On the Particles Transport Between Embedded Clusters

Florin Despa
Department of Theoretical Physics,
Institute of Atomic Physics,
POBox MG - 6, Măgurele, Bucharest, R - 76900, România
e-mail: despa @ roifa. if. ro
Fax: 40. 1. 312. 2247

Vladimir Topa
Institute of Physics and Technology of Materials,
POBox MG - 7, Măgurele, Bucharest, R - 76900, România

Abstract: Diffusional interactions within the Ostwald Ripening process are analyzed in the present paper. An off-centre diffusion approach is performed to point out the direct correlation between the size of clusters. Herein the diffusion solution is derived as a function of both the growing and shrinking cluster sizes. Also, it is shown that the frequency transfer of particles between the shrinking cluster and the growing one may acquire high values due to the medium polarization. As a result, the temporal power law of the cluster growth derived in this theoretical model differs from that predicted by the LSW theory. Experimental data for Ag clusters embedded in a KCl matrix are analyzed both by the present theory and by the LSW theory.
1 Introduction.

As it is well known, one can distinguish two regimes in the phase separation process following the formation of nuclei. The initial stage is the growth of these nuclei by the condensation of solute on their surface. The second stage is known as the Ostwald Ripening (OR) process where the particles flow from shrinking clusters to growing ones.

The kinetics of domain growth in the late stages of diffusion-limited spinodal decomposition Ostwald Ripening (OR) have been studied by a variety of methods \([1, 2, 3, 4, 5, 6, 7, 8]\). The Lifshitz, Slyozov and Wagner (LSW) theory predicts that the average droplet radius \(R\) grows with time \(t\) as \(R(t) = \Gamma t^{\alpha}\), where \(\Gamma = \text{const.}\) and \(\alpha = 1/3\) and that the distribution of droplet sizes reaches a material-independent universal form when properly scaled. Most simulations and experiments measure \(\alpha\) exponents in the range 0.15 to 0.25 \([1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]\), below the theoretical value \(\alpha = 1/3\). Moreover, the measured size distributions are typically broader than the LSW prediction.

This discrepancy has been attributed either to diffusion effects at an interface or the inadequacy of mean field description for the systems or to insufficiently long simulation times. Several authors have developed improved theoretical models that take into account interaction effects \([3]\). These models involve expansions in power of the parameter \(\sqrt{\phi}\) (where \(\phi\) is the volume fraction of the minority phase), whose importance was first recognized by Tokuyama and Kawasaki \([23]\). To first order in \(\sqrt{\phi}\), interactions give rise to two types of corrections: a direct correlations between droplet pairs where small droplets are likely to be surrounded by large ones as well as a "medium polarization" in which the rate of evolution of a droplet is not only a function of its radius \(R\), but also of the droplets within a neighborhood of size \(\xi\). The models reproduce the broadening of experimental distributions while predicting that correlations do not alter the value of the LSW exponent \(\alpha\) just as observed in experiments. Recent experimental results \([24]\) have revealed the above types of correlation.
effects in the two-dimensional coarsening process. Thus, according to the direct correlation
effect small (large) cluster are more likely to be found near large (small) ones. The other
correlation effect, experimentally observed, is a medium polarization according to which the
rate of change of the size cluster is determined not only by its size but also by the influence
of others in its surroundings. Thus, the medium polarization around two nearby clusters
promotes the accelerated shrinkage of one and growth of the other, the rates of shrinkage
and growth being larger than if both clusters were isolated. Taking into account these cor-
relation effects it has been proven \[25\] that within an *off-centre diffusion* approach \[26, 27\]
the temporal law of the *OR* process in two-dimensions can be, under some circumstances,
different from that predicted by the *LSW* theory.

The purpose of this paper is an examination of the cluster growth where the dynamic
is dominated by the coarsening process. As in the previous case of the *OR* in two-dimensions
\[25\], we will suppose that the particles transport from shrinking cluster to growing one occurs
by an *off-centre diffusion* mechanism \[26, 27\]. The identifying of the *Markowian chains* (as
within the *Flux over Population Method* \[28\]) is based on a local feature of the medium,
according with, the small cluster (which disappears during the *OR* process) is likely to be
surrounded by the greater ones (which increase by the incorporation of mass into them). In
this way, the diffusion solution will be determined as a function of both the growing and
shrinking cluster sizes. Also, it is shown that the frequency transfer of particles between
the shrinking cluster and the growing one may acquire high values due to the medium
polarization. Particular properties of the clusters are included in the model. As a result, the
temporal power law of the cluster growth derived in this theoretical model differs again, as
in the two-dimensional case, from that predicted by the *LSW* theory. Some experimental
results on the growth of the *Ag* clusters embedded in a *KCl* matrix will be analyzed by the
present theory.

It must be pointed out that the present approach of the three-dimensional *OR* process
can work only under assumption that the correlation effects occur (especially, the direct correlation between the cluster sizes). This fact can exist if the clusters nucleate and grow at dislocation lines and/or at grain boundaries (situation which is frequently supposed for clusters embedded in solid matrix [29]).

Far to elucidate the controversy regarding the general theory of the OR process (especially related to the famous $\frac{1}{3}$), the off-centre diffusion approach of OR gives, at least, a real way to account for the correlation effects. Moreover, this distinguishes from the others in this branch by the fact that the clusters act as entities in theirself and, consequently, the temporal power law of OR is derived in connection with their particular properties [25].

2 Off-centre Diffusion Approach of the OR Process.

As we have said in the previous section, according to the direct correlation effect within the two-dimensional OR process experimentally observed by Krichevsky and Stavans [24], small (large) clusters are more likely to be found near large (small) ones. Supposing that this fact is appropriate also in three-dimensions, let us examine the effect of such a correlation on the diffusion process in the OR phenomenon. Consequently, we will assume the situation which is shown in Fig. 1, where there exist a cluster of $N$ sites slightly displaced around the position of the large cluster and, only $N_o$ sites ($N_o < N$) around the position of the small cluster. These off-centre sites (the "kinks" of the cluster surface) serve both to the particles motion on the cluster surface [30] and as available sites for the particles transfer from the shrinking (small) cluster to growing (large) cluster [25, 26, 27]. In the following, we assume that the motion among the available sites of the same cluster is described by the frequency $p_o$ while the transfer frequency from shrinking (small) cluster to growing (large) one is $p$, $p_o \gg p$. In this way, the particles leave the "kink" sites of the surface of the shrinking cluster and "condense" in the "kink" sites of the nearest-neighbour growing cluster. The equations
for the \( N_o \) concentrations \( n_i(x, t), i = 1, N_o \), can readily be written as:

\[
\frac{\partial n_1}{\partial t} = p_o \sum_{i=1}^{N_o} (n_i - n_1) + p \sum_{j=1}^{N} (n_j(x + \xi) - n_1)
\]

\[\vdots\]

\[
\frac{\partial n_{N_o}}{\partial t} = p_o \sum_{i=1}^{N_o} (n_i - n_{N_o}) + p \sum_{j=1}^{N} (n_j(x + \xi) - n_{N_o}).
\]

We perform the power-series expansion of the concentration function in (1). Since, as usual in diffusion processes, we are interested only in slowly varying functions in time and space \[26\], \[27\], we may neglect the terms containing the first-order derivatives in the series expansion of (1). Equations (1) can, therefore, be approximated by

\[
\frac{\partial n_1}{\partial t} = p_o \sum_{i=1}^{N_o} (n_i - n_1) + N_1 \frac{1}{2} p \xi^2 \frac{\partial^2 n_1}{\partial x^2}
\]

\[\vdots\]

\[
\frac{\partial n_{N_o}}{\partial t} = p_o \sum_{i=1}^{N_o} (n_i - n_{N_o}) + N \frac{1}{2} p \xi^2 \frac{\partial^2 n_{N_o}}{\partial x^2},
\]

whose Fourier transforms read

\[
n_{1q} \left( \omega - N_1 \frac{1}{2} p \xi^2 q^2 \right) + n_{2q} p_o + \ldots + n_{N_o q} p_o = 0
\]

\[\vdots\]

\[
n_{1q} p_o + \ldots + n_{(N_o-1) q} p_o + n_{N_o q} \left( \omega - N_1 \frac{1}{2} p \xi^2 q^2 \right) = 0.
\]

Looking at the system of equations (2) and at their Fourier transforms we can see that the problem amounts to finding the lowest eigenvalue of a system of equations which has the general matrix form \[27\],

\[
A = p_o A_o + p A_1 + A_2.
\]

Here, \( A_o \) describes the diffusion among the off-centre sites belonging to the same cluster; \( A_1 \) corresponds to the second-order expansion of the concentration functions; and \( A_2 \) includes
the higher-order contributions of the derivatives. We note that in the long-wavelength limit $A_2$ vanishes. The lowest eigenvalue can be obtained by a perturbation [27] given by

$$\omega = \pi A_1 n = \frac{1}{2} N p \xi^2 q^2,$$

(5)

where $n$ is the (column) vector adjoint to eigenvector

$$\mathbf{n} = N^{-\frac{1}{2}} (1, 1, \cdots, 1).$$

(6)

The diffusion solution is given by

$$n(x, t) = \frac{n_0}{\sqrt{2\pi N p \xi^2 t}} \cdot \exp \left( -\frac{x^2}{2 \cdot N p \xi^2 t} \right).$$

(7)

This equation gives the particles number per unit length at the time $t$ and at the distance $x$ due to the diffusion of an initial $\delta$-form concentration of particles. $N$ is in direct proportion with the cluster surface and, in a crude approximation, can be expressed by

$$N \approx \frac{1}{2} \cdot \frac{R^2}{a_o^2},$$

(8)

where $a_o$ is the atom radius and $R$ the radius of the growing cluster. The above equation establishes that, due to the geometrical obstructions, see Fig. 1, only half of the peripheral off-centre sites (the "kinks") are available to receive diffusing particles.

The diffusing particles come, in the $OR$ process, from shrinking cluster and, indeed, we must take into account its dissociation rate. As it is well known, the cohesive energy per atom decreases with decreasing cluster size [31] and, therefore, the dissociation rate for shrinking clusters become considerably greater in comparison with growing ones. This is important to gain physical insight in the $OR$ process. The shrinking or growing of an cluster begins from a critical radius that depends on its size. A common definition of the critical radius states that it is the radius of a droplet which is instantaneously neither growing nor shrinking. The dissociation rate is related, in the $RRK$ theory ($Rice, Ramsperger,$
Kassel) \[32\], to both the thermal energy \( E_o = E_o(T) \) (\( T \) stands for the temperature) and the dissociation energy of the particle \( E_D \),

\[
K(T) = \nu \left[ \frac{E_o - E_D}{E_o} \right]^{s-1}.
\] (9)

Here, \( \nu \) is the vibrational frequency, \( s \) is the number of vibrational degrees of freedom of the cluster and \( T \) is the temperature. One seems that the excitation of the cluster, ultimately, causes heating and dissociation and that to a large extent the excitation mechanism is decoupled from the dissociation. Thus, with such a simplification, the dissociation rate can be calculated by (9). In this way, we may find the total amount of dissociated particles from the shrinking (small) cluster during the thermal annealing as

\[
n_o = W \cdot K(T) \cdot t,
\] (10)

where \( W \) accounts for the surface atoms of the cluster and \( t \) is the time of the thermal annealing. Further, the \( n_o \) entering in equation (7) is replaced by the above amount.

The other correlation effect, theoretically assumed in \[23\] and experimentally observed in two-dimensional OR \[24\], is a medium polarization according to which the rate of change of the size cluster is determined not only by its size but also by the influence of others in its surroundings. Thus, the medium polarization around two nearby clusters promotes the accelerated shrinkage of one and growth of the other, the rates of shrinkage and growth being larger than if both clusters were isolated. The medium polarization is due to the electrostatic interaction between the charges associated with each shrinking (negative charge) or growing (positive charge) cluster. This charge is proportionally to the rate of change of the cluster area. The medium polarization consists in the appearance of an electrostatic potential

\[
\Phi(r) = C e^{-\frac{r}{D}},
\] (11)

as solution of the Poisson - Boltzmann equation \[33\]. \( C \) is a constant depending on the cluster size and \( D \) is the Debye length. The Debye length is in inverse proportion with
where \( M \) is the number of clusters within the neighborhood of the reference cluster (the shrinking or growing cluster). Indeed, the activation energy for particles transfer from shrinking cluster to growing one is considerably lowered due to this electrostatic potential \( (\Phi) \), thereby enhancing the transfer frequency (see eq. 7)

\[
p = \nu \exp (-\beta (E_b - e\Phi)),
\]

where \( E_b \) denotes the threshold energy for activation, \( \nu \) is a prefactor, and \( \beta = (K_B T)^{-1} \). In this way the medium polarization accelerates both the shrinkage of a small cluster and the growth of a large one. As we have said in the introduction part, this correlation effect (as well as the former) can be properly understood for embedded clusters in solid matrix only if the nucleation sites, which really promote the growth of clusters, occur at dislocation lines or/and at grain boundaries \[29\].

Diffusing particles added to a growing cluster having an initial critical radius \( R_o \) leads to an increase in its radius to \( R \);

\[
n = \rho \frac{4\pi}{3} \left( R^3 - R_o^3 \right),
\]

where \( \rho \) is the particles concentration in the cluster. Also, taking into account (7) we can express \( n \) by

\[
\int_{R_o}^{R} n (\xi - R, t) dR = \frac{WK(T)}{\sqrt{\alpha_o \xi^2}} \sqrt{t} \cdot \int_{R_o}^{R} \frac{1}{R} \exp \left( -\frac{(\xi - R)^2}{\alpha_o \xi^2 t} \right) dR,
\]

where \( \xi \) stands for the separatrix between the shrinking cluster and the growing one. For large \( t \) and as \( \xi \approx R \)[24] the exponential function vanishes and the above equation becomes

\[
\frac{R^3 - R_o^3}{\ln \frac{R}{R_o}} = \frac{WK(T)\alpha_o}{\rho \sqrt{\pi \alpha_o \xi^2}} \sqrt{t}.
\]

The last equation gives the time \( t \) for an increase of the cluster radius from a radius \( R_o \) to \( R \) by an off-centre diffusion mechanism . Indeed, the diffusion process is related to the frequency transfer \( p \) and, as we have said, within the particular dependencies of \( p \) we must take into account (11).
3 Experimental.

Metal clusters can be produced with ease in solid matrix [29]. For example, electrolytical or additive colouring of the alkali halide crystals containing relatively high impurity concentration (≈ 10^{18} impurities per cm^3) lead, directly, to cluster formation [29, 35, 36]. Another, more adequate, method in order to study the kinetic aspects of the embedded clusters is the thermal annealing of alkali halide crystals containing negative metallic ions [34, 35]. This method advantages a better control of the cluster size but, it must be pointed out that the obtaining of the negative metallic ions is, generally, more difficult to do, this process requiring appropriate conditions related to the external factors as temperature, electric field as well as the filling factors; when large impurity concentration (≈ 10^{18}) is used then insignificant amount of the negative metallic centres are obtained. In the present paper, we show the experimental data for metallic clusters obtained by thermal annealing of the KCl : Ag^- samples.

KCl single crystals containing Ag^+ ions in a concentration of 5 · 10^{17} ions/cm^3 have been grown by the Kyropoulos method in air. Under electrolytical colouring performed by an usual device in air at 573K and at 8000 V/cm we obtain samples containing Ag^- negative metallic centres (see the initial (1) peak at 290 nm in the Fig. 2a) as well as few small silver clusters (see the initial (1) peak at 380 nm in Figs. 2a and b). Thermal annealing at a given temperature of the KCl : Ag^- samples leads, progressively, both to the decrease of the Ag^- amount and to the obtaining of the other, more and more, clusters (see the rise trend of the absorption curves). A possible scenario for the conversion of the Ag^- ions towards Ag^o centres and/or cluster states begins with Ag^- + kT ↔ F + Ag^o (the F means F centre and the Ag^o means an interstitial silver atom) [34]. The following step after the above reaction should be the precipitation of the silver atoms.

Also, during the thermal annealing, the clusters have an increase trend of their sizes.
Experimentally, this fact can be observed by a change of the optical spectra; the absorption maximum shifts, progressively, towards high wavelengths. In Figs. 2a the evolution of the optical spectra for the sample is shown with respect to the time of annealing at 800K; the first absorption maxima are due to $Ag^-$ centres (290 nm), the second absorption maxima are due to silver clusters and the third, very slight peaks are due to the $F$ centres (550 nm). Another set of optical spectra, corresponding to a thermal annealing at 920K, is shown in Fig. 2b. In this figure we have eliminated the absorption maxima corresponding to the $Ag^-$ centres.

As we can observe, besides the formation of the silver clusters, the thermal treatment of the samples containing $Ag^-$ leads to the appearance of the $F$ centres (the second peak in the right side of the figures). The $F$ centre peak (550nm) has, as it is well known and as one can observe in the Figs. 2a and b, no shift during the thermal annealing. In contrast with the $F$ centre behaviour, the absorption maximum of the silver clusters moves, as we can see, towards the high wavelengths in . Curiously enough, despite the fact that both the samples arise from the same $KCl:Ag^-$ crystal, the thermal annealing at 920K provides a better production and conservation of the $F$ centres (see Fig. 2b). However, a long time annealing will lead to destroy all the $F$ centres.

From the optical spectra, the cluster radii are determined using electrodynamic (Mie) theory \[37\]. Application of this theory to large metal clusters is successful and a review of the method as well as more complementary features are given in the book of Vollmer and Kreibig \[37\]. The extinction cross section is given by

$$\sigma_{ext} = \frac{2\pi}{k^2} \sum_{L=1}^{\infty} (2L+1) \text{Re} \left( a_L + b_L \right),$$ \hspace{1cm} (16)

where $k$ is the wavevector and $a_L$ and $b_L$ are coefficients containing Bessel and Hankel functions which depend on the complex index of refraction of the particle, the real index of refraction of the surrounding medium and the size parameter $x = k \cdot R$. The $R$ is the cluster radius.
radius. For clusters larger than about 10nm the size dependence of the optical spectra is an extrinsic cluster size effect due to electrodynamics of the excitation which is governed only by the dimension of the particle with respect to the wavelength of the light.

In Figs. 3a and b it is shown the time of the thermal treatment and the corresponding increase of the cluster radii for the thermal annealing both at 800K and at 920K. The shapes of the curves are identically which means that no influence of the F centres on the cluster size evolutions exists. Consequently, in the following we will discuss only a set of experimental data (920K).

4 Results.

As it is well-known one can distinguish two regimes in the cluster growth process. The initial stage of cluster increase, following the formation of nuclei, is, in our case, due to the conversion of the negative metallic centres (see the decrease trend of the Ag\(^{-}\) peak (270 nm)). Thus, the main stage of the phase separation proceeds as a uniform growth of a number of precipitate particles from the supersaturated matrix. In this way, during the thermal treatment, the cluster radius increases initially due to the addition of particles coming from the source of the solute ions. When this concentration decreased, the increase of cluster radius is due, mainly, to particle transport from small clusters to larger ones. This is the second stage in the cluster growth process which is known as the Ostwald Ripening (OR) . It must be pointed out that the delimiting of the boundary between the two increasing regimes is difficult to do, but one supposes that the OR regime begins usually before the solute concentration decreases considerably . In Fig. 4 we have shown the theoretical curve (equation 15) derived within the off-centre diffusion approach, the theoretical curve corresponding with the LSW theory and the experimental curve for the increase of the cluster radius in the OR stage for a thermal annealing at 920K. We have approximated the
start of the OR process around of the $R = 16\,\text{nm}$. For the theoretical calculus (the *off-centre diffusion* approach) we have used appropriate values for dissociation energy as $E_D = 0.7\,\text{eV}$ and for the threshold energy of the particles transfer as $E_b - e\Phi = 1\,\text{eV}$. One can say that there is an agreement between the theoretical curve derived within the *off-centre diffusion* approach and experimental curves. This agreement becomes much better for larger radii ($R > 18\,\text{nm}$). In contrast to the former, the agreement between the LSW theory and the experiment is very good for $17\,\text{nm} < R < 19\,\text{nm}$ and more poor in the rest.

5 Conclusion.

In summary, by the present paper, we have analyzed how the correlation effects [23, 24] can be taken into account within an *off-centre diffusion approach* of the OR process. The time dependence of the cluster growth derived by this theoretical approach, under the assumptions established in the introductory part, differs from that predicted by the *LSW theory* but agrees with the most simulations and experiments in the sense that $\alpha < \frac{1}{3}$ [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. It must be pointed out that though the dynamics is different from that predicted by *LSW* theory and, one seems that there is a better agreement of the theoretical approach presented here with the experimental data for larger clusters ($R > 18\,\text{nm}$), this fact do not invalidate the known theoretical results [1, 2, 3, 4, 5, 6, 7, 8]. A source of this difference could consist within the stress effect in the host matrix and/or the correlation effects do not exist in three-dimensional case. Consequently, the experimental data going over $R = 20\,\text{nm}$ and a careful study of the stress effect should be helpful.

Beforehand to check again the agreement between the theory and the experiment we can see that this approach is distinguished from the others in this branch by the fact that the clusters act as individual entities and, hereby, allowing of the introduction of the cluster properties according with the recent discoveries [31]: the cohesive energy, the dissociation
rate for the shrinking cluster, the mobility of the particles inside the cluster which promotes the quasi-sphericity of the cluster shape, the cluster kinks as the sites from where the particles leave the surface of the shrinking cluster or the sites where these particles condense on the surface of the growing cluster. However, despite of a relative agreement only between theory and experiment below $R = 18\text{nm}$ we may say that the results are encouraging in further pursuing of this off-centre diffusion approach. Also, we may say that a careful investigation on the transfer frequency $p$ (within which the explicit form of the electrostatic potential due to medium polarization should take into account) can rise the agreement between the experimental and theoretical data.

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The way of the particles transport between the shrinking cluster and the growing one. The particles leave the surface of the shrinking cluster from the ”kink positions” (the $N_{off}$ -centre sites) and ”condense” in the ”kink positions” (the $N_{off}$ - centre sites) of the growing cluster.

The changes of the absorption spectra during thermal treatment at 800K and at 920K. The second peak in (b) is due to the F centres.

The increase of the cluster radius $R$ (Å) versus the time $t$ (min.) of the thermal treatment at 800K and at 920K.

The time $t$ (min.) of thermal treatment at 920K for the increase of the Ag cluster radii $R$ (Å) at different sizes in the OR stage.

- □ - experimental,
- - theoretical (off centre diffusion approach),
- † - theoretical (LSW theory).

The Ag clusters are embedded in the KCl matrix.