



## A size quantization of atomic space in metals under high temperature

Filippov ES

National Research Technological University “MISA”, Russia

DOI: <https://doi.org/10.33545/26647575.2019.v1.i1a.14>

### Abstract

It is considered proofs of a size quantization (linear and bulk) in processes of phase transformations from polymorphic to a boiling at high temperature.

It is shown that atomic space between atomic and ionic radii is divided into the ready  $K\lambda$  cells (where  $K$  - nearest neighbors,  $\lambda = h/mc$ ), that is - the atomic coordination space is discrete for the placing  $K\lambda$ . It is shown also, that cell-  $K\lambda$  is the result of exchange interaction photoppon + electron  $\rightarrow \lambda$  between emitter and absorber of photons. The model  $\pm K\lambda$  may be employed both the nontransition metals and transition and also its has been employed into the analysis of the formed of the amorphous structure by the freezing of the liquid metals. It is shown also particularity of the model  $K\lambda$  for noble metals and the formation of the hexagonal structure and also phase transformations: ordinary crystallization and bcc - fcc and also bcc – hcp. It is considered processes the melting, the boiling and the formed of clusters.

**Keywords:** ionic and atomic radii, electronic density, fluctuation density, volume of melting and boiling, cluster heat transfer, amorphous structure, photon

### Introduction

It is considered new nontraditional approach into analysis of processes at high temperature from the recrystallization for solid state to the boiling for liquid state. The reason - it is not possible to use the band theory. Because nontraditional approach was chosen: We go around this theoretical difficulty by considering the probability distribution of the electron density in the coordinate space. It is allowed to determine reasons of the formation different structures (bcc, fcc and hcp) at the crystallization and the polymorphic transformations and processes of a melting and a boiling and also it has been employed into the analysis heat transfer <sup>[1, 2]</sup>. Two theoretical problems are analyzed by using a review of research works <sup>[1, 2]</sup>: a structure of liquid metals and principle of a size quantization both continual approximation (factor 0,65) and solid spheres (factor  $4/3\pi$ ), connecting with average-statistical number shorts neighbors (6,5) in chaotic packing by using simplest ratio:  $4/3\pi/6,5 = 0,65$ . These geometrical factors have been correlated with the wave space  $\lambda_F/2\pi$  and atomic-ionic space, which is divided into the ready  $K\lambda$  cells (where  $\lambda = h/mc$ ,  $K$  –nearest neighbors)[1,2]. Thus it is the essence of given article: the combination of all relationships ratios by means of analysis of all phases transformations from polymorphic (fcc-bcc, bcc-hcp) to a boiling.

### Initial data.

A pseudo – potential approximation of the electron – ion interaction has been by the initial premise for model - theoretical studies. This is allowed to research the electron density fluctuations in the coordinate space between radii atom ( $r_a$ ) and ionic ( $r_i$ ).

We took advantage of the results presented in [1,2], where the calculation (in limits of the model free electrons) parameter  $R$  (the half-with on the probability distribution over the coordinate of interatomic distance), corresponding to the maximum of the electron density fluctuation, was revealed based on the assumption on the electron density fluctuation.

The parameter  $R$  is determined in interatomic space from combinations and shapes caused by the uncertainty principle and the best use of the interatomic space, that is predetermined by values  $r_a$ ,  $r_i$  and  $\lambda_F/2\pi$  [1,2]. This conclusively may write as  $R = f(\lambda_F/2\pi)$ :

$$2\pi r = 2\pi r_i + n\lambda_F/2\pi \quad (1)$$

Where at  $n=1$   $r = R_c$  and  $n=2$   $r = R$  ( $r_i$  – is crystal – chemical radius).

Here values  $R$  and  $R_c$  are determined by the standing wave arising during the formation of the self- closing orbital  $2\pi r = n\lambda$  (a circle of radius  $r$  comprises an integer number of wave lengths).

Main assumption is a follows: the value  $R$  is a coordinate per  $r$  of maximum probability at the electron density distribution between  $r_a$  and  $R_c$  in pseudo- potential approximation, that is:

$$R = [(r_a + R_c)/2]. \quad (2)$$

Here we have on the one hand geometrical values ( $R, R_c$ ) and with other - the function of wave length ( $\lambda_F$ ). Besides we have empirical simplest correlations:

$$R_c = r_i + K\lambda/Z \pm n \lambda, \quad (3)$$

Where  $n = 0, 1, 2$ . and where  $K$  – nearest neighbors,  $\lambda = h/mc$ ,  $Z$  is number of valence electrons.

This relation is associated with the electron – photon interaction in the coordinate atomic space in the interaction mode photon + electron  $\rightarrow \lambda$ . If values  $R, R_c$  and  $K\lambda$  are considered as main dimensional features, then (according to [1,2]) a chain of interactions can be obtained for coordinate space:

A volume of a sphere in pseudo- potential field:

$$4/3\pi (r_a^3 - r_i^3) / K = R^3 \quad (4)$$

(and also  $4/3\pi R^3 = 4/3\pi r_i^3 + r_s^3 Z$ , where  $r_s = 1,92 \lambda_F / 2\pi$ ); A surface of sphere in pseudo- potential field:

$$4\pi R^2(K\lambda) = (r_a^3 - r_i^3) Z^{1/3}. \quad (5)$$

Here we must note adiabatic approximation: atomic sphere can have not the ideal form but the atomic volume is remained constant.

Thus coordinate space between ions can be represented by values  $r_a, r_i, R, R_c$  and  $\lambda, \lambda_F, Z$  by using all variants: as an orbital, as spheres, as a surface. Besides we have grounded assumption - the discrete of atomic space per  $K\lambda$ , although in empirical form. Hence there are grounds to the analysis of the high temperature processes, a name – to heat transfer.

## Modeling of the heat transfer

### 1. Linear relations.

High temperature is associated with contact of atomic spheres in vibration mode: its maximal number is  $K$ - neighbors; minimal distance of an interaction is  $\lambda$  (smaller then  $\lambda$  can't be). The heat energy is associated with electron + photon interaction in atomic space has an excess ( $+K\lambda$ ) or a deficit ( $-K\lambda$ ) in the mode: photon + electron  $\rightarrow \lambda$  between emitter and absorber photons.

Since the parameter  $R$  has been determined by bond energy (according to [1] we have:  $U(r) = e^2/4\pi\epsilon_0 (Z/KR)$ ), then the value  $R$  should to establish the equilibrium between an emitter and an absorber in vibration mode ( $R - K\lambda$ )  $\leftrightarrow$  ( $R + K\lambda$ ):

$$R + K\lambda = r_a - K\lambda/Z; \quad (6)$$

$$R - K\lambda = R_c + K\lambda/Z; \quad (7)$$

$$R_c - r_i = K\lambda/Z. \quad (8)$$

Were the value  $1/Z$  is the restriction of the absorber of photons.

Here the accurate to (1,2)  $\lambda$  has been for 14 of metals (alkali and alkaline earth, Pb, Al, In, Cd and Zn).

These data allow us to conclude that the value of  $K\lambda$  corresponds to the maximum level of probability for the exchange interaction of conduction electrons of  $K$  atoms according to the scheme: electron + photon  $\rightarrow \lambda$ . Combining Eqs.(2-8) and using the relation for determined  $R$ , we get:

$$R - R_c = K\lambda(1/Z + 1); R - r_i = K\lambda(2/Z + 1); r_a - R_c = 2K\lambda(1/Z + 1); r_a - R = K\lambda(1 + 1/Z);$$

$$R_c - r_i = K\lambda/Z.$$

These data are confirmed by line correlation between  $r_a, r_i$  and  $K\lambda$ :

$$r_a = r_i + K\lambda (1/Z + 1) + K\lambda (1/Z + 1) + K\lambda/Z \pm n\lambda, \quad (9)$$

where  $n = 0, 1, 2$  for 14 metals (alkali, alkali-earth, Pb, Al, In, Cd and Zn).

Thus, it can be assumed that the atomic space between  $r_a$  and  $r_i$  is divided into the ready  $K\lambda$  cells. Its number must be discrete for  $K\lambda$ . Therefore, the heat energy transfer (the change in the intensity of the atomic-vibrational mode) in this space is represented in the model of two fluxes exchanging by fluctuations of the electron density in the  $\pm K\lambda$  mode.

Here  $R$  is determined by the bond energy  $U(r) = (e^2 / 4\pi\epsilon_0) (Z/K)1/R$ .

### Liquid State.

A liquid state fits precisely into model of heat transfer of solid state.

Here two values are determined the model of the heat transfer:  $\sigma/2$  – semi-diameter of hard sphere (Percus-Yevic) and  $K = K_{SP}$ ,

where  $K_{SP} = 6,5 = 1/12(1+2+\dots+12)$  (the average statistical number of nearest neighbors [1,2]). According to [1,2] we have:

$$\sigma/2 - r_i = r_a - R_c$$

and according to Eqs. (2-8):  $r_a - R_c = 2 K\lambda(1/Z + 1)$ . Hence we have:  $\sigma/2 - r_i = 2 K\lambda(1/Z + 1)$  and for the value  $\sigma/2$  we are obtained:

$$\sigma/2 = K \lambda + R, \tag{10}$$

where clusters have  $K = 12,8$  for not overheated liquid nearly  $T_{melt}$ ;

$$\sigma/2 = \lambda K_{12} + R_{sp}, \tag{11}$$

where  $R_{SP}^3 / 0,65 = (0,65r_a^3 - r_i^3)$  and  $\lambda K_{12} = 12\lambda$  is maximal number ready cells ( $K\lambda$ ) for placing theirs in atomic continuum (not neighboring) superheating liquid at  $T_{boil}$  with an accuracy less than 3% for 14 research metals.

Here, factor  $0,65 \approx 0,643 = 4/3\pi / 6,5$  is the transition from atomic spheres  $4/3\pi r_a^3$  to atomic continuum  $0,65 r_a^3$ , where  $0,65r_a^3 = (\sigma/2)^3$ . Consequently, factor 0,65 is a constant similar to  $4/3\pi$  and  $6,5 = 1/12(1+2+\dots+12) = K_{sp}$  statistical average number of nearest neighbors.

Hence, it follows:  $\sigma/2 = R + \lambda K$ ;

$$\sigma/2 = R_{sp} + \lambda K_{12},$$

These data allow to make conclusion about adequate approach to modeling of heat transfer via the exchange – fluctuation interaction between atomic spheres per  $K\lambda$  ready cells.

### Bulk

The volume of the liquid metal at the melting temperature can be calculated in two variants: for absolutely chaotic packing (or SP-statistical packing):

$$V_{melt} = 4/3\pi r_a^3 / 0,65 \tag{12}$$

and with allowance for maximum possible fluctuations (clusters) of the atomic density  $V_o$  (at 0K) and  $V_{boil}$  (at  $T_{boil}$ )

$$V_{melt} = 0,65 V_o + 0,35 V_{boil}. \tag{13}$$

Here all three reference points ( $V_o$ ,  $V_{melt}$  and  $V_{boil}$ ) lie on one straight line with  $V_{melt}$  in the center. From here it follows that there are grounds to accept the value 0,65/0,35 for the ratio cluster / SP.

According to experimental data [1,2] we have  $V_{boil} / V_o = 1,23 \pm 0,03$  and  $V_o = V_a + 0,35V_a$  and  $V_{boil} = 1,23V_o = 1,23(V_a + 0,35 V_a) = 1,67 V_a \approx 1,70 V_a$ , where  $0,35 V_a$  is a void volume at  $K = 12$  and other part  $0,35V_a$  is the result of the thermal wide. Thus atomic system have two volume of a void. Hence it follows:  $V_{boil} = 1,70V_a$ .

As a whole, the model cluster / SP is represented by 0,65  $\approx$  0,643 part of clusters and 0,35 part SP can be write as: 0,643 (0,74)  $\approx$  0,47, where 0,74 is the factor of maximal packing into a cluster and 0,643 =  $4/3\pi / 6,5$  is the probability of random cluster packing. Here the calculated value 0,47 coincides with  $\eta = 0,44 - 0,47$  obtained by numerical solution of the Percus – Yevic equation [1,2].

### Electronic subsystem.

The approximation of the liquid metal structure by atomic density fluctuations allow us to consider the balance of interatomic voids in the model cluster / SP in according to parts 0,65 / 0,35. For cluster 0,65(0,35) at  $K=12$ . For SP 0,35(0,65) at  $0,65r_a^3 = (\sigma/2)^3$ . Here we obtain in fact the equality of volumes interatomic voids:

$$0,65(0,35) r_a^3 \approx 0,35(0,65) r_a^3 = (\lambda_F / 2\pi)^3 z, \tag{14}$$

Where  $z$  – a valence.

It is the equality of densely packed clusters and of absolutely disorderly packing (SP) in the continual approximation Eq. (13) is satisfied for the solid spheres ( $\sigma/2$ ) approximation:

$$0,35 (4/3\pi r_a^3) / K_{sp} = (\lambda_F/2\pi)^3 z \tag{15}$$

Where  $4/3\pi / K_{sp} = 0,65$  and it corresponding  $0,65r_a^3 = (\sigma/2)^3$ .

Hence it follows the dynamic equilibrium  $r_a \leftrightarrow \sigma/2$  which is confirmed by fluctuation SP as an emitter of the excessive energy and cluster as the energy receiver. This energy (E) can be transferred by radiation from SP is attained under condition  $h\nu_{max} / kT_{boil} = 2,82$  (the emission law):

$$E = (e^2/4\pi\epsilon_0) (1 / \sigma/2 - 1 / r_a) z^{1/3}, \quad (16)$$

Where  $0,35 E = 2,82 \text{ kTboil}$ .

Further, electronic subsystem of the boiling is connected with the value  $V_{\text{boil}} = 1,70 V_a = (1,70 4/3\pi) r_a^3 = 7,1 r_a^3$ , where the value 7,1 is  $(1,92)^3 = (2\pi r_s / \lambda_F)^3$ .

Consequently, the value  $V_{\text{boil}}$  is determined by the values of atomic radius and  $\lambda_F$ .

### Modeling of processes the melting and the boiling.

The grown the value of thermal expansion  $\Delta V_t$  from OK to  $T_{\text{melt}}$  should have a limit. Its yields the following relationship:  $\Delta V_t^{1/3} = r_a - r_i$  at  $T_{\text{melt}}$  [1,2]. On the other hand (liquid phase) we have:

For metals with bcc structure:  $\Delta V_t = (V_{\text{melt}} - V_0)_8 = R_{12}^3$ ,

where  $V_0$  (at OK) is determined at  $K=8$  and  $R_{12}$  at  $K=12$  from Eq. (2).

For metals with fcc structure:  $\Delta V_t = (V_{\text{melt}} - V_0)_{12} = R_{12}^3$ ,

where both  $V_0$  and  $R_{12}$  are determined at  $K = 12$  from Eqs.(2,4).

Thus, for metals with bcc structure we have:

$$R_8^3 = R_{12}^3 + \Delta V_t. \quad (17)$$

For hexagonal layer-by-layer packed (6+6) Cd and Zn:

$$\Delta V_t = (V_{\text{melt}} - V_0)_6 = R_8^3, \quad (18)$$

where  $V_0$  is determined at  $K=6$  and  $R_8^3$  at  $K=8$ .

Analogous process is also reproduced in polymorphic fcc(hcp)  $\rightarrow$  bcc transformations in the solid phase:

$$\Delta V_t + R_{12}^3 = R_8^3. \quad (19)$$

The process of the boiling is determined by the value  $R_{12}$ , as well as, the melting with fcc structure:

$$\Delta V_t + R_{12}^3 = 2R_{12}^3, \text{ (or } \Delta V_t = R_{12}^3), \quad (20)$$

where the value  $\Delta V_t$  is corresponded by the value interatomic void  $0,35 V_a$  at  $K=12$ . The general tendency is toward an increase in the number of the nearest neighbors during thermal expansion [1,2], or cells for a placing  $\lambda K_{12}$  (as for the boiling). Thus all points of phase transformations are connected with grand value  $R$ .

### Volume correlations for heat transfer.

Here we have the ground for the examination of the model of high temperature heat transfer in two forms: both fixed orbital ( $R, R_c, r_a$ ) and a sphere, having variable radius but in limits from  $r_a$  to  $r_i$ .

Using assumption of ready cells-  $K\lambda$  into the coordinate space, we may write a chain of correlations in according to the principle uncertainty:

$$4\pi R^2 K\lambda = (r_a^3 - R_c^3) Z^{1/3}; \quad (21)$$

$$4\pi R_c^2 K\lambda = R^3 Z^{1/3} \quad (22)$$

$$4\pi [1/2(r_a + r_i)]^2 K\lambda (1/Z + 1) = r_a^3 / k_p = r_a^3 + R^3 \equiv V_2; \quad (23)$$

$$4\pi [1/2(r_a + r_i) - K\lambda/Z]^2 K\lambda/Z = R^3; \quad (24)$$

$$4\pi [1/2(R + r_i)]^2 K\lambda (1/Z + 1) = r_a^3 \equiv V_3; \quad (25)$$

$$4\pi [1/2(R + r_a)]^2 K\lambda (1/Z + 1) = 2r_a^3 \equiv V_1; \quad (26)$$

$$4\pi r_i^2 K\lambda (1/Z + 1) = R^3 / k_p = R^3 + R_c^3 \quad (27)$$

Eqs. (21-27) are established per 14 metals with an accuracy  $\pm 5\%$  in average.

Where:  $4\pi [1/2(r_a + r_i)]^2 K\lambda = \Delta V_{\text{emitter}}$ ;  $4\pi [1/2(r_a + r_i)]^2 K\lambda/Z = \Delta V_{\text{absorbent}}$ . Hence, we obtain:

$\Sigma \Delta V = \Delta V_{\text{emitter}} + \Delta V_{\text{absorbent}} = 4\pi [1/2(r_a + r_i)]^2 K\lambda (1/Z + 1)$  and also for other relations (24-27).

Here the value  $1/Z$  (it is into relations as  $K\lambda/Z$ ) is the limitation in an absorption of photons by conduction electrons (a valence).

Further we have:  $r_a^3 / k_p$  and  $R_c^3 / k_p$ , where  $k_p$  is the coefficient of the packing (0,68-0,74);

$k_p = V_a / (V_a + V_{voids}) = r_a^3 / (r_a^3 + R^3) = R^3 / (R^3 + R_c^3)$ , where  $V_a$  is atomic volume.

Here we have the value  $V_{voids}$  is coincided with values  $R^3$  and  $R_c^3$ .

Hence:  $R^3 / r_a^3 = (1 - k_p) / k_p = R_c^3 / R^3$  and we obtained:  $R = r_a(0,78-0,705)$  and  $R_c = R(0,78-0,705)$ .

Hence it follows that a placing of  $K\lambda$ -cells into coordinate space from  $r_a$  to  $r_i$  must be connected with relation:

$$R = [\Delta V_{voids}]_R^{1/3}; \quad (28)$$

$$R_c = [\Delta V_{voids}]_c^{1/3}$$

On the basis of Eq. (21-27) where  $R - R_c = K\lambda(1/Z + 1)$ , we may write:

$$[\Delta V_{voids}]_R^{1/3} - [\Delta V_{voids}]_c^{1/3} = K\lambda(1/Z + 1). \quad (29)$$

Hence, we can assume that elementary distance of thermal vibration has been corresponded to the fluctuation - exchange cell  $\pm K\lambda$ . Here the geometrical volume ( $r_a^3 / k_p$ ) has been corresponded to the physical ( $R$  and  $R_c \sim f(\lambda_F/2\pi)$ ) and to the electron- photons interaction in any point of the atomic space between  $r_a^3/k_p$  and  $R^3/k_p$  simultaneously. Thus, we may assume that geometrical interatomic space is a continual, having different forms in according to the principle uncertainty. We may conclude also that heat transfer is connected with the transition and the exchange voids volumes into the interval from  $r_a$  to  $r_i$  and ves in the mode heating - cooling.

Besides, we should be noted relationships in Eq.(23,25,26) between values  $V_1, V_2, V_3$  and the packing factor  $k = 0,74(0,68)$ , which is corresponded to normal values of the lattice (bcc and fcc) -  $V_2$  and the reciprocal lattice in relationships (in wave aspect) between  $V_1/V_2$  and  $V_3/V_2$  (i.e. for alkali, alkali-earth metals it is 0,74 and Mg,Al,Pb...it is 0,68):

$$V_2/V_1 \approx k; V_3/V_2 \approx k \quad (30)$$

The following relations between  $2r_a^3, r_a^3/k$  and  $1r_a^3$  correspond to the value of  $k$  of the reciprocal lattice (in geometric aspect):

$$2/1, 35 \approx 1,47; 1/1,35 = 0,74;$$

$$2/1, 47 \approx 1,35; 1/1,47 = 0,68.$$

Thus two forms of the atomic- ion interaction (the geometric and wave) are corresponded to the model of heat transfer, which is represented by the model of two fluxes exchanging by fluctuations of the electron density in the  $\pm K\lambda$  mode [2]. Heating mode is the fluctuation flux from the atomic periphery ( $r_a$ ) to the ionic core ( $r_i$ ). Cooling mode - vise versa. The equilibrium state is the compensation of electron density fluctuation ( $\pm K\lambda$ ) and it is corresponded to the compensate values packing factor  $k$  (wave and geometric) by reciprocal and normal lattice accordingly.

### Consequences from the model of heat transfer.

#### 1. Principle uncertainty.

Seven relations in Eqs. (21-27) have been by main idea of all combinations: emitter  $K\lambda$  + absorber  $K\lambda/Z$  of electron - phonon interaction must exist in frames of values  $\lambda_F/2\pi$  and in frames principle uncertainty only. The latter is cleared up in follows moments: in Eq.(22) values  $R$  and  $R_c$  are const. by the spread of electronic charge  $Z$  to  $Z^{1/3}$  per atomic sphere and contrary if  $Z$  is const. then value of the radius is var. that is average value between  $R, R_c, r_a$  and  $r_i$  as it shown in Eqs. (21,22).

Thus, principle uncertainty may present in the following scheme: If atomic radius is const, then  $Z^{1/3}$  and if atomic radius is var. then  $Z$  is const.

#### 2. Peculiarity of heat transfer for Cu, Ag and Au.

Here we get the degradation of values  $R$  and  $R_c$ , as we have:

For Cu and Ag:  $r_a - r_i = 0,32$  :-  $0,28 \text{ \AA}$ , then it is corresponded to  $\lambda K = 0,29 \text{ \AA}$ ;

For Au:  $r_a - r_i = 0,045 \text{ \AA}$ , then it is corresponded to  $2\lambda = 0,048 \text{ \AA}$ .

Consequently, we have the distance  $r_a - r_i = n\lambda$  from  $n=2$  for Auto 12 for Ag and Cu, escaping of  $R_c$  and  $R$ . This is a justification of superior heat transfer of these metals, as

$r_a - r_i = n \lambda$  directly and  $n$  is minimal possible value.

#### 3. Peculiarity of hexagonal structure (6+6) Cd and Zn.

For Cd:  $r_a^{\max} - r_a^{\min} = 0,152 \text{ \AA} \approx K\lambda$ ;

For Zn:  $r_a^{\max} - r_a^{\min} = 0,140 \text{ \AA} \approx K\lambda$ ,

Where  $K\lambda = 6\lambda = 0,145 \text{ \AA}$  and  $r_a^{\max}$  and  $r_a^{\min}$  are determined from the lattice parameters  $[a]$  and  $[c]$  and where average value  $1/2$

$(0,152 + 0,140) = 0,146 \text{ \AA}$  is very near value to  $K\lambda = 0,145 \text{ \AA}$ .

#### 4. Transition metals.

Here we have limits in the determining and the calculating of values  $R$  and  $R_c$  so s-d zone and d- zone of electronic system have the influence on  $k_F$ . For example, for Ni it is  $k_F \approx 0,55a.u.$  (s-d zone) and  $k_F \approx 0,81a.u.$  (d-zone), that is  $k_F \neq const.$

However, it can be assumed that  $R_c \rightarrow r_i$ . This assumption allows us to determine both  $R = (r_a + r_i) / 2$  and the equality of fluxes fluctuations (an excess  $+K\lambda$  with a deficit  $-K\lambda$ ) as:

$$R - r_i = nK\lambda \pm \lambda, \text{ and also } r_a - R = nK\lambda \quad (31)$$

where  $n = 1,2$ . For example Ni ( $\text{\AA}/\text{atom}$ ):  $R = (1,26 + 0,72)/2 = 0,99$ ;

$$R - r_i = 0,99 - 0,72 = 0,27;$$

$$K\lambda = 12 \cdot 0,024 = 0,29,$$

Where  $0,27 \approx 0,29$  at  $n = 1$ .

For example, Y:  $R = (1,64 + 0,88)/2 = 1,26$ ;

$$R - r_i = 1,26 - 0,88 = 0,38;$$

$$2K\lambda = 2 \cdot 8 \cdot 0,024 = 0,38,$$

Where  $n = 2$ .

Eq. (31) is fulfilled accurate in limits  $\pm 4\%$  for: Ni, Cu, Mo, Nb, Y, Ti ... similarly Eq.(6-9) for nontransition metals.

#### 5. Amorphous state.

According to data [3] the value  $(r_a - r_i)/K$  is the dimensional criterion for the analysis of the formation of amorphous intermetallic combinations at diffusion heating of films (dusty materials) pure metals  $A_xB_yC_z$ , where x,y,z are combination parts.

Main approximation: it is the freezing of atomic exchange between fluctuation states of clusters ( $K=12,8$ ) and statistical packing atomic ( $K_{SP} = 6,5 = 1/12(1+2+3 + \dots + 12)$ ). This state may to determine as frozen crystallization, where cannot carry out the development neither crystallization from SP state (fluctuation) nor from cluster state (fluctuation). This momentary a freezing can be realized in ideal conditions of heat transfer only. According to Eq. (9) these conditions may create on a distance  $r_a - r_i$ , where a cell  $K\lambda$  has been comprised by integer number n, namely:

$$(r_a - r_i) = n\lambda K \quad (32)$$

Where  $K = 12,8$  for a cluster and  $K_{SP} = 6,5$  for SP; integer number  $n = 1,2,3$ . However integer number n has the limit ( $n=3,0$ ) so according to Eq. (9):

$$r_a - r_i = 2K\lambda (1/Z + 1) + K\lambda/Z,$$

Where we have  $r_a - r_i = 3,5 K\lambda$  at  $Z_{min} = 2$  and  $r_a - r_i = 2,6 K\lambda$ , if  $Z_{max} = 5$ .

Therefore conditions of a freezing for atomic exchange may write in the following way:  $n_{cluster} = n_{SP} \leq 3,0$ .

Hence ideal condition - this is the equality of cells ( $n\lambda$ ) of cluster state with absolute chaotic packing. This equality of cells ( $n\lambda$ ) may carry out by using coefficients x,y,z (composite parts) in dusty films at an joint of their layers of pure metals  $A_xB_y$  and  $A_xB_yC_z$ . For example it is for pair metals  $A_xB_y$ :

$$x [(r_a - r_i)/\lambda K_{12,8}]_A + y [(r_a - r_i)/\lambda K_{12,8}]_B = (x,y) [(r_a - r_i)/\lambda K_{SP}]_{A,B} \quad (33)$$

Hence we have:  $\sum n_{cluster A,B} = n_{SPA,B} = n$  (integer: 1,0-3,0).

Adequacy of the Equality (33) may demonstrate by using experimental data taken from a review article of Johnson W.L. [4].

1)  $Ni_{0,31}Y_{0,69}$

$$(0,69\Delta r_Y^{(8)} + 0,31\Delta r_{Ni}^{(12)}) / \lambda = (0,69\Delta r_Y^{(6,5)}) / \lambda$$

$$3,2 \approx 3,1$$

Where  $\Delta r_Y^{(8)} = (r_a - r_i)/8$ ;  $\Delta r_Y^{(6,5)} = (r_a - r_i)/6,5$  and ets.

$$\sum n_{clusters Y, Ni} \approx n_{SP Y} \approx n$$

$$3,2 \approx 3,1 \approx 3,0.$$

2)  $Ti_{31}Nb_{22}Cu_{47}$ .

$$\text{First variant: } (0,31\Delta r_{Ti}^{(12)}) / \lambda = (0,22\Delta r_{Nb}^{(8)}) / \lambda = (0,47\Delta r_{Cu}^{(6,5)}) / \lambda.$$

$$0,91 \approx 0,92 \approx 0,96 \approx 1,0$$

$$n_{cluster Ti} \approx n_{cluster Nb} \approx n_{SP Cu} \approx n$$

$$\text{Second variant: } (0,31\Delta r_{Ti}^{(8)} + 0,22\Delta r_{Nb}^{(12)}) / \lambda = (0,47\Delta r_{Cu}^{(6,5)} + 0,22\Delta r_{Nb}^{(6,5)}) / \lambda$$

$$2,0 \approx 2,07 \approx 2,0$$

$$\sum n_{clusters Ti, Nb} \approx \sum n_{SP Cu, Nb} \approx n$$

3)  $Al_{55}Nb_{45}$

$$(0,45\Delta r_{\text{Nb}}^{(12)} + 0,55\Delta r_{\text{Al}}^{(12)}) / \lambda = (0,55\Delta r_{\text{Al}}^{(6,5)}) / \lambda$$

$$3,0 \approx 3,2 \approx 3,0$$

$$\Sigma n_{\text{clusters Nb,Al}} \approx n_{\text{SP Al}} \approx n$$

$$4) \text{Ni}_{40}\text{Nb}_{60}$$

$$(0,40\Delta r_{\text{Ni}}^{(12)} + 0,60\Delta r_{\text{Nb}}^{(8)}) / \lambda = (0,60\Delta r_{\text{Nb}}^{(6,5)}) / \lambda$$

$$3,2 \approx 3,15 \approx 3,0$$

$$\Sigma n_{\text{clusters Ni,Nb}} \approx n_{\text{SP Nb}} \approx n$$

Thus the equality  $n_{\text{clusters}} = n_{\text{SP}} \approx 1,0 - 3,0$  is the ground to take into consideration as ideal condition for momentary freezing of atomic exchange between clusters and chaotic SP. Here we have successful combination of metals at minimal and maximum values ( $r_a - r_i$ ). For instance: Cu,Ni  $\rightarrow (r_a - r_i) = 0,32 - 0,54 \text{ \AA}$  (it is min.) and Al,Ti  $\rightarrow (r_a - r_i) = 0,94 - 0,86 \text{ \AA}$  (it is max.). In this case a probably is increased for equalize  $n_{\text{cluster}}$  to  $n_{\text{SP}}$ , using coefficients x,y,z.

### Usual crystallization.

Analysis of the crystal nuclei appear is founded to model of the liquid state: clusters, having ordered packing of atoms and a completely chaotic packing or statistical packing (SP) in the correlation 0,65/0,35 [2]. Main calculation parameter R (corresponds to the maximum level of the electron density fluctuation in pseudo - potential approximation) is determined by a model of the thermo-vibration atomic spheres, leading to the separating on cluster and SP in the fluctuation mode:

$$\text{For cluster } R^3 = 4/3\pi(r_a^3 - r_i^3)/K \text{ and for SP } R_{\text{SP}}^3 = 4/3\pi[(\sigma/2)^3 - r_i^3]/K_{\text{SP}} \quad (34)$$

Where  $K=12, 8,6$  and  $K_{\text{SP}} = 1/12(1+2+\dots+12) = 6,5$  is an average statistical number of nearest neighbors at equation -probably occurrences of all of the dispositions from 1 to 12 [1-3]. The value  $\sigma$  (diameter hard sphere) is defined both using the experimental diffraction data (Perqus-Yevic) and in theoretical models of liquid state as  $(\sigma/2)^3/r_a^3 = 0,65$  or  $\sigma/2 = 0,867 r_a$  [1-3].

Here we make main assumption: at the phase transition point, the same level of the maximum electron density fluctuation is reached. This means the same level of values of R calculating in Eqs.(1,2,4). Hence one may write the basic equation of crystallization or a condition of equilibrium of two phases - the solid and liquid:

$$R_{12,8,6} = R_{\text{SP}} = R_{\text{F}} \quad (35)$$

An analysis of these values R indicates that Eq. (34) is fulfilled for metals with bcc - structure (alkaline and alkaline-earth metals) at  $R_{\text{SP}}/0,65^{1/3}$  (or  $R_{\text{SP}}/0,867$ ), i.e. at  $K=8$  in Eq. (23) and it fulfilled at  $K=12$ :

$$R_{\text{SP}}/0,867 = R_8 = R_{\text{F}}; R_{\text{SP}} = R_{12} = R_{\text{F}} \quad (36)$$

The transition from SP to crystal nuclei ( $\sigma/2 \rightarrow r_a$ ) is connected with coefficient  $0,65^{1/3}$  [1-3]. These data give reason to assume that the crystal lattice, having  $K=8$ , is formed from SP at  $\sigma/2 \rightarrow r_a$  and on the contrary: the crystal lattice with  $K=12$  is formed from clusters with  $K=12$  without the preliminary transition  $\sigma/2 \rightarrow r_a$ .

This choice of a mechanism for a process of the crystallization is determined by the value  $R_{\text{F}}$  in Eq. (1) and only probably.

Metals having a structure bcc (alkaline and alkaline- earth) have clusters  $K=12$  at the melting [2]. Hence, we may write:

1. For the dynamic equilibrium of crystal nuclei (bcc) - SP:  $R_8^3 = R_{\text{SP}}^3/0,65$ .
2. For the dynamic equilibrium of cluster ( $K=12$ ) - SP:

$$R_{12}^3 = R_{\text{SP}}^3.$$

3. For the dynamic equilibrium of crystal nuclei (bcc,  $K=8$ ) - cluster ( $K=12$ ):  $R_8^3 = R_{12}^3/0,65$ .

Here it should be noted the balance of volumes between crystal nuclei (and cluster) and SP at theirs the dynamic equilibrium:

$$4/3\pi r_a^3 = K_{\text{SP}}(\sigma/2)^3. \quad (37)$$

$$\text{Hence may write: } 4/3\pi/K_{\text{SP}} = (\sigma/2)^3/r_a^3 = 0,643 \approx 0,65. \quad (38)$$

Therefore, a factor 0,65 is the grounded physical value perfectly. Values  $\pi$  and  $K_{\text{SP}} = 6,5$  are const. Therefore 0,65 and the ratio 0,65/0,35 is const., determining the ratio cluster/SP [1,2].

For Cd and Zn having a hexagonal layered structure (6+6) Eq. (35) fulfilled with the correction of the  $R_{\text{SP}}$  values by a factor 0,867, i.e.:  $R_6 = R_{\text{SP}}/0,867$ , according to [1].

Here we may to conclude that a structure of the liquid state of any metals is the dinamic equilibrium state clusters with  $K=12$  and SP at their ratio 0,65/0,35 [1-3].

Probably clusters with  $K=8$  and  $K=6$  can't exist in equilibrium conditions for the liquid metals.

### Polymorphic transformation bcc $\leftrightarrow$ fcc.

The process of polymorphic transformation can be represented as a result of a change of  $r_i$  for  $R_c$  and the volume of spheres  $4/3\pi (r_a^3 - r_i^3)/K$  for the continuum  $(r_a^3 - R_c^3)/K$  caused by a decrease in the fluctuation processes and an increase in the tendency to restoration of the band structure. Hence, taking into account Eqs. (1,4,5,11) we can write the phase equilibrium condition:

$$R_8 = R_{12} = R_F \quad (39)$$

Where  $R_8 = [4/3\pi (r_a^3 - r_i^3)/8]^{1/3}$  and  $R_{12} = [Z^{1/3}(r_a^3 - R_c^3)/4\pi\lambda 12]^{1/2}$  and  $R$  from Eq. (1).

### Polymorphic transformation bcc $\leftrightarrow$ hcp.

A large number of metals is crystallized in the bcc lattice with a subsequent transition to the hcp with a very small compression along the [c] axis at  $[c]/[a] < 1,633$  (where 1,633 corresponds to the close sphere packing). The magnitude of compression should be in limits  $n\lambda$  according to Eq. (9) (where  $n=0,1,2$ ).

The deformation of a lattice along [c] axis in  $n\lambda$  is led to same value of the deformation along [a] axis in according to the uncertainty principle.

Compressing an atomic sphere by  $\lambda$  from above and below along the [c] axis, we obtain [c] -  $2\lambda$  (flattening along the [c] axis). The elongation [a] +  $2\lambda$  along the [a] axis by  $\lambda$  from both sides corresponds to this value [c] -  $2\lambda$  in accordance with the principle of uncertainty (total volume has not changed for 12 neighbors). Here we obtain inverse ratio  $([c] + 2\lambda)/([a] - 2\lambda) \approx 1,633$  (an ideal ratio  $[c]/[a] = 1,633$  of a cubic close sphere packing). It is fulfilled for 12 metals from Re, Os.... to Hf, Gd..., using the model  $2\lambda$  and experimental data [c] and [a] for these metals.

It is supposed that the appearance of the structure hcp and the transformation bcc  $\rightarrow$  hcp at a very small changes in  $n\lambda$  (where  $n = 1,2$ ) is connected with relations  $R_c \leftrightarrow r_i$  and  $r_a \leftrightarrow r_i$  in Eqs.(3,9) where the imprecision of the calculation  $R_c$  and  $r_a$  is corresponded to a same small value  $n\lambda$  (where  $n = 1,2$ ).

Thus, based on the analysis of the electron -ion interaction within the consideration of the probability distribution of electron density in the coordinate space can be concluded that there is a size quantization over  $n\lambda$  and a bulk quantization over  $4\pi R^2\lambda$  under high-temperature for any phase transformations and heat transfer.

### References

1. Filippov ES. Model of High Temperature Phase Transitions in Metals. Russ. Phys. J. 2015; 58(12):72-76.
2. Filippov ES. Model of Melting and Heat Transfer in Metals. Applied Physics Research. 2017; 9(2):1-4.
3. Filippov ES. Quantomization by number nearest neighbors in metals. Izv. Vyssh. Uchebn. Zaved. Chern. Metallurg, 2009, 9.
4. Johnson WL. Thermodynamic and kinetic aspects of the crystal to glass transformation in metallic materials // Progress material science. 1989; 30(2):81-134. (Pergamon Precc).