(6)

Substituting (6) into (2), we will find parameters

$$\left.\begin{aligned}a_{11} &= 1\\a_{22} &= x\\a_{12} &= -x\alpha_1[1 - x(\alpha_1 - \alpha_2/\alpha_1)\gamma]\\a_{21} &= x\big[1 + x(1 - \alpha_1\gamma - (1 - \alpha_2)\beta)\big]\gamma\end{aligned}\right|$$

(7)

for $x < 1/\gamma$ and zero coefficients at $(\varphi \cdot \chi)$ and $(\vec{\nabla}\varphi \cdot \vec{\nabla}\chi)$ [10]. Here, $\alpha_1 = K_{12}/K_{11} \sim 1$, $\alpha_2 = K_{22}/K_{11} \sim 1$, and $\gamma = 1 - (1 - \alpha_1)\beta$ are the alternating-sign factor. As a result, Eq. (2) to x^2 becomes

$$f/\beta nT = \frac{(1+x\gamma)^2}{2}\varphi^2 + \frac{(1+x\alpha_1\gamma)^2}{2}\frac{K_{11}}{\beta T}\left(\vec{\nabla}\varphi\right)^2 + \frac{x\big[1+x(1-\alpha_1)^2\beta\big]}{2\beta}\chi^2 + \frac{x^2(\alpha_2-\alpha_1^2)}{2}\frac{K_{11}}{\beta T}\left(\vec{\nabla}\chi\right)^2$$

$$-\frac{(1+x\gamma)^3}{6}\varphi^3 - \frac{x(1-\alpha_1)+x^2(1-\alpha_2)\gamma}{2}\varphi^2\chi - \frac{x^2(1-\alpha_1)^2}{2}\varphi\chi^2$$

(8)

Labeling $\quad a_0 = 1 + x\gamma, \quad b_0 = 1 + x\alpha_1\gamma, \quad c = \big[1 + x(1-\alpha_1)^2\beta\big]/\beta, \quad \lambda = 1 - \alpha_1 + x(1-\alpha_2)\gamma, \quad$ and $\vec{\rho} = \vec{r}\sqrt{\beta T/K_{11}}$, we will obtain

$$\Delta F(\varphi, \chi) = nK_{11}\sqrt{K_{11}/\beta T} \int_{V\left(\frac{\beta T}{K_{11}}\right)^{3/2}} d^3\rho \left[\frac{a_0^2}{2}\varphi^2 + \frac{b_0^2}{2}\left(\vec{\nabla}\varphi\right)^2 - \frac{a_0^3}{6}\varphi^3\right.$$

$$\left. + x\left(\frac{c}{2}\chi^2 + x\frac{\alpha_2 - \alpha_1^2}{2}\left(\vec{\nabla}\chi\right)^2 - \frac{\lambda}{2}\varphi^2\chi - x\frac{(1-\alpha_1)^2}{2}\varphi\chi^2\right)\right]$$

(9)

What sense have the parameters of order, φ and χ? We obtain $\varphi \approx (\Delta_1 + \Delta_2)/n$ and $\chi \approx (\Delta_2/x - \Delta_1)/n$ out of (6) when $\alpha_i \approx 1$ and $x < 1$. Then, φ is the reduced TPO of liquid, and χ expresses the reduced CPO for clustering the initially homogeneous liquid alloy to microregions of different composition, that is, the parameter, χ, describes the compound fluctuation field as opposed to the parameter, φ, which describes the topological fluctuation field.

Each of these fields can be presented as a set of oscillations of averaged corresponding collective modes that are Fourier images of topological and compound fluctuations of the liquid alloy. They are defined by Green functions, $G(\varphi)$ и $G(\chi)$ [12].

In the integral (9), Hamiltonian (2) defines the change of free energy of weak-interacting long-wave phonons and clusters in the double alloy. In the adiabatic approximation, one can take into account only the given ordering (φ, χ) without caring of other variables of the system. Then, we will define the equilibrium fields, $\varphi(\vec{\rho})$ and $\chi(\vec{\rho})$, in the minimum of $\Delta F(\varphi, \chi)$ [8]. This condition looks like Euler variation equation which for the entered parameters of order gives equations [10].

$$\left. \begin{aligned} -b_0^2 \vec{\nabla}^2 \varphi + a_0^2 \varphi - a_0^3 \varphi^2/2 &= x\left[\lambda \varphi \chi + x(1 - \alpha_1)^2 \chi^2/2\right] \\ x(\alpha_1^2 - \alpha_2) \vec{\nabla}^2 \chi + c\chi - \lambda \varphi^2/2 &= x(1 - \alpha_1)^2 \varphi \chi \end{aligned} \right| \tag{10}$$

Using the standard diagram techniques [11] for averaged collective variables, one can reduce the task for weak-interacting phonons and clusters to solve the equations of proper-energetic functions of interacting quasi-particles [10]. For this, we use an averaged correlator $\langle \phi(\vec{\rho}) \cdot \phi(\vec{\rho}\,') \rangle$ which is Green function at $\vec{\rho}\,' = 0$ [8]:

$$G_\varphi\left(\vec{\rho}\right) = \left\langle \varphi\left(\vec{\rho}\right) \cdot \varphi(0) \right\rangle \tag{11}$$

In such case, one can present the effects of alloy fluctuation nonhomogeneity as the integrals containing correlation functions, $G_\varphi(\vec{\rho})$ and $G_\chi(\vec{\rho})$ or their spectral densities

$$\left. \begin{aligned} \left\langle \varphi\left(\vec{k}\right) \cdot \varphi\left(\vec{k}\,'\right) \right\rangle &= G_{\vec{k}}(\varphi)\delta\left(\vec{k} - \vec{k}\,'\right) \\ \left\langle \chi\left(\vec{k}\right) \cdot \chi\left(\vec{k}\,'\right) \right\rangle &= G_{\vec{k}}(\chi)\delta\left(\vec{k} - \vec{k}\,'\right) \end{aligned} \right| \tag{12}$$

obtained by Fourier conversion:

$$\left. \begin{aligned} \varphi\left(\vec{\rho}\right) &= \int e^{i\vec{k}\vec{\rho}} \varphi\left(\vec{k}\right) d^3k/(2\pi)^3 \\ \chi\left(\vec{\rho}\right) &= \int e^{i\vec{k}\vec{\rho}} \chi\left(\vec{k}\right) d^3k/(2\pi)^3 \end{aligned} \right| \tag{13}$$

where $\varphi(-\vec{k}) = \varphi^*(\vec{k})$ and $\chi(-\vec{k}) = \chi^*(\vec{k})$. According to Wiener-Khinchin theorem, $G_i(\vec{\rho})$ and $G_{\vec{k}}(i)$ ($i = \varphi, \chi$) are equivalent functions because they are connected by Fourier conversion

$$G_i\left(\vec{\rho}\right) = \int G_{\vec{k}}(i) e^{i\vec{k}\vec{\rho}} d^3k/(2\pi)^3 \tag{14}$$

Thanking δ-normalization of $\varphi(\vec{k})$ and $\chi(\vec{k})$, one can change the differential equations (10) to the algebraic ones for Fourier-images of Green functions: $G_{\vec{k}}\left(\varphi\right) = \langle|\varphi(\vec{k})|^2\rangle$. We will calculate them in approximation of the perturbation theory by means of iterations and Neumann series of Feynman diagrams [13].

3. The formalism of Feynman diagrams

For "bare" phonon propagator $G^0_{\vec{k}}(\varphi)$, determined by the first equation of system (10) without the member on the right ($x = 0$), we have [10]

$$\left(a_0^2 + b_0^2 k^2\right) G^0_{\vec{k}}(\varphi) = \left(a_0^3/2\right) F_{\vec{k}}\left[G^0_\varphi\left(\vec{\rho}\right)\right] \tag{15}$$

where $F_{\vec{k}}[G^0_\varphi(\vec{\rho})]$ is the iteration procedure presented by the chain

$$\tag{16}$$

which is converted into the recurrence form [12]

$$\tag{17}$$

and has the analytic solution

$$G^0_{\vec{k}}(\varphi) = \left(a_0^2 + b_0^2 k^2 - \Sigma_0\left(\vec{k}\right)\right)^{-1} > 0 \tag{18}$$

under the condition: $|\Sigma_0(\vec{k})|/(a_0^2 + b_0^2 k^2) < 1$. Here, $\Sigma_0(\vec{k})$ is the proper-energetic function expressed by the equation [10]

$$\Sigma_0\left(\vec{k}\right) = \frac{a_0^6}{8} \int \frac{d^3 p}{(2\pi)^3} g_{\vec{p}}(\varphi) g_{\vec{k}-\vec{p}}(\varphi) \tag{19}$$

and $g^{\vec{p}}(\varphi) = \left(a_0^2 + b_0^2 p^2\right)^{-1}$ as the solution of (15) with unit on the right. From the second equation of system (10) without the member on the right, we obtain the equation for "bare" cluster propagator, $G^0_{\vec{k}}(\chi)$ [10]:

$$\left[c + x\left(\alpha_2 - \alpha_1^2\right) k^2\right] G^0_{\vec{k}}(\chi) = \frac{\lambda}{2} F_{\vec{k}}\left[G^0_\varphi\left(\vec{\rho}\right)\right] \tag{20}$$

The solution of this equation converted into the recurrence form has the graphic form

$$\tag{21}$$

and the analytic one under the conditions, $|\Pi_0(\vec{k})|/[c + x(\alpha_2 - \alpha_1^2) k^2] < 1$ and $|\vec{k}| < 1$:

$$G^0_{\vec{k}}(\chi) = \left[c + x(\alpha_2 - \alpha_1^2)k^2 - \Pi_0\left(\vec{k}\right)\right]^{-1} > 0 \tag{22}$$

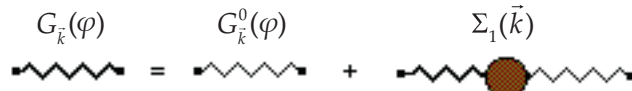Here, $\Pi_0(\vec{k})$ is the phonon-proper-energetic function determined by the equation [10]

$$\Pi_0\left(\vec{k}\right) = \frac{\lambda^2}{8}\int\frac{d^3p}{(2\pi)^3}G^0_{\vec{p}}(\varphi)G^0_{\vec{k}-\vec{p}}(\varphi) \tag{23}$$

The solution (22) of the Eq. (20) defines the propagator of induced compound field entering in Hamiltonian (9), that is, the clusters are generated *forcedly by phonons* unlike their free field with the propagator, $G^0_{\vec{k}}(\varphi)$, whose fluctuations are formed spontaneously.

The natural development of this idea is the "bootstrap" hypothesis [14] which consists in the following. The fluctuations of CPO, χ, arising at the interaction of phonons deform partially the density-fluctuations field, φ, "dressing" the propagator, $G^0_{\vec{k}}(\varphi)$, by the proper-energetic function

$$\Sigma_1\left(\vec{k}\right) = x^2\lambda^2\int\frac{d^3p}{(2\pi)^3}G^0_{\vec{p}}(\varphi)G^0_{\vec{k}-\vec{p}}(\chi) + \frac{x^4(1-\alpha_1)^4}{8}\int\frac{d^3p}{(2\pi)^3}G^0_{\vec{p}}(\chi)G^0_{\vec{k}-\vec{p}}(\chi) \tag{24}$$

defined by the members of the first equation of system (10) on the right. The graphic and analytic solution of this equation is [10]

$$G_{\vec{k}}(\varphi) \qquad G^0_{\vec{k}}(\varphi) \qquad \Sigma_1(\vec{k})$$

$$\tag{25}$$

and

$$G_{\vec{k}}(\varphi) = \left[1/G^0_{\vec{k}}(\varphi) - \Sigma_1\left(\vec{k}\right)\right]^{-1} > 0 \tag{26}$$

This formula makes sense under the obvious condition $|\Sigma_1(\vec{k})|G^0_{\vec{k}}(\varphi) < 1$.

Now, one can analytically express the first (topological) bootstrapping of deformed CPO field by replacing function, $G^0_{\vec{k}}(\varphi)$, in (23) by "dressed" phonon propagator, $G_{\vec{k}}(\varphi)$:

$$\Pi_1\left(\vec{k}\right) = \frac{\lambda^2}{8}\int\frac{d^3p}{(2\pi)^3}G_{\vec{p}}(\varphi)G_{\vec{k}-\vec{p}}(\varphi) \tag{27}$$

and its substitution in the formula (22) instead of $\Pi_0(\vec{k})$. It is possible under the condition: $|\Pi_1(\vec{k})|/[c + x(\alpha_2 - \alpha_1^2)k^2] < 1$. Taking into account the member in the second equation of system (10) on the right gives for propagator, $G^0_{\vec{k}}(\chi)$, the proper-energetic function in the final form

$$\Pi_2\left(\vec{k}\right) = x^2(1-\alpha_1)^4 \int \frac{d^3p}{(2\pi)^3} G^0_{\vec{p}}(\chi) G_{\vec{k}-\vec{p}}(\varphi) \tag{28}$$

This is expressed in graphic and analytic forms by

$$G_{\bar{k}}(\chi) \qquad G^0_{\bar{k}}(\chi) \qquad \Pi_2(\vec{k})$$

$$\tag{29}$$

and

$$G_{\vec{k}}(\chi) = \left[1/G^0_{\vec{k}}(\chi) - \Pi_2\left(\vec{k}\right)\right]^{-1} > 0 \tag{30}$$

under the condition $|\Pi_2(\vec{k})|G^0_{\bar{k}}(\chi) < 1$.

Thus, one can find the fluctuation fields of the liquid density and compound in the form of autocorrelation functions of impurity concentration, x, and the parameters $(\alpha_1, \alpha_2, \beta)$ by means of the graphic, algebraic, and integral Eqs. (17)–(19) and (21)–(30).

4. The coherent propagators of phonons and clusters

One can find the solutions of the Eq. (10) in the form of phonons and clusters that are averaged on ensemble of the casual states defined by Hamiltonian (9). The representation of own functions of this Hamiltonian by flat waves with $k = |\vec{k}| < 1$ is a good approximation for the impurity content far from the saturation of liquid alloy.

For dilute solutions ($x \ll 1$), one can restrict the proper-energetic functions (19), (24), (27), (28) by the second degree of k and present the propagators (18), (22), (26), (30) in the form [10].

$$\left.\begin{aligned}
G^0_{\bar{k}}(\varphi) &= \left(a^0 + b^0 k^2\right)^{-1} \\
G_{\vec{k}}(\varphi) &= \left(a + bk^2\right)^{-1} \\
G^0_{\bar{k}}(\chi) &= \left(u^0 + v^0 k^2\right)^{-1} \\
G_{\vec{k}}(\chi) &= \left(u + vk^2\right)^{-1}
\end{aligned}\right| \tag{31}$$

At such restriction, it is easy to find all the proper energetic functions. For this, we will substitute (31) into (24), (27), and (28) and transform these multiple integrals to the kind

$$I_{lm}(k) = \int_0^\infty (\sigma_l + \tau_l p^2)^{-1} \left(\sigma_m + \tau_m|\vec{k}-\vec{p}|^2\right)^{-1} d^3p/(2\pi)^3 = arctg\left(\frac{\Lambda_l \Lambda_m k}{\Lambda_l + \Lambda_m}\right)/4\pi\tau_l\tau_m k \tag{32}$$

where $\Lambda_l = \sqrt{\tau_l/\sigma_l}$. Under the condition of $k < 1/\Lambda_l + 1/\Lambda_m$, one can transform (32) into Taylor expansion on k up to the second member [10]:

$$I_{lm}(k) \cong \frac{\Lambda_l \Lambda_m}{4\pi \tau_l \tau_m (\Lambda_l + \Lambda_m)} \left[1 - \left(\frac{\Lambda_l \Lambda_m}{\Lambda_l + \Lambda_m} \right)^2 \frac{k^2}{3} \right] \tag{33}$$

Substituting (33) into (19), (24), (27), and (28), we will obtain

$$\Sigma_0(k) = \frac{a_0^5}{64\pi b_0^3} \left(1 - \frac{b_0^2 k^2}{12 a_0^2} \right) \tag{34}$$

$$\Sigma_1(k) = \frac{x^2}{4\pi v^0} \left[\frac{\lambda^2}{b^0 \left(\sqrt{\frac{a^0}{b^0}} + \sqrt{\frac{u^0}{v^0}} \right)} + \frac{x^2 (1 - \alpha_1)^2}{16\sqrt{u^0 v^0}} \right] - \frac{x^2 k^2}{12\pi v^0} \left[\frac{\lambda^2}{b^0 \left(\sqrt{\frac{a^0}{b^0}} + \sqrt{\frac{u^0}{v^0}} \right)^3} + \frac{x^2 v^0 (1 - \alpha_1)^2}{64\sqrt{(u^0)^3 v^0}} \right] \tag{35}$$

$$\Pi_1(k) = \frac{\lambda^2}{64\pi \sqrt{ab^3}} \left(1 - \frac{bk^2}{12a} \right) \tag{36}$$

$$\Pi_2(k) = \frac{x^2 (1 - \alpha_1)^2}{4\pi b v^0 \left(\sqrt{\frac{a}{b}} + \sqrt{\frac{u^0}{v^0}} \right)} \left(1 - \frac{k^2}{3 \left(\sqrt{\frac{a}{b}} + \sqrt{\frac{u^0}{v^0}} \right)^2} \right) \tag{37}$$

Now using formulas (18), (31), and (34), we will obtain

$$\left. \begin{aligned} a^0 &= a_0^2 \left(1 - \frac{(a_0/b_0)^3}{64\pi} \right) \\ b^0 &= b_0^2 \left(1 + \frac{(a_0/b_0)^3}{768\pi} \right) \end{aligned} \right| \tag{38}$$

The parameters (u^0, v^0) can be obtained by means of (22), (31), (36), and the comment to (27)

$$\left. \begin{aligned} u^0 &= c - \frac{\lambda^2}{64\pi \sqrt{ab^3}} \\ v^0 &= x(\alpha_2 - \alpha_1^2) + \frac{\lambda^2}{768\pi \sqrt{a^3 b}} \end{aligned} \right| \tag{39}$$

At last, the mutual solution of (26) and (30) gives the parameters of "dressed" phonon and cluster propagators, $G_{\vec{k}}(\varphi)$ and $G_{\vec{k}}(\chi)$:

$$\left. \begin{aligned} a &= a^0 - \frac{x^2}{4\pi v^0} \left(\frac{\lambda^2/b^0}{\left(\sqrt{\frac{a^0}{b^0}} + \sqrt{\frac{u^0}{v^0}} \right)} + \frac{x^2 (1 - \alpha_1)^2}{16\sqrt{u^0 v^0}} \right) \\ b &= b^0 + \frac{x^2}{12\pi v^0} \left(\frac{\lambda^2/b^0}{\left(\sqrt{\frac{a^0}{b^0}} + \sqrt{\frac{u^0}{v^0}} \right)^3} + \frac{x^2 (1 - \alpha_1)^2}{64\sqrt{(u^0)^3/v^0}} \right) \end{aligned} \right| \tag{40}$$

$$u = u^0 - \frac{x^2(1-\alpha_1)^2}{4\pi b v^0 \left(\sqrt{\frac{a}{b}} + \sqrt{\frac{u^0}{v^0}}\right)}$$

$$v = v^0 + \frac{x^2(1-\alpha_1)^2}{12\pi b v^0 \left(\sqrt{\frac{a}{b}} + \sqrt{\frac{u^0}{v^0}}\right)^3} \qquad (41)$$

It means that the renormalization procedure of the model (9) parameters carries out isomorphic transformation of weak-interacting fields of TPO and CPO into the ensemble of free "dressed" phonons and clusters with Hamiltonian

$$\Delta F(\varphi, \chi) = nK_{11}\sqrt{K_{11}/\beta T} \int_{V\left(\frac{\beta T}{K_{11}}\right)^{3/2}} d^3\rho \left[\frac{a}{2}\varphi^2 + \frac{b}{2}\left(\vec{\nabla}\varphi\right)^2 + x\left(\frac{u}{2}\chi^2 + \frac{v}{2}\left(\vec{\nabla}\chi\right)^2\right)\right] \qquad (42)$$

under the condition $a > 0$ and $u > 0$. In this representation, the correlation functions for TPO and CPO functions look like:

$$G_\varphi(\rho) = \left(\frac{\beta T}{K_{11}}\right)^{3/2} \frac{\exp\left(-\frac{\rho}{\Lambda_\varphi}\right)}{4\pi\beta\rho nb}$$

$$G_\chi(\rho) = \left(\frac{\beta T}{K_{11}}\right)^{3/2} \frac{\exp\left(-\frac{\rho}{\Lambda_\chi}\right)}{4\pi\beta\rho nv} \qquad (43)$$

where $\Lambda_\varphi = \sqrt{b/a}$ and $\Lambda_\chi = \sqrt{v/u}$. It is easy to see that $G_i(\rho) \propto \rho^{-1}$ at $\rho < \Lambda_i$, and this function exponentially works for zero, when $\rho > \Lambda_i$.

It is clear that the Eq. (40) is obtained under the condition: $k < 1/\Lambda_\varphi^0 = \sqrt{a^0/b^0}$, that is equivalent to $|\vec{\rho}| > \Lambda_\varphi^0$, that is, the relation, $G_\varphi\left(\vec{\rho}\right) \sim |\vec{\rho}|^{-1}$, is valid for the interval, $\Lambda_\varphi^0 < |\vec{\rho}| < \Lambda_\varphi$.

Under the condition: $|\vec{\rho}| < \Lambda_\varphi^0$, it is necessary to replace the correlator, $G_{\vec{k}}(\varphi)$, by the "bare" propagator, $G_{\vec{k}}^0(\varphi)$, with the parameters (39).

Thus, the TPO fluctuations in the liquid alloy are characterized by various behaviors in small and large scales in comparison with Λ_φ^0. In the case of $|\vec{\rho}| < \Lambda_\varphi^0$, density fluctuations of liquid do not feel impurities. When $\Lambda_\varphi^0 < |\vec{\rho}| < \Lambda_\varphi$, the liquid matrix is inhomogeneous in the form of impurity colloids, and for $|\vec{\rho}| > \Lambda_\varphi$, such heterogeneity is not observed at all [10].

5. Stratification of impurity by density fluctuations of liquid alloy

The structural modification of the liquid alloy at varying the system parameters $(x, \alpha_1, \alpha_2, \beta)$ is characterized by changing the correlation radii Λ_ϕ and Λ_χ of Green functions (43). They

define the characteristic ranges of observed TPO and CPO fluctuations [8]. Therefore, the concentration dependence, $\Lambda_i(x)$, is interested to consider for different $(x, \alpha_1, \alpha_2, \beta)$ of the model (9). At the same time, one should remember that this model is applied only in Taylor expansion (2) of $f(\Delta_i, \vec{\nabla} \Delta_i)$ under the conditions [11]: $x < 1/4|1 + (\alpha_i - 1)\beta|$ and $\langle |i|^2 \rangle_{\Lambda_i} << 1$ that are reduced to: $\sqrt{b^3/a}, \sqrt{v^3/u} >> (e - 2)\sqrt{\beta(T/2z|J_{11}|)^3}/e(1 + z)$ [10].

The solutions of Eqs. (38)–(41) obtained under these conditions are illustrated in **Figures 1–4** by the graphs of functions, $\Lambda_\phi(x)$ and $\Lambda_\chi(x)$, in logarithmic coordinates for the ranges: $0.095 < \alpha_1^2 < \alpha_2 \leq 1.4$ and $10 \leq \beta \leq 150$. The last one characterizes liquid metals where the alloy components have a tendency for demixing at $\alpha_1^2 < \alpha_2$ in contrast to clustering at $\alpha_1^2 > \alpha_2$. The structural features of such alloy are discussed below.

One can see that the correlation radius of phonons (Λ_ϕ) is practically not changed with growing the impurity concentration as opposed to the correlation radius of impurity demixing (Λ_χ) which increases: the higher values of α_i at $\alpha_1^2 < \alpha_2$, the more is. At the same time, increasing β partially decreases this effect (compare **Figures 3** and **4**) [10].
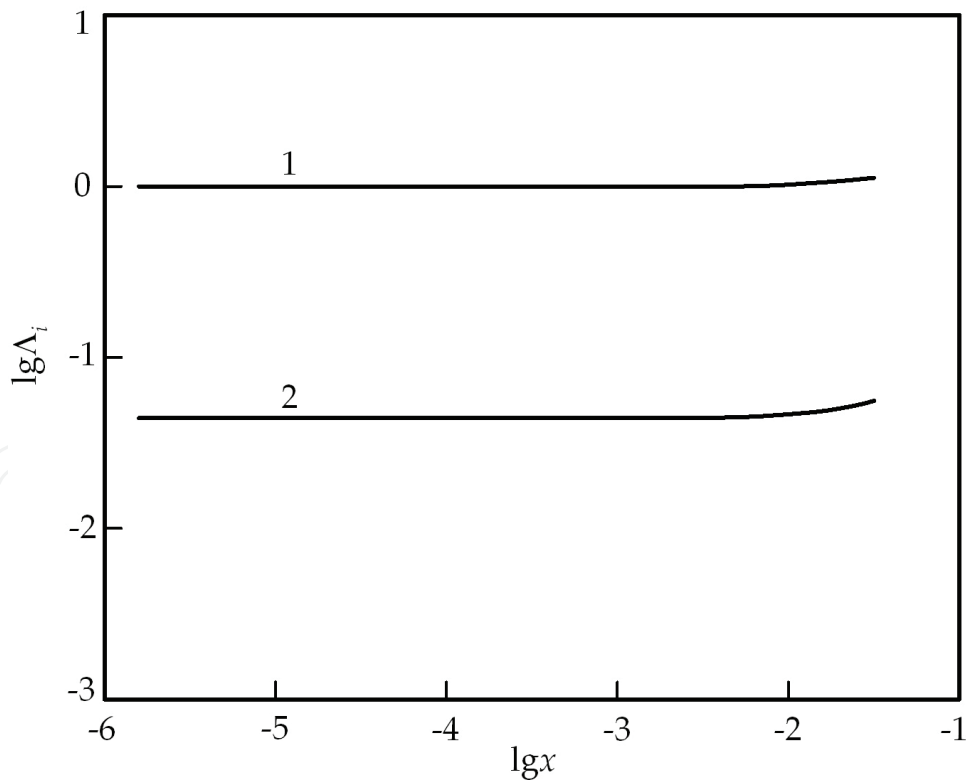

Figure 1. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.31$, $\alpha_2 = 0.1$, and $\beta = 10$.
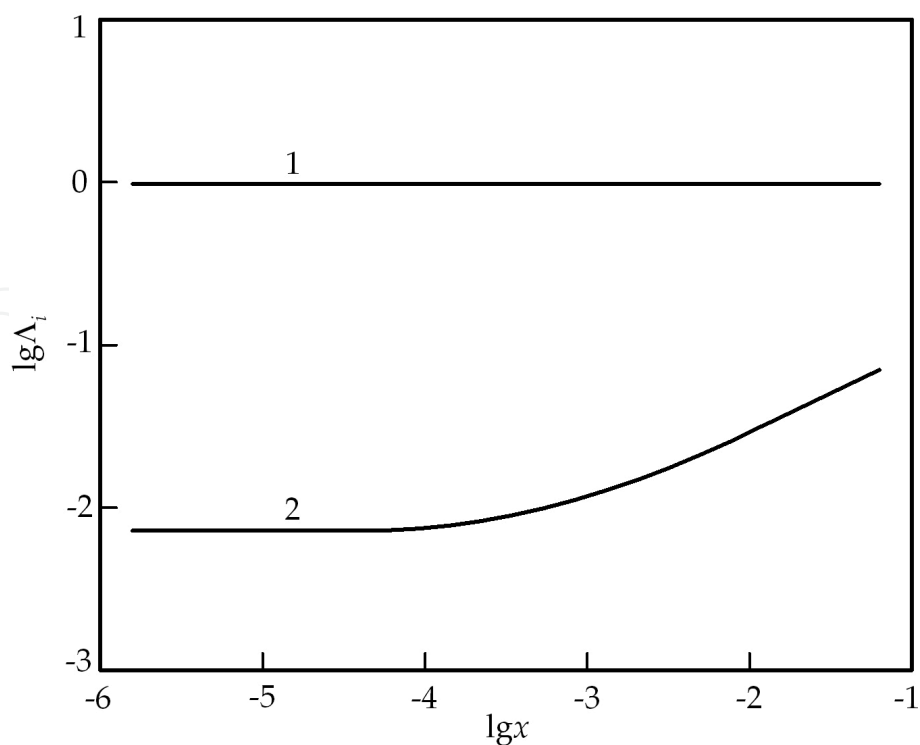
Figure 2. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.89$, $\alpha_2 = 0.8$, and $\beta = 10$.
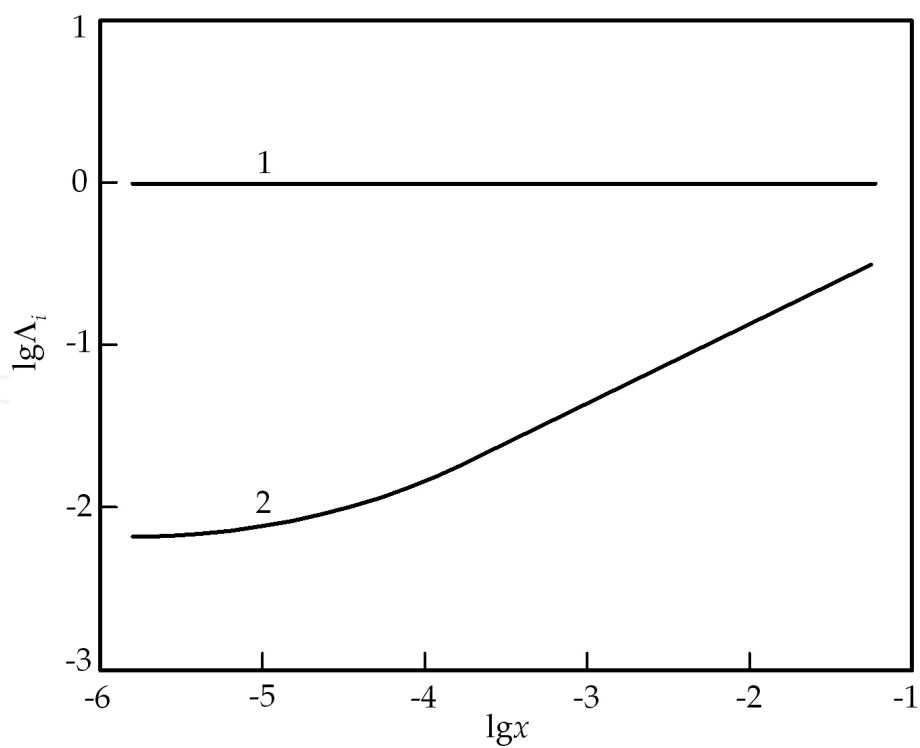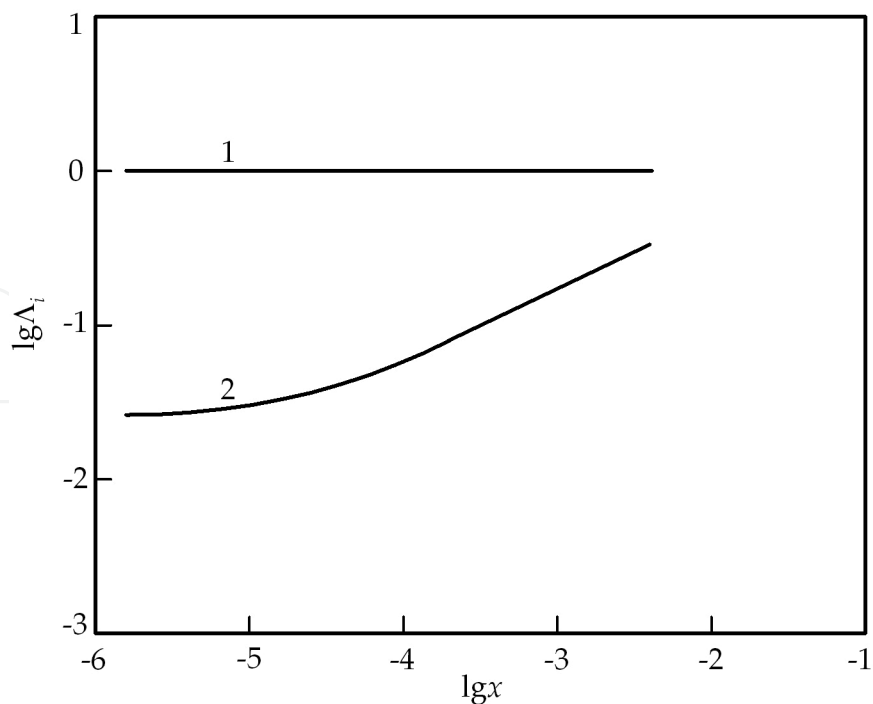

Figure 3. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 1.1$, $\alpha_2 = 1.4$, and $\beta = 10$.

Figure 4. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 1.1$, $\alpha_2 = 1.4$, and $\beta = 150$.

6. Impurity clustering induced by alloy density fluctuations

At $\alpha_1^2 > \alpha_2$, the graphs of lg $\Lambda_\phi(x)$ and lg $\Lambda_\chi(x)$ are shown in **Figures 5–8** for $\alpha_1 = 0.6$, $\alpha_2 = 0.3$, and for four values of β in the range of 10–150.
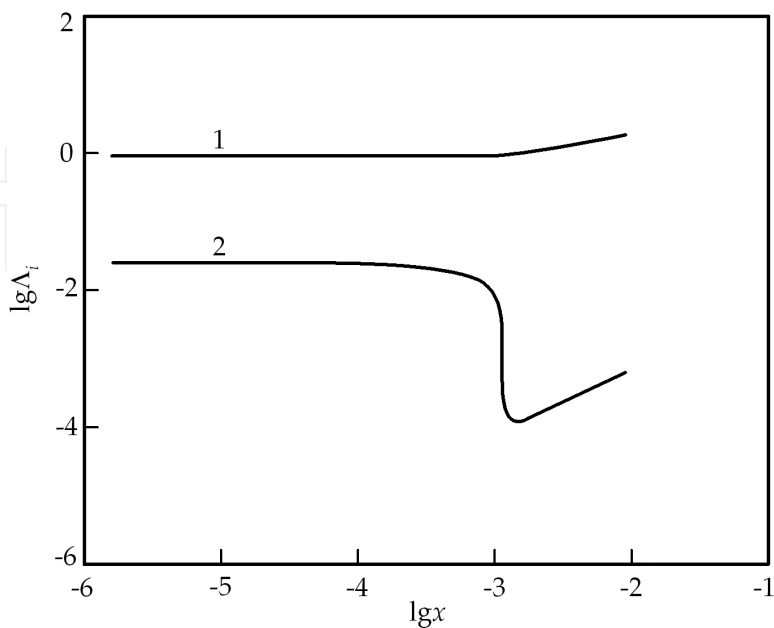

Figure 5. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.6$, $\alpha_2 = 0.3$, and $\beta = 10$.
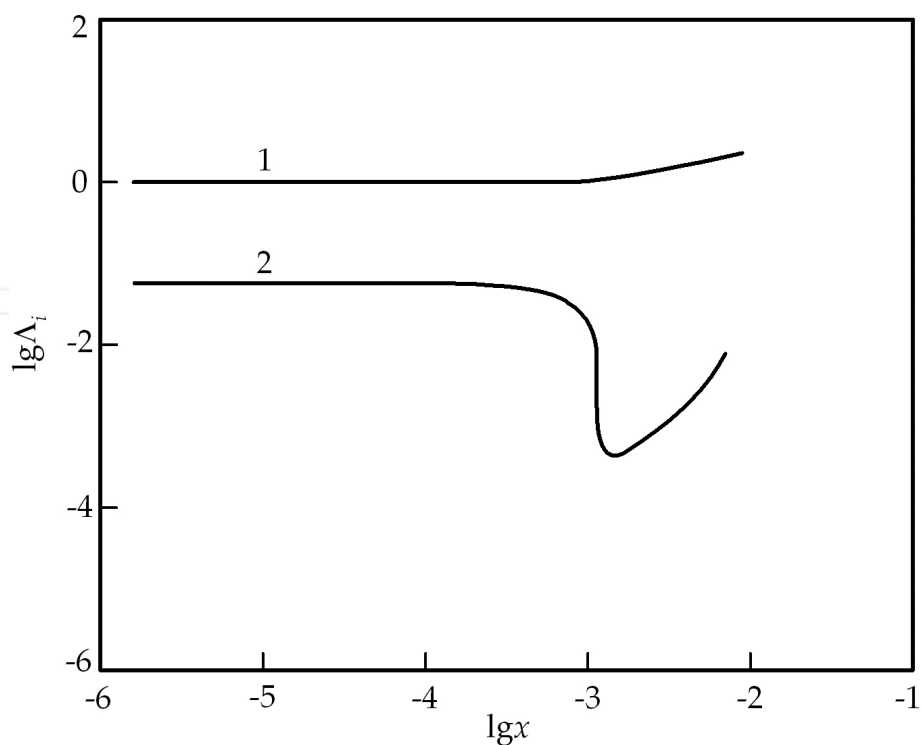
Figure 6. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.6$, $\alpha_2 = 0.3$, and $\beta = 50$.
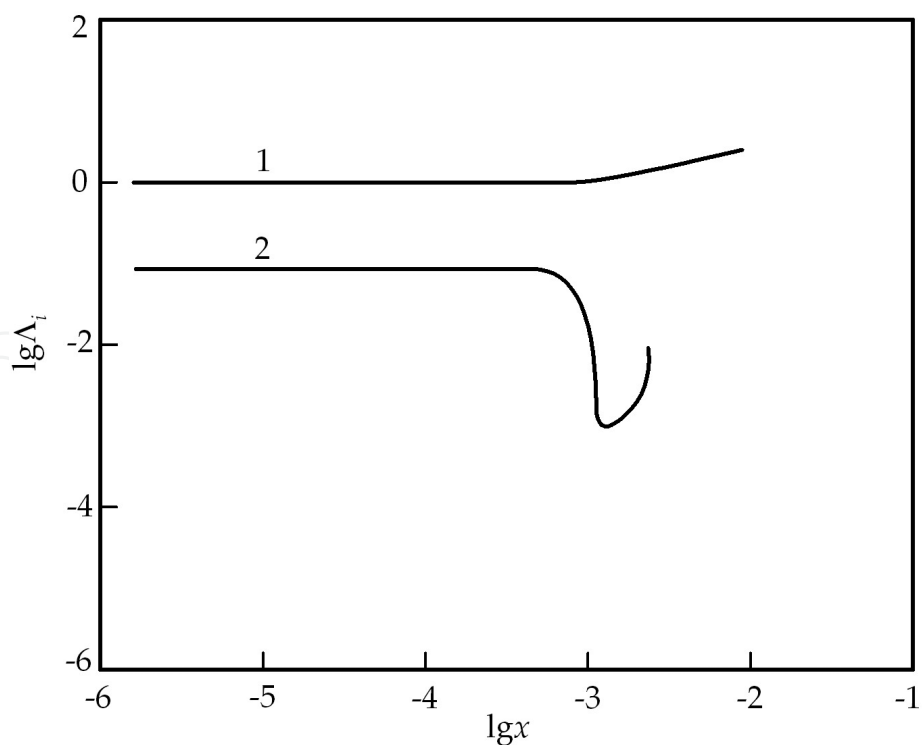

Figure 7. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.6$, $\alpha_2 = 0.3$, and $\beta = 100$.

Figure 8. The graphs of lg $\Lambda_\varphi(1)$ and lg $\Lambda_\chi(2)$ as functions of the impurity concentration, lg$x$, at $\alpha_1 = 0.6$, $\alpha_2 = 0.3$, and $\beta = 150$.
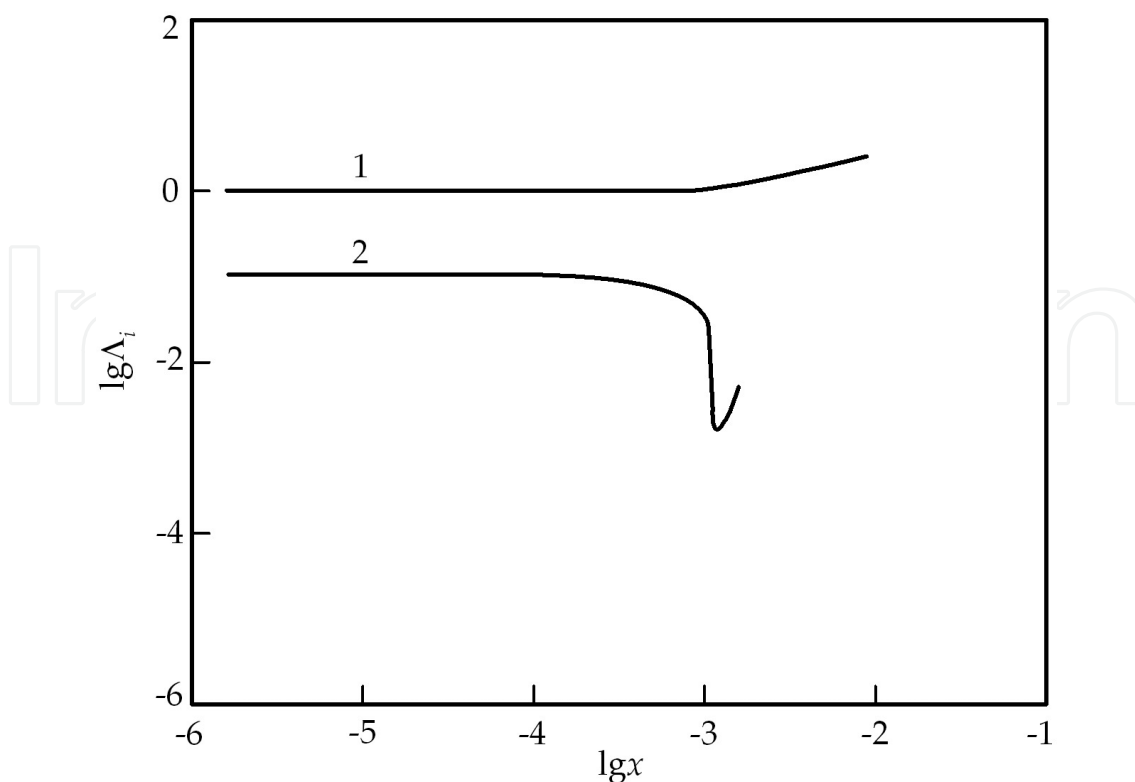
It turned out that Λ_χ decreases sharply at some critical point, x_c. This indicates the decay of CPO fluctuations of double alloy into compound clusters on the background of long-wave density fluctuations of liquid. One can see that the range of impurity concentration of clusters existence decreases with growing the rigidity, β, of condensed matter.

At the same time, x_c does not practically change because this point is defined by the value of $\alpha_1^2 - \alpha_2$ which is constant. The following sharp increase of the CPO correlation radius (see **Figures 7** and **8**) is interpreted as aggregation of clusters [10]. The observed growing of TPO correlation radius, $\Lambda_\phi(x)$, can be caused by impurity precipitations that do more lengthy the density fluctuations.

7. Conclusions

According to the two-parametric model represented above, density fluctuations of liquid induce mono-ordering impurity in micro-regions at $\alpha_1^2 < \alpha_2$ (see **Figures 2–4**) and its clustering with basic component at $\alpha_1^2 > \alpha_2$ (see **Figures 5–8**). Such self-organization of liquid alloy has no thermodynamic singularities of the first-order phase transition because it has continuous character without the potential jump and concerns only to change the impurity state in liquid alloy, that is, it is interpreted as a component phase transition of the first order [15].

The scale of this transition increases with growing the concentration and bond force of impurity particles and it decreases with growing the rigidity of condensed matter inclined to stratification of components $(\alpha_1^2 < \alpha_2)$. For opposite components inclined to clustering $(\alpha_1^2 > \alpha_2)$, the composition fluctuations of double alloy decay to local states in the form of quasi-molecular fluctuations.

By renormalizing parameters of this model, we have transformed weakly interacting fluctuations to free "dressed" phonons and clusters whose autocorrelation functions are characterized by various behaviors in small and large scales in comparison with the atomic spacing. In the first case, density fluctuations of liquid do not feel impurities. In the intermediate scale, the liquid matrix is inhomogeneous in the form of colloids, which is not observed at the large scales. Dynamics of such liquid is characterized by diffusion modes of solvent and oscillations of impurities.

At the same time, any liquid can be composed from two structures. The first of them represents finite and ramified clusters from almost tetrahedrons having common faces in pairs. The second is locally less dense which includes micropores as elements of free volume of liquid.

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