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Size-Induced Freezing Effect in Monte-Carlo Simulations of Phase Separation Kinetics in Nanoparticles

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Abstract. The separation kinetics in a binary nanoparticle is studied by means of two-dimensional Monte-Carlo sampling and Ising-type model, where the species exchange positions due to vacancy mechanism. The model is developed in case of a free nanoparticle with a coating shell. The kinetics is shown to depend on the size of a nanosystem. We demonstrate a distinct size-induced freezing effect on kinetics of separation.

1. Introduction

Nanosciences aim at understanding the nanoobjects for their control, manipulation and application. Modern nanomaterials sciences include the numerical simulations as a practical way of validating the theoretical approaches through the use of computer experiments. Despite the high interest, the evolution of nanostructured systems at the first stages of their synthesis (nucleation) and their structural peculiarities are still poorly understood [1]. Understanding of nucleation in nanostructured systems, such as nanoparticles, is of obvious significance for further fabrication of new nanomaterials with desired properties.

In this respect, the Monte-Carlo (MC) method is one of the effective methods for the phase transition analysis in metallic nanosystems and is proved to be efficient for calculation of equilibrium properties of systems, estimation of the phase stability limits, etc [2].

Due to their unique behaviour, metallic nanoparticles are the subject of fundamental and applied works [1-4]. Nanoparticles are not always uniform. In many circumstances, they consist of a core phase, surrounded by another phase, forming the shell of the particle. This is the case for elemental particles surrounded by their oxide, metal core in another metal shell, etc. It is also observed that some other metastable phases become stable when surrounded by another shell [3]. In some circumstances, core-shell structures seem to appear spontaneously, while alloying occurs for other alloys [4]. Despite their differences, from the viewpoint of structural stability, three main problems need to be addressed: i) the effect of size; ii) the effect of defects on their internal structures; iii) the stability of metallic nanoparticles under external conditions and fields. All these problems have not been completely solved both from the theoretical and experimental points of view.

Most of the current works on metallic particles and clusters concern elemental ones [5-6]. Furthermore, usually the diffusion in mixtures consisting of two sort atoms is modeled by Kawasaki direct exchange dynamics. This is not a satisfactory representation of the diffusion in real alloys, where atoms can change places easily due to empty neighboring sites [7-8]. In the present communication, we study the process of vacancy-mediated phase separation in a nanoparticle (with a diameter in the range of 1 - 100 nm) consisting of atoms of two different types, A and B, and describe the corresponding evolution of the process in the finite volume. We treat the case of a binary metallic nanoalloy $A_{1-X}B_X$ with the initial composition X_0 as a supersaturated nanosystem whereas a nucleus of a new phase has another stoichiometry X_n, $X_n \neq X_0$. Here, the only allowed microscopic motion is the exchange between the vacancy and one of the nearest neighbour atoms. Doing this, we present 2D Monte-Carlo simulations and focus on the aspects related to the kinetics.

It is well documented that nucleation in nanosystems and thermodynamic properties of nanosystems differ qualitatively from those in macroscopic phases, for the size of the nucleus is comparable to the size of the mother phase [9-11]. Also, the smaller the particle is the diffusion coefficient should be bigger and as a consequence the kinetics is faster. As we shall see in case of vacancy-mediated solid-to-solid transition in coated nanoparticles one can observe the opposite behaviour.

The paper is structured as follows. In the next section we describe the basic assumptions of MC method for microscopic theory of diffusion and the presentation of the two-dimensional MC model of a decomposing nanoalloy. In section 3, we investigate the kinetics of nucleation and phase separation in a small isolated particle and its peculiarities related to the influence of size, supersaturation and existence of the particle shell. Concluding remarks are presented in section 4.

2. Model

In the classical diffusion theory, as investigated by Frenkel in 1960s, atoms may exchange their positions due to three simple main mechanisms: i) interstitial mechanism; ii) vacancy-mediated mechanism and iii) exchange mechanism or the so called Kawasaki dynamics [8,12]. Here, we consider only one of the simplest and the most probable mechanisms seen in metal alloys, namely the vacancy-mediated mechanism.

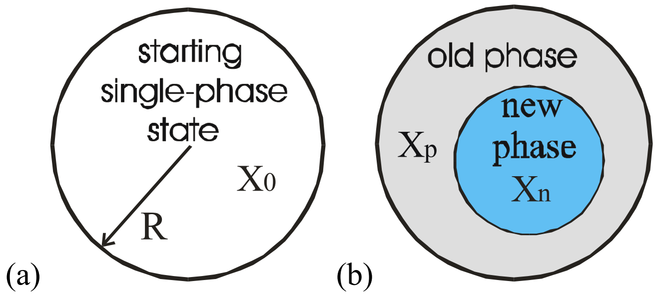

Fig. 1. Schematic representation of possible phase transition mode in a nanoparticle: (a) – single phase particle of composition X_0 at the initial stage, (b) – the same particle in a two-phase state after the nucleation with composition redistribution being taken into account. X_p – composition of ambient parent phase, X_n – concentration in the new-born phase, R – radius of a nanometric isolated particle.

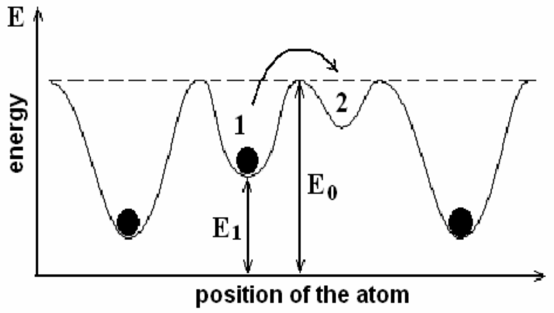

Fig. 2. Sketch-model of the barrier for the diffusion jump: for the atom jumping from position 1 into position 2. The activation energy Q, for 1→2 diffusion jump, is determined as the difference $E_0 - E_1$. The smaller the value E_1 is the larger the energy barrier $Q=E_0 - E_1$ for diffusion becomes.

When the temperature, T, is changed, first order phase transitions may take place. Let us assume that a small isolated initially supersaturated particle of the binary alloy is quenched into the two-phase region. Then one should observe the phase transition from the single phase state to the two-phase state [9-11]. Due to the limited matter reservoir, the nucleation process might differ from the usual bulk one [13-15]. In figure 1 we represent the possible evolution mode of phase transition in a single-phase particle. The "kinetic decoding" of the transformation (a)→(b) is visualized in the framework of the two-dimensional MC simulations.

Consider basic model of vacancy-mediated diffusion. The activation energy for a diffusion jump, Q, is evaluated as follows. Let us assume (figure 2) that the energies of the positions of the atom in the lattice are different, while the barrier height E_0 in the crossover point of potential energy relief is the same for all the atoms [16]. The depth of the well, where the atom is located, depends on its nearest environment, that is the value E_i for the at i-th atom can be determined within the first coordination sphere by Ising-type model:

$$E_i = \sum_{j=1}^{Z} \Phi_{X_i Y_j} \ . \tag{1}$$

Here Z is the number of nearest-neighbour atoms of the vacancy. The value of the activation energy Q for microscopic diffusion of the atom of type X (here X = A, B), going from point 1 to point 2 (figure 2), is given by quantity: $Q=E_0-E_1$. In general, if the *i*-th atom adjoins the vacancy, the height at the activation energy barrier for diffusion jump of the vacancy towards *i*–th direction is expressed by:

$$Q_i=E_0 - E_i. \tag{2}$$

The residence time algorithm uses the 'forced' jump into randomly selected *i*-direction (*i* labels the direction). The probability of one diffusion jump into each direction is given by ratio:

$$p_i = \frac{\nu_i}{\sum_{j=1}^{Z} \nu_j} = \frac{\nu_{0i} \cdot e^{\frac{-Q_i}{kT}}}{\sum_{j=1}^{Z} \nu_{0j} \cdot e^{\frac{-Q_j}{kT}}} = \frac{\nu_{0i} \cdot e^{\frac{E_i}{kT}}}{\sum_{j=1}^{Z} \nu_{0j} \cdot e^{\frac{E_j}{kT}}} \ . \tag{3}$$

Here ν_i is the frequency of the atom-vacancy interchange in the *i*–th direction, j is the number adjacent to the vacancy atom. Having obtained the p_i values, one finds the successful jump direction by randomly generating R and comparing it with the p_i, ν_{0i} is the vacancy-*i*-atom exchange characteristic frequency [2,7-8].

Furthermore, as mentioned above, nanoparticles often consist of a core phase, surrounded by another phase, being a shell of a particle [3-4]. So, in the following MC simulations, we assume that the nanoparticle consists of a main nanoalloy in the core and a thin shell (figures 3-4). The core is a binary nanoalloy with two species A and B. The shell properties differ from the core ones, so that we use a third type of atoms for the surface film and call them C atoms. This gives the opportunity to investigate the influence of the shell on the dynamics of phase separation and the growth of a new phase inside the nanoparticle. Why?

The configuration energy of the system is obtained by means of the Ising type Hamiltonian, taking into account interatomic nearest-neighbour pair potentials. A single vacancy was introduced at random into the two-dimensional nanoparticle. Each pair of atoms is characterized by the pair interaction potential Φ_{XY}, where the subscripts X and Y can accept one of the values A (for atoms A), B (for the species B), C (for shell atoms) and V (for vacancy). For a system of N_{tot} lattice sites consisting of N_A sites occupied by the A-species and N_B sites occupied by the B-species, the configurational energy of the whole system can be written following the Ising-type model:

$$E = \frac{1}{2} \sum_{i=1}^{N_{tot}} \sum_{j=1}^{Z} \Phi_{X_i Y_j} \ , \tag{4}$$

where the external summation is carried out over all lattice sites N_{tot} of the system, while the internal summation only over the points within the first coordination sphere of the i-th lattice point. Here, Z=4.

Let us consider the model of a separating alloy. In our opinion, the kinetic model of reactive diffusion introduced here is adapted to regular solutions, because it takes into account nearest-neighbour interatomic pair potentials. Following the simple theory of a regular solid solution, binary alloys can be investigated by the criteria of mixing and separation (also so-called as demixing). In order to describe the separating nanoalloy, we assume that pair interaction potentials Φ_{AA} and Φ_{BB} are equal and smaller than Φ_{AB}, so that the so-called energy of ordering or mixing energy $E_{mix}=0.5(\Phi_{AA}+\Phi_{BB})-\Phi_{AB}$ is negative. During the process of phase transition our initially saturated solution should be separated into a phase containing mainly A atoms and a phase consisting of B atoms. From this standpoint, the stability criteria of the mixture as a function of composition and of the temperature can be conveniently discussed by calculating the first and second differentiatives of the configurational Helmholtz free energy g(X) as a function of composition X. They correspond to the zeroes of $\partial g(X)/\partial X$ and $\partial^2 g(X)/\partial X^2$. The last conditions define the metastability gap on the g(X) curve (given further).

Our computer simulations are performed for different number of atoms N_{tot} in the nanoparticle: between 10^3 and 10^8 (so the vacancy concentration varies as 1/ N_{tot} from 10^{-3} to 10^{-8}). The temperature T is taken to be equal to T=300 K. Pair interaction potentials are taken to be symmetric: $\Phi_{AA}=\Phi_{BB}=-5\cdot10^{-20}$ J, $\Phi_{AB}=\Phi_{BA}=-4.3\cdot10^{-20}$ J in all experiments, except when explicitly noted. The component mobilities, that is the jump frequencies for the exchange of the vacancy with species A and B, are estimated as $\nu_{0A}=\nu_{0B}=10^{14}$ s^{-1}, respectively. The frequencies ν_{0C} for vacancy-shell exchange is varied between 0 and $10\cdot\nu_{0A}$. In present calculations it is assumed that $\Phi_{AC}=\Phi_{BC}=\Phi_{CC}$ and $\Phi_{VX}=0$. The potential Φ_{CC} has been varied between -10^{-20} J and -10^{-15} J and is taken as $\Phi_{CC}=-5.5\cdot10^{-20}$ J if else is not specified.

Being given the above parameters for the regular solution model, one obtains $\partial g(X)/\partial X=0$ at X=0.0008 and X=0.9992, whereas $\partial^2 g(X)/\partial X^2=0$ at X=0.077 and X=0.923, respectively. So, the alloy is calculated to be metastable, when $0.0008<X<0.077$ and $0.923<X<0.9992$. It is absolutely unstable when $0.077<X<0.923$.

The algorithm of calculation is the following. First, we design the initial configuration of the atoms in the treated nanosystem, by random distribution of A and B atoms into the square lattice and by fixing the initial composition X_0 of B-species. Then we introduce one single vacancy into a randomly found place of the nanoalloy. We determine the probabilities p_i (3) for diffusion jumps of the vacancy into all directions by taking into account the energies E_i (1) of the nearest-neighbour atoms. At last, by generating the random number R and comparing it with the values p_i, we find the successful jump direction and realize the exchange procedure, as explained above.

It is worth noting that the shell properties are such that neither the atoms nor the vacancy can escape out of the core of the nanoparticle. (This is realized by introducing a smaller frequency for vacancy-shell jump as compared with the vacancy-core frequency.)

The following parameters are studied as functions of the MC steps number (MCS): the number of new phase precipitates (small clusters), their volume, overall size.

Furthermore, only those clusters were considered as the clusters of the new phase with minimal dimensions, which were composed of not less than $N_{min}=10$ atoms of the sort B only.

It is also useful to calculate the average size <N> of new phase clusters. Let *f(N)* represent the number of new phase clusters consisting of N atoms each, at a fixed number of MCS. Then, <N> is defined as:

$$< N >= \frac{\sum_{N=10}^{N_{\max}} N\cdot f(N)}{\sum_{N=10}^{N_{\max}} f(N)} \tag{6}$$

where N_{max} is the number of atoms in the largest cluster of the new phase. The denominator indicates the total number of the new phase clusters in the treated system:

$$\text{CN}\equiv \sum_{N=10}^{N_{\max}} f(N) \tag{7}$$

It is worth noting that all MC simulations and results may also be checked by visual observation.

3. Size-induced freezing effect

Our simulations start from a structure of N_{tot} atoms (figures 3a and 4a). The initial composition X_0 corresponds to the (thermodynamically) metastable state.

The model shows that, in accordance with the theoretical thermodynamic estimations for nanosystems, there is no separation in very small particles as well as in case of small supersaturation [11,13-15]. The increase of N_{tot}, at small and fixed X_0, leads to the possibility of nucleation of one new phase embryo inside the particle. The same reasoning is applied with respect to the increase of supersaturation X_0 at a fixed size of N_{tot}.

In the usual treatment of nucleation, it is assumed that the reservoir of matter is very large, so that there is no problem of matter supply during the nucleation process itself. In a nanosystem, the reservoir of matter is finite. Therefore, the total amount of one of the chemical components may be too small for the synthesis of even one critical nucleus. To see this, let us consider a binary isolated nanoparticle (figure 1a). Let X_0 be the mole fraction of B-species in the particle (in the parent phase) before nucleation, X_n is the stoichometry or mole fraction of B-species in the new formed phase ($X_n \neq X_0$), N_{tot} and N_n are the total numbers of atoms in the parent and new phases, respectively.

Let us assume that only a single new phase embryo of critical size N^*_n can appear (figure 1b). At that, the embryo of the new phase will need to keep atoms B from the parent phase. This condition gives the estimation for minimal number of atoms N^*_{tot} of a nanoparticle, where the transition may appear: $N^*_{tot}=N^*_n \cdot X_n/X_0$. The last equation is the matter conservation law. Obviously, if the number of atoms N_{tot} of the whole particle is less than N^*_{tot}, the nucleation becomes impossible: the total number of atoms B is even not enough for the synthesis of a single stable nucleus. In our case $N^*_n=N_{min}=10$ is taken and $X_n \approx 1$, then $N^*_{tot} \approx 10/X_0$ and say, for $X_0=0.05$, one obtains $N^*_{tot} \approx 200$.

Actually, the prohibition of separation in the small particle (at X_0, when the alloy is unstable in the bulk) indicates the increasing of solubility of components. So, the MC simulations confirm the theoretical result of thermodynamical approach that, in small particles, the solubility of the components increases as compared with the bulk case [10-11]. Obviously, such behaviour is related to the finite size effect.

Furthermore, when N_{tot} increases, one observes the competitive nucleation of a few, and then many, nuclei in one particle.

To investigate the effect of the shell, we consider different values of Φ_{CC}. When $\Phi_{CC} >> \Phi_{AA}$ and $\Phi_{CC} >> \Phi_{AB}$, the vacancy never remains in the core part: it always finishes in the shell. Here, the vacancy mainly moves along the core-shell boundary. Therefore, the diffusion in the core is inhibited and there is no phase transition at all: $\langle N \rangle = 0$.

When Φ_{CC} is decreased such that $\Phi_{CC} << \Phi_{AA}$, the opposite behaviour is observed: the vacancy ‘prefers’ to be inside the core of the particle and the diffusion along the core-shell boundary does not take place. In this case, the nucleation and separation are homogeneous-like. This may be verified visually, as shown in figures 3 and 4.

In order to fully investigate the role of the shell, one will also have to vary ν_{0C}. When $\nu_{0C}=0$ (or $\nu_{0C} << \nu_{0A}$ at nearly the same potentials Φ_{AA}, Φ_{BB}, Φ_{AB} and Φ_{CC}), it turns out that the vacancy exchange inside the core part is preferred. The opposite behaviour is observed when $\nu_{0C} >> \nu_{0A}$. Physically, $\nu_{0C}=0$ means that the vacancy can not go out of the particle, can not exchange with the shell atoms, but it can move along the core-shell boundary of the particle and be inside the core part.

The effect of the shell on the nucleation mechanism is presented in figures 3-4. Here we present two evolution modes of transition: homogeneous and heterogeneous, depending on potential Φ_{CC}: $\Phi_{CC}=-5 \cdot 10^{-18}$ J for the figure 3 and $\Phi_{CC}=-5.5 \cdot 10^{-20}$ J for the figure 4. From the above results, it turns out that the properties of the shell may be very important for determining the mechanism of nucleation and separation in a nanosystem. Care has to be taken in the study and modelling of the phase transition processes taking place in coated nanofilms and nanoparticles.

The observation of the evolution of the system shows that there exists a correlation between the size of the new formed phase and its shape. This correlation may be reduced to one simple conclusion: the greater the nucleus size is the more close its shape to the circular one is (see also figure 4). This result is related to the fact that pair potentials Φ_{AB} (characterizing the surface tension of the nucleus) are not interrelated with the crystallographic orientations of the lattice.

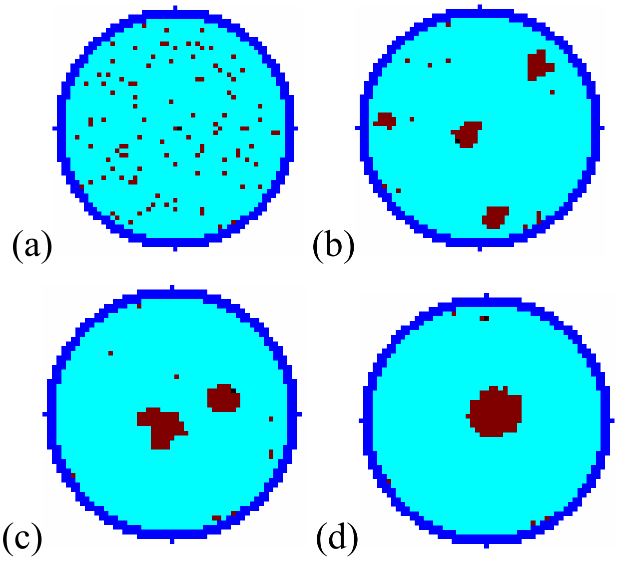

Fig. 3 Simulated microstuctures of the nanoalloy at different stages of the evolution: (a) – initial supersaturated nanoparticle, (b) – 10^7 MCS, (c) – $4{\cdot}10^7$ MCS, (d) – $4.5{\cdot}10^7$ MCS. The B-atoms are indicated by black points. Shell consists of C atoms. At the last stage the new phase nucleus is in the center of the nanoparticle. Parameters are taken as: $X_0=0.05$, $\Phi_{AA}=\Phi_{BB}=-5{\cdot}10^{-20}$ J, $\Phi_{AB}=-4.3{\cdot}10^{-20}$ J, $\nu_{0A}=\nu_{0B}=\nu_{0C}=10^{14}$ s^{-1}, $\Phi_{CC}=-5{\cdot}10^{-18}$ J, $N_{tot}=2000$.

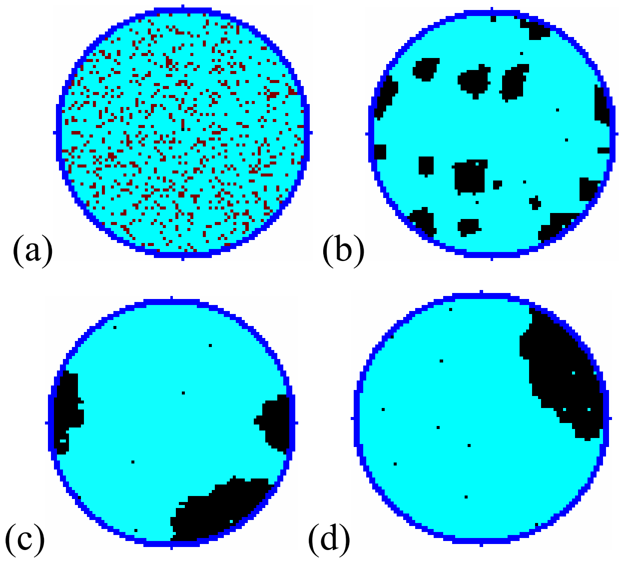

Fig. 4 Fragments of evolution of the separating nanoparticle – ‘in situ’: from the initial stage of multiple nucleation until the last stage of coalescence and coagulation: (a) – initial supersaturated nanoparticle of composition $X_0=0.05$, (b) – $2.5{\cdot}10^7$ MCS, (c) – 10^{10} MCS, (d) – $5{\cdot}10^{10}$ MCS. The B-atoms are indicated by black points. Shell consists of C atoms. Parameters: $N_{tot}=5000$, $\Phi_{AB}=-4.3{\cdot}10^{-20}$ J, $\Phi_{AA}=\Phi_{BB}=-5{\cdot}10^{-20}$ J; $\Phi_{CC}=-5.5{\cdot}10^{-20}$ J, $\nu_{0A}=\nu_{0B}=10^{14}$ s^{-1}, $\nu_{0C}=0$ s^{-1}, $X_0=0.1$.

The kinetics in our MC simulations shows a nearly power law for average size <N> (6) from time, t (here, the MCS):

$$\langle N\rangle(t) - \langle N\rangle(0)=\alpha{\cdot}t^{\beta}, \tag{8}$$

where β is the dynamic exponent and α is the coefficient of proportionality. The initial average cluster size <N>(0) is small (smaller than N_{min}), so it may be taken as zero. The equation (8) is then rewritten as:

$$\langle N\rangle(t)=\alpha{\cdot}t^{\beta}. \tag{9}$$

We found that kinetic quantity β depends on the number of atoms in the treated system (figure 5 and figure 6), so it is size-dependent.

The MC simulations also allow us to investigate ‘in situ’ the time dependence of the number of new formed clusters in the nanoparticle. We see that at initial MCS, the number of new formed clusters increases up to a maximum, corresponding to the transition between the nucleation regime to coalescence and coagulation. At high MCS, the number of clusters tends to 1 (one nucleus of a thermodynamically given size).

The rate of the relaxation process is clearly shown by the value of exponent β depending on N_{tot} (9). For the first time, we show that β is varied within the 0.05-0.5 range and depends on the number of atoms N_{tot} in the treated system. At high N_{tot}, β tends to increase. Also, we see the new and very important results: i) the smaller the system is the smaller the β is, that is the slower the relaxation process (figure 6) at last stages becomes, ii) the smaller the particle is the faster the first nucleation stage is (figure 5). It is worth noting that these effects are not equilibrium thermodynamic ones, they are kinetic. The first result is not obvious and even seems to be the ‘opposite’ kinetic behaviour. We call it as “size-induced freezing effect” on kinetics.

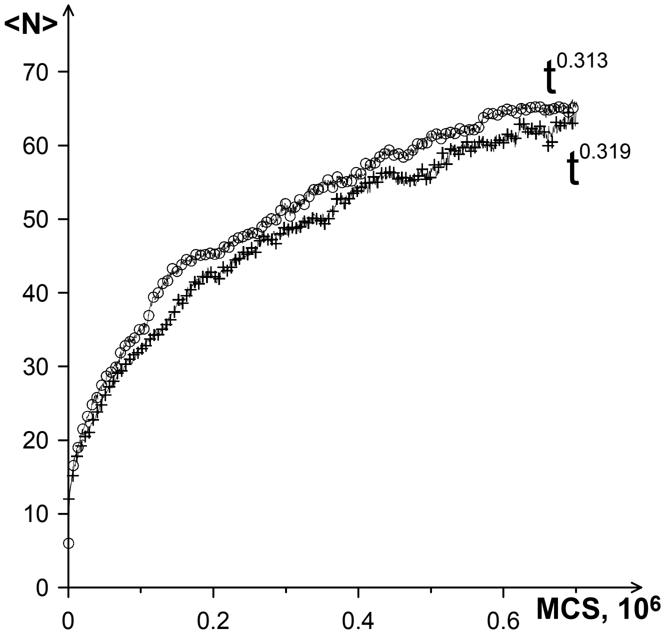

Fig. 5 Average size <N> versus MCS for different values N_{tot}: N_{tot}=5000 (○) and N_{tot}=8000 (+). At high MCS, <N>(t) enters a saturation regime. Parameters: $\Phi_{AB}=-4.3\cdot10^{-20}$ J, $\Phi_{AA}=\Phi_{BB}=-5\cdot10^{-20}$ J; $\Phi_{CC}=-5.5\cdot10^{-20}$ J, $\nu_{0A}=\nu_{0B}=10^{14}$ s^{-1}, $\nu_{0C}=0$ s^{-1}, $X_0=0.05$. The simulations are averaged by 22 independent program starts.

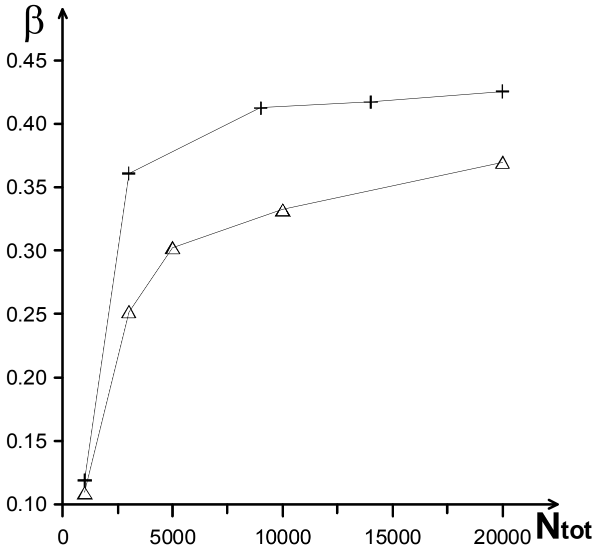

Fig. 6 Averaged value of exponent β versus number of atoms N_{tot} – size-induced freezing effect for different temperatures T=150K (+), T=300K (Δ) while other parameters are the same: $\Phi_{AB}=-4.3\cdot10^{-20}$ J, $\Phi_{AA}=\Phi_{BB}=-5\cdot10^{-20}$ J; $\Phi_{CC}=-5.5\cdot10^{-20}$ J, $\nu_{0A}=\nu_{0B}=10^{14}$ s^{-1}, $\nu_{0C}=0$ s^{-1}, $X_0=0.05$. Each point is averaged over 22 realizations.

Generally speaking, compared with the bulk materials, nano-sized ones are characterized by the fact that the ratio of the number of surface to volume atoms is not small and so one can expect that the diffusion should be induced by the surface effect of nanoparticles and be dominated by surface atoms of nuclei. At the same time it is well-known that the surface diffusion is usually faster than the bulk one (due to preferable places of defects). From this, the smaller the whole particle is the bigger the effective diffusion coefficient should be. This is shown, for example, by finding diffusion activation energy at different approaches: i) by molecular dynamics simulations of study the melting evolution of metal nanoparticle, ii) in the experimental diffusion results of nitrogen atoms into bcc Fe and Ag into Au nanoparticles, iii) due to thermodynamic approximation based on size-dependent melting temperature [17-20]. We see that in our case, that is, in case of vacancy-mediated diffusion and separation (solid-to-solid transition) in coated nanoparticles it is not so.

Let us try to explain why for the smaller systems the nucleation stage is fast whereas coarsening is slow (figure 5). Our explanation is based on the existence of effective 'bulk' diffusion at the nucleation stage and on the size constraints at coarsening stage. The decreasing of the relaxation kinetics in the nanoparticle means that, in the framework of the present model, small volumes constrain the diffusion processes (effective diffusion coefficient D decreases) whereas the effective concentration of the vacancies is increased as compared with the larger volumes.

For very short times vacancy has not yet visited all parts of the nanoparticle. So, for initial times the process should be dominated by the bulk diffusion of vacancy and atoms in the core part of the nanoparticle. The effective bulk diffusion coefficient should be proportional to vacancy concentration C_v ($C_v=1/N_{tot}$), correlation factor and jump frequency. From this, $D\sim C_v\sim 1/N_{tot}$. Hence, the smaller the system is the bigger the effective vacancy concentration is, the bulk diffusion and initial stage – nucleation process are faster. This is verified in figure 5a, where parameters are taken as: $\Phi_{AB}=-4.3\cdot10^{-20}$ J, $\Phi_{AA}=\Phi_{BB}=-5\cdot10^{-20}$ J; $\Phi_{CC} = -5.5\cdot10^{-20}$ J, $\nu_{0A}=\nu_{0B}=10^{14}$ s^{-1}, $\nu_{0C}=0$ s^{-1}, $X_0=0.05$. We see that the average size <N> curve for N_{tot}=5000 (○) is higher than for N_{tot}=8000 (+)

at the initial stage whereas at the last stage the dependences are opposite: $\langle N\rangle \sim t^{0.313}$ for $N_{tot}=5000$ and $\langle N\rangle \sim t^{0.319}$ for $N_{tot}=8000$.

On the other hand, one can estimate the diffusion coefficient of vacancy (or atoms) using the Einstein equation $D\sim\langle[r(t)-r(0)]^2\rangle\cdot(4t)^{-1}$, where t is the diffusion time, r is the position of the vacancy (or an atom), $\langle[r(t)-r(0)]^2\rangle$ is the mean square displacement. The vacancy starts the motion from the center so that $r(0)=0$. So for longer times of coarsening (which we present by formula (9) and compare in figure 5) we can assume for the moment that interface diffusion plays a key role. So in the coarsening process in a nanosystem, r(t) would be replaced by up estimation value R; that is maximal displacement is limited by the particle radius R. Hence, at long times $D\sim R^2/t$ or as estimation for our two-dimensional model $D\sim N_{tot}/t$, that is proportional to the size of the nanoparticle and inversely proportional to the time considered. Thus, for two different sizes R and the same time, the effective diffusion coefficient during the coarsening in smaller system should be slower and it tends to zero, $D\rightarrow 0$, when $t\rightarrow\infty$. This is the case when thermodynamic constraints (size of the system, interaction potentials and initial set of parameters) suppress the kinetics of coarsening.

Other arguments may be related to the fact that the probability distribution of the vacancy position is not uniform (correlation factor in diffusion coefficient D). However, we expect that an adequate explanation of these results is related to the interface diffusion and to size and atom composition dependence on the corresponding diffusion coefficient, which is not included in this discussion. A more quantitative statistical analysis is needed for quantitative understanding of the size effect on vacancy diffusion in the present model of decomposition in a nanoparticle. The corresponding analysis is going on for 3D MC sampling and will be presented elsewhere.

Another surprising result of the present model is that the separation process goes much faster at low temperatures (figure 6). This result is also looks opposite to the common view according to which the rate of separation should be higher for higher temperatures. Assuming again that the present model follows the simple theory of a regular solid solution, we can understand such behaviour by investigating the temperature dependence and the criteria of mixing and separation. It is well known that the width of the gap at Helmholtz free energy g(X) dependence on composition increases with decreasing the temperatures. From this, the decrease of T leads to increase of supersaturation, that is, to increase of the bulk driving forces for separation.

4. Summary and Concluding Remarks

The present model clarifies the specific features of phase separation in nanovolumes. In accordance with the proposed model the power law for the mean size $\langle N\rangle$ of the new phase particles appears: $\langle N\rangle(t)=\alpha\cdot t^{\beta}$. The kinetic exponent β characterizes the rate of relaxation process and depends on the size of a nanosystem, temperature and composition. We obtained the new kinetic behaviour - size-induced freezing effect: the smaller the system is the slower the separation process at coarsening stage is and the faster the nucleation stage is.

Depending on the shell properties, the nucleation of a new phase may be either heterogeneous (on the external surface) or homogeneous (in the core of the particle).

The development of a new three-dimensional model is now in progress in order to prove the scheme and results and in order to compare with the real experimental observation and satisfactory explanation of diffusion effects. Results of 3D model show the similar ‘freezing’ behaviour.

The model introduced here may be useful in the analysis of the other phase transitions in small systems, in bulk nanocrystalline materials and closely related problems.

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