

References

1. Hill, T.L.: Thermodynamics of Small Systems, I, II; New York, Amsterdam, 1963, 1964
2. Ulbricht, H.; Schweizer, J.; Mähne, R.; Schweitzer, F.: Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions, Teubner, Leipzig, 1988
3. Meakin, P.: The Growth of Fractal Aggregates and Their Fractal Measures; In: Domb, C.; Green, M.S.; Ledowitz, J.L.: Phase Transitions and Critical Phenomena; Volume 12, London, New York, 1980, p. 335-469
4. Pfeifer, H.; Dehne, W.; Siegel, H.: Ann. Phys., 7, 42, H. 4-6 (1985) 496
5. Jeamish, J.R.; Hikata, A.; Tell, L.; Elbaum, C.: Phys. Rev. Lett. 50, 6 (1983) 425
6. Fink, H.-P.: Dissertation A, Universität Rostock, 1976
7. Paterson, L.: Phys. Rev. Lett. 52 (1984) 1621
8. Hewett, T.A.: 61. annual Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans (1986)
9. Maloy, K.J.; Feder, J.; Jossang, T.: Phys. Rev. Lett. 55 (1985) 2688
10. Stokes, J.P.; Veltz, D.A.; Gollub, J.P.; Dougherty, A.; Robbins, M.D.; Chaikin, P.M.; Lindsay, H.M.: Phys. Rev. Lett. 57 (1986) 1718
11. Daccord, G.: Phys. Rev. Lett. 58 (1987) 479  
Daccord, G.; Lenormand, R.: Nature 325 (1987) 41
12. Ulbricht, H.; Pohlmann, M.: Wiss. Z. Univ. Rostock, Math.-Naturw. Reihe 28, 3 (1979) 229
13. Ulbricht, H.; Pohlmann, M.: Wiss. Z. Univ. Rostock, Math.-Naturw. Reihe 30, 1 (1981) 47
14. Schmalzer, J.; Schweitzer, F.: Z. phys. Chem. (Leipzig) 271 (1990) 565
15. Witten, T.A.; Sander, L.M.: Phys. Rev. Lett. 47 (1981) 1400  
Witten, T.A.; Sander, L.M.: Phys. Rev. 3 27 (1983) 5686
16. Chen, J.D.; Wilkenson, D.: Phys. Rev. Lett. 55 (1985) 1892

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NUCLEATION AND CLUSTER GROWTH IN SMALL CAVITIES  
WITH DIFFUSION INTERACTION

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1. Introduction

Most of the well known theories of nucleation and cluster growth deal with a cluster size distribution where the space coordinates of the clusters are neglected. Such a mean cluster distribution,  $f(n,t)$ ,  $n$  being the cluster size, involves the appropriate information of the phase transition in systems, where exchange processes (e.g. via diffusion) proceed much more faster than the process of cluster formation and growth /1,2/. This situation of a well mixed system is realized e.g. in gases and simple liquids.

Finite size effects in such systems, which are obtained from a conservation of the total particle number, result in a global depletion of free particles during the phase transition. This effect leads to a three step scenario of the phase transition, consisting of (1) nucleation, (2) simultaneous growth of clusters, (3) Ostwald ripening, which has been widely discussed in previous papers (see e.g. /3/ and references therein).

A quite different situation is given in systems where the characteristic time scale of nucleation is of the same order as the relaxation time of the imbedding matrix, e.g. in glass forming melts /4/. Here local effects, say the local supersaturation, play the important role, because long range order relaxations mostly are impossible because of elastic strains /5/ and small diffusion coefficients. Since the system is spatially highly inhomogeneous, the appropriate cluster distribution is given by  $f(n(r),t)$ , where the cluster size depends on the space coordinate  $r$ .

The box model give us a quite simple model to include the space dependence of the phase transition. We will discuss here two cases:

(i) The boxes act as a grid which divides the system volume  $V$  into a number of small subvolumes  $v(i)$ , where the index  $i$  gives us the space coordinate of the box. In this way we have a discrete space division. Long range order exchanges are now considered by means of coupling parameters between the subvolumes. — This model allows us e.g. the investigation of diffusion zones in the vicinity of the clusters.

(ii) Moreover, the nature creates also real box systems, e.g. the pores in zeolites or the cavities in gels. These pores, cavities are connected by small tunnels or passages, which allow a diffusion of particles /6/. The diameter of such cells ranges between 5 and 80 nm;  $10^2$  to  $10^4$  particles are included in one cell /7/. That means, we have here a realization of the former discussed /2,3,8/ small system, but it is not closed, but connected with the neighboring small systems.

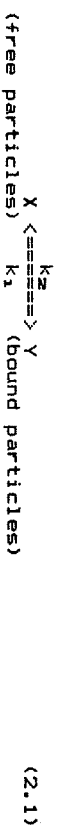
The first stage of the phase transition, nucleation, in such small cavities is mainly governed by the conditions (supersaturation) in the box, whereas the further stages, growth of clusters, result from the diffusion of free particles from neighboring boxes /9/.

The basic ideas developed in the following describe both cases from an uniform point of view, where a number of special cases can be easily derived from.

## 2. Model of Interacting Boxes

We discuss now a system with the volume  $V$  which is divided into  $z$  small subvolumes  $v^*$  characterizing the box volume. The boxes are distinguished by an index  $i = 1, 2, \dots, z$ .

In the system a phase transition occurs, characterized by the reaction between two kinds  $X$  and  $Y$



The values of  $X$  and  $Y$  differ from box to box and depend on time, therefore we introduce the state vectors:

$$\begin{aligned} \underline{X}(t) &= \{X_1(t), X_2(t), \dots, X_z(t)\} \\ \underline{Y}(t) &= \{Y_1(t), Y_2(t), \dots, Y_z(t)\} \end{aligned} \quad (2.2)$$

Further, we assume that the kind  $X$  can diffuse, whereas the kind  $Y$  in every box is concentrated in only one cluster of size  $n$ , which cannot move. The total particle number  $N_j$  of box  $j$ , is now given by the number of free particles,  $N_{j,j}$ , and the cluster of size  $n_j$ . Equivalent to (2.2) we have the space-dependent distributions:

$$\begin{aligned} \underline{N}_j(t) &= \{N_{j,1}(t), N_{j,2}(t), \dots, N_{j,n_j}(t)\} \\ \underline{n}(t) &= \{n_1(t), n_2(t), \dots, n_z(t)\} \end{aligned} \quad (2.3)$$

Because of diffusion interaction between the boxes yields:

$$N_j = N_{j,j} + n_j \neq \text{const.} \quad (2.4)$$

but for a fixed total particle number of the system we obtain:

$$\sum_{j=1}^z N_j = \sum_{j=1}^z (N_{j,j} + n_j) = N_{\text{free}} = \text{const.} \quad (2.5)$$

## 3. Stochastic Description of Nucleation and Diffusion — the Multivariate Master Equation

In the framework of a stochastic description we discuss the probability  $P(\underline{N}_j, \underline{n}_j, t)$ , to find a given space- and time dependent distribution of free particles and clusters in the box system. The change of  $P(\underline{N}_j, \underline{n}_j, t)$  is given by the multivariate master equation /10/. With respect to reaction (2.1) and for a non-diffusing component  $Y$  this equation reads:

$$\begin{aligned} \frac{\partial P(\underline{X}, \underline{Y}, t)}{\partial t} &= \sum_{i,j} \{ d_{i,j}^+ (X_i+1) P(\underline{X}_i+1, \underline{X}_j-1, \underline{X}, \underline{Y}, t) \\ &\quad - d_{i,j}^- (X_i) P(\underline{X}_i, \underline{X}_j, t) \} \\ &\quad + \sum_i \{ k_1 (Y_i+1) P(\underline{X}_i-1, Y_i+1, \underline{X}, \underline{Y}, t) \\ &\quad - k_2 (X_i+1) P(\underline{X}_i+1, Y_i-1, \underline{X}, \underline{Y}, t) \} \\ &\quad - \{ k_{11} (Y_i) + k_{21} (X_i) \} P(\underline{X}, \underline{Y}, t) \} \end{aligned} \quad (3.1)$$

The values  $\underline{X}^*, \underline{Y}^*$  denotes those elements of the vectors (2.2) which have not changed, the changed elements are explicitly written down.

The first term of eq. (3.1) expresses the change of free particles due to diffusion processes to/from neighboring boxes with a transition rate  $d_{i,j}$  ( $N_{i,i}$ ) between the boxes  $i$  and  $j$ . It yields  $d_{i,j} = 0$  for non-adjacent boxes.

The second term of eq. (3.1) considers the changes of the free and bound particles due to reaction (2.1), where the transition rates  $k$  depend on the actual values of  $X$  and  $Y$ .

In order to make now assumptions for the transition rates, we suppose, that the formation and growth or the diminution of the clusters explicitly depend on the conditions inside the box only. In this way we choose the transition rates for the cluster growth and shrinkage in a former proved form /2,3/:

$$W(N_{1,J}-1, n_{2,J}+1 | N_{1,J}, n_{2,J}) = \alpha n_{2,J}^{2/2} N_{1,J} / V^* \equiv W_{R-}(N_{1,J}) \quad (3.2)$$

$$W(N_{1,J}+1, n_{2,J}-1 | N_{1,J}, n_{2,J}) = \alpha n_{2,J}^{2/2} N_0(n_{2,J}) / V^* \equiv W_{R+}(N_{1,J}) \quad (3.3)$$

The transition probability of cluster growth (3.2) increases with the cluster surface and with the density of free particles inside the box. The parameter  $\alpha$  characterizes the time scale of the implementation of particles into the cluster, it depends on the surface tension and the sticking coefficient.

The transition probability of cluster shrinkage (3.3) is again proportional to the cluster surface and depends on the equilibrium concentration of free particles above the curved cluster surface,  $N_0(n_{2,J}) / V^*$ . This value depends on the cluster size and the saturation concentration  $c_{eq}(T)$  via /8/:

$$\frac{N_0(n_{2,J})}{V^*} = c_{eq}(T) \exp \left\{ \frac{2B}{k_B T} n_{2,J}^{-1/2} \right\} \quad (3.4)$$

where  $B$  is a constant with respect to the surface tension.

Additional to eq. (3.2) it holds for the creation of dimers:

$$W(N_{1,J}-2, 2 | N_{1,J}, 0) = \alpha N_{1,J} (N_{1,J}-1) / V^* \quad (3.5)$$

The transition probabilities of diffusion of free particles are chosen in analogy to refs /11, 12/ as:

$$W(N_{1,J}-1 | N_{1,J}) = \sum_m D_{jm} N_{1,J} / V^* \equiv W_D^-(N_{1,J}) \quad (3.6)$$

$$W(N_{1,J}+1 | N_{1,J}) = \sum_m D_{mj} N_{1,m} / V^* \equiv W_D^+(N_{1,J}) \quad (3.7)$$

$D_{1,j}$  is the coupling constant between the boxes. It yields:

$$D_{mj} = D_{jm} \text{ for adjoining boxes (Index } m)$$

$$D_{1,j} = 0 \text{ for non-adjoining boxes}$$

$$(3.8)$$

The coupling constant is related to Fick's diffusion coefficient

$D_F$  via  $D_{1,j} = D_F / l^2$ , where  $l$  is the characteristic length of the system, e.g. the box diameter.

We use further the abbreviations:

$$a(n_{2,J}) = \alpha n_{2,J}^{2/2} / V^*; \quad d_{1,j} = D_{1,j} / V^* \quad (3.9)$$

and for  $d_{1,j}$  not explicitly depending on space, also  $d_{1,j} = d$ .

The transition rates for the change of free particles in box  $i$  are now composed from two parts:

$$W(N_{1,J}+1 | N_{1,J}) = W_{R+} + W_D^+ \\ = a(n_{2,J}) N_0(n_{2,J}) + \sum_m d_{mj} N_{1,m} \quad (3.10)$$

$$W(N_{1,J}-1 | N_{1,J}) = W_{R-} + W_D^- \\ = N_{1,J} \{ a(n_{2,J}) + \sum_m d_{jm} \} \quad (3.11)$$

It depends on the ratio of the two kinetic prefactors  $a(n_{2,J})$  and  $d_{1,j}$  whether the reaction or the diffusion processes will govern the kinetics of cluster formation (reaction or diffusion limited cluster growth) and thereby the cluster distribution.

#### 4. Deterministic Description of the Distributions

The deterministic equations for the vectors (2.3),  $N_i$  and  $\Omega_i$ , agree with the mean values equations which can be derived from  $P(N_i, \Omega_i, t)$  by means of the relation:

$$\langle N_{1,J}(t) \rangle = \sum_{\langle N_{1,J} \rangle} N_{1,J} P(\langle N_{1,J}, \Omega_{1,J}, t) \quad (4.1)$$

which results with the master equation (3.1) in /13/:

$$\frac{d \langle N_{1,J} \rangle}{dt} = \sum_k \Delta_k \langle N_{1,J} \rangle < W^*(N_{1,J}) \rangle \quad (4.2)$$

where  $k = \{+, -\}$  and  $\Delta_{+} = +1$ ,  $\Delta_{-} = -1$  (dimer decay  $\Delta = +2$ , dimer creation  $\Delta = -2$ ). By means of the transition probabilities (3.10), (3.11) we obtain:

$$\langle \dot{N}_{1,J} \rangle = \langle a_{1,J} N_0(n_{2,J}) + \sum_m d_{mj} N_{1,m} - N_{1,J} \{ a(n_{2,J}) + \sum_m d_{jm} \} \rangle \quad (4.3)$$

or, with respect to eq. (4.4):

$$\langle \dot{n}_{2,J} \rangle = \langle W_{R-}(N_{1,J}) - W_{R+}(N_{1,J}) \rangle = \langle a(n_{2,J}) \langle N_{1,J} - N_0(n_{2,J}) \rangle \rangle \quad (4.4)$$

$$\langle \dot{N}_{1,J} \rangle = - \langle \dot{n}_{2,J} \rangle + \sum_m d_{jm} \langle N_{1,m} - N_{1,J} \rangle \quad (4.5)$$

Eq. (4.5) means a system of equations for  $j = 1, \dots, z$ . If the total particle number of the system is conserved, it follows from (2.5):

$$\sum_{j=1}^z \langle N_{1,j} \rangle = - \sum_{j=1}^z \langle n_j \rangle \quad (4.6)$$

and therefore for the diffusion:

$$\sum_{j=1}^z d_{jm} \langle N_{1,m} - N_{1,j} \rangle = 0 \quad (4.7)$$

In order to compare the results for the deterministic equations of cluster growth in box systems with the known equations derived for well mixed systems /3/, we turn to a continuous description of space, that means  $\langle n_j \rangle = n(r)$  and  $\langle N_{1,j} \rangle = N_1(r)$ , and introduce the Radius of the assumed spherical cluster by

$$R^3(r) = n(r)/(4\pi c_\alpha/3) \quad (4.8)$$

By means of

$$\frac{2B}{3k_B T} n^{-1/3}(r) = \frac{d_0}{R(r)} \quad ; \quad d_0 = \frac{2\sigma}{c_\alpha k_B T} \quad (4.9)$$

do being the capillary length,  $\sigma$  the surface tension and  $c_\alpha$  the density of the cluster, eq. (4.4) now reads as follows:

$$\dot{R}(r) = \frac{\alpha c_{mg}(T)}{(4\pi c_\alpha/3)^{1/3}} \left\{ \frac{N_1(r)}{c_{mg} V^*} - \exp \frac{d_0}{R(r)} \right\} \quad (4.10)$$

After using power expansions and introducing the critical radius by

$$R_{cr}(r,t) = d_0 / \ln \{ N_1(r,t)/c_{mg} V^* \} \quad (4.11)$$

we arrive finally at the deterministic growth equation

$$\dot{R}(r,t) = \alpha \frac{c_{mg}(T) d_0}{(4\pi c_\alpha/3)^{1/3}} \left\{ \frac{1}{R_{cr}(r,t)} - \frac{1}{R(r,t)} \right\} \quad (4.12)$$

Eq. (4.12) formally agrees with the known deterministic kinetics of gaseous systems /2/. But now the cluster size,  $R(r)$ , depends on the space coordinate, and the critical radius,  $R_{cr}(r)$ , too. That means, we have no global value of  $R_{cr}$ , which acts as a selection parameter for all clusters - but only a local selec-

tion. It depends on the local conditions (density of free particles inside the box and diffusion interaction with the surroundings) if  $R(r)$  is larger or smaller than the critical radius  $R_{cr}(r)$  at the same point, if the cluster can grow further or not.

On the other hand, the time dependent change of  $R_{cr}(r,t)$  is connected with the change of free particles  $N_1(r)$  by:

$$\frac{d \ln N_1(r,t)}{dt} = - \frac{d_0}{R_{cr}} \frac{d \ln R_{cr}(r,t)}{dt} \quad (4.13)$$

With respect to eq. (4.5) this means, that  $R_{cr}(t)$  depends both on the time scales of reaction and of diffusion, expressed by  $\alpha$  and  $d$ . According to whether  $\alpha$  or  $d$  dominates, we expect a quite different behaviour of the critical radius.

### 5. Evaluation of Stationary States

In order to evaluate stationary solutions of eq. (4.5), we introduce first the potentials  $V$  and  $\psi$  by assuming the evolution of the values  $n_j$  and  $N_{1,j}$  as a motion in a potential mountain:

$$\frac{d}{dt} \langle n_j \rangle = \frac{\partial V(N_{1,j})}{\partial N_{1,j}} = f(N_{1,j}, n_j) \quad (5.1)$$

$$\frac{d}{dt} \langle N_{1,j} \rangle = - \frac{\partial \psi(N_{1,j})}{\partial N_{1,j}} = - \frac{\partial V(N_{1,j})}{\partial N_{1,j}} + \sum_m d_{jm} \langle N_{1,m} - N_{1,j} \rangle \quad (5.2)$$

$f(N_{1,j}, n_j)$  is the reaction function with the related potential  $V(N_{1,j})$  with respect to box  $j$ .

$\psi(N_{1,j})$  is the Landau-Ginzburg functional with respect to the whole system. For continuous variables it has the known form /12/:

$$\psi \{x(r)\} = \int d\mathbf{r} [ V(x(r)) + \frac{1}{2} D (\nabla x)^2 ] \quad (5.3)$$

In the considered case of a discrete box system we get with the additional factor (1/2) for the sum over  $j$  and with  $d_{j,j} = d_{j,j} = d$ :

$$\psi(N_{1,j}) = \sum_j [ V(N_{1,j}) + (1/4) d \sum_m \langle N_{1,m} - N_{1,j} \rangle^2 ] \quad (5.4)$$

The stationary states, expressed by the vector  $N_{1,stat}$  are obtain-

ned from a variational derivation of  $\psi(N_{1j})$ . If the restrictive condition (4.6) holds, we need additionally a Lagrange parameter  $\lambda$ , which result in the system of equations:

$$\begin{aligned} x(N_{1j}) &= \sum_{j=1}^Z \langle N_{1j} \rangle + n_{1j} = 0 \\ \frac{\partial}{\partial N_{1j}} \{ \psi(N_{1j}) + \lambda x(N_{1j}) \} &= 0; \quad j = 1, \dots, z \end{aligned} \quad (5.5)$$

If no particle conservation holds, every derivation  $\partial \psi(N_{1j}) / \partial N_{1j}$  must vanish independently. Let us discuss now these two cases in detail.

(i) No particle conservation holds

For this case we receive from  $\partial \psi(N_{1j}) / \partial N_{1j} = 0$ :

$$\langle n_j \rangle = d \sum_m \langle N_{1m} - N_{1j} \rangle; \quad j = 1, \dots, z \quad (5.6)$$

That means that the cluster growth or shrinkage is in balance with the diffusion of free particles to/from the box.

A special solution of eq. (5.6) is given by  $\langle n_j \rangle = 0$ , that means an equilibrium state of the cluster, expressed by the condition:

$$N_{1j}^{state} = N_0(n_j) = c_{0j}(T) V^* \exp \{ 2B/3k_B T n_j^{1/3} \} \quad (5.7)$$

From the condition  $\langle n_j \rangle = 0$  results because of eq. (5.6) directly, that the same number of free particles is in all boxes. That means, we have here the homogeneous case, where in all boxes the cluster has the size  $n_j^{state}$  and the particle number is  $N_{1j}^{state}$  (5.7).

Moreover, also inhomogeneous stationary solutions should exist, where the situation in the boxes is different. From eq. (4.5) results:

$$N_{1j}^{state} = \frac{N_0(n_j) + [d/a(n_j)] \sum_m N_{1m}^{state}}{1 + m[d/a(n_j)]} \quad (5.8)$$

In the limit  $d \rightarrow 0$  we receive the homogeneous solution again, that means, diffusion is the reason for the possibility of inhomogeneous stationary states.

(ii) Particle conservation holds

For this case we must solve the system of equations (5.5). We

get first:

$$\langle n_j \rangle - d \sum_m \langle N_{1m} - N_{1j} \rangle + \lambda = 0; \quad j = 1, \dots, z \quad (5.9)$$

Summing over all equations, for the Lagrange parameter results:

$$\lambda = - \frac{1}{z} \sum_{j=1}^Z \langle n_j \rangle = \frac{1}{z} \sum_{j=1}^Z \langle N_{1j} \rangle \quad (5.10)$$

This sum define us a mean value, indicated by "x"; that means,  $\lambda$  give us the mean velocity of cluster growth or the mean velocity of the free particles changes:

$$\lambda = - "n" = "N_1" \quad (5.11)$$

In the considered case the stationary states instead of eq. (4.12) result from the system of equations:

$$\langle n_j \rangle - d \sum_m \langle N_{1m} - N_{1j} \rangle = "n" = - "N_1"; \quad j = 1, \dots, z \quad (5.12)$$

The special solution of eq. (5.12), which supposes all  $\langle n_j \rangle = 0$ , coincides with the homogeneous solution (5.8). The inhomogeneous solutions, if existing, are now given by:

$$N_{1j}^{state} = \frac{N_0(n_j) + [d/a(n_j)] \{ \sum_m N_{1m}^{state} - "N_1" \}}{1 + m[d/a(n_j)]} \quad (5.13)$$

where "N<sub>1</sub>" gives an addition coupling between the equations.

6. Numerical Simulations and Discussion

Finally we want to evaluate the time- and space-dependent cluster distribution of the box system numerically. Therefore we discuss a linear system of 50 boxes forming a ring, that means, box "1" and box "50" are neighbours. The total number of particles is conserved to 5000.

Initially in every box  $N_{1j} = N_2 = 100$ . free particles (no clusters) are included. The initial supersaturation is given by  $Y = N_{1j}/N_0 = 5$ . We assume now, that during the first time step nucleation occurs, which is governed only by the conditions inside the box. For the given constraints, the critical cluster size for the closed box is calculated as 15 particles (cluster radius  $R = 0.6975$  nm); the stable cluster size of the closed

box, which results from the depletion of free particles, remains 46 particles (cluster radius  $R = 1.013$  nm).

In order to make proper assumptions about the initial cluster distribution, a Gaussian-like distribution around the critical cluster size is presumed. From this distribution 50 cluster sizes are randomly chosen with respect to their frequency  $f$  (see Fig. 1). If  $f$  is smaller than 1 the clusters sizes are neglected (that means size 0). But, as to be seen in Fig. 1, this is the case only for clusters smaller than 9 and larger than 21 particles.

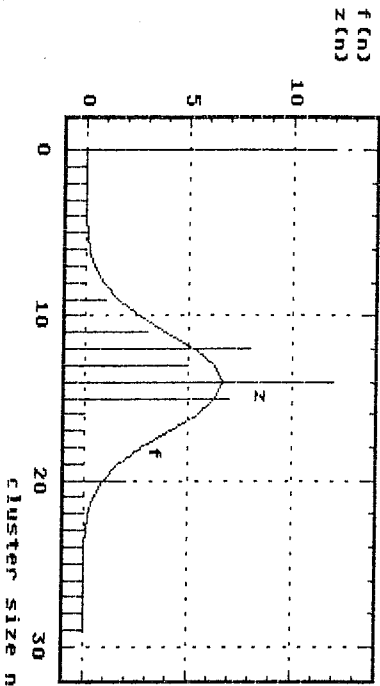


Fig. 1: Gaussian-like cluster distribution  $f(n)$  around the critical cluster size ( $n = 15$ ) and randomly chosen initial cluster  $z(n)$  distribution after nucleation period

For times  $t > 1/d/a$  (where  $d$  characterizes the time scale of the diffusion and  $a$  the time scale of the reaction) a coupling between the boxes exists via diffusion; that means the further growth of clusters can occur also at the expense of the neighbouring boxes. We have now to solve numerically the whole system of reaction-diffusion equations (4.4), (4.5).

Different time steps of the evolution of the space- and time dependent cluster size distribution are presented below in terms of the cluster radius and the critical radius of the different boxes.

Fig. 2a gives the cluster radius and the critical radius inside the closed boxes after the nucleation period.

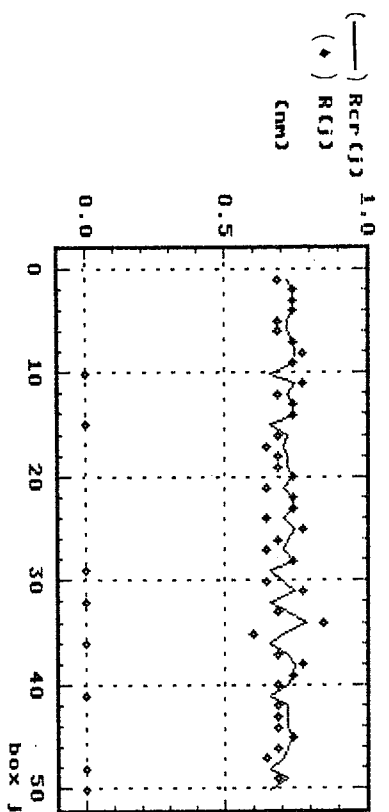


Fig. 2a: Cluster radius  $R(j)$  and critical radius  $R_{cr}(j)$  (—) versus box number for  $t = 1$  time step ( $d/a$ )

The following snapshots show the evolution with time (see Figs. 2b-e).

The evolution of the time- and space-dependent cluster distribution leads to the following conclusions:

- (1) Slightly subcritical clusters (e.g. with 13 particles, compared to the critical cluster size of 15) are able to grow to a supercritical size, if the diffusion from the neighbouring boxes is large enough to decrease the local critical radius by an influx of free particles.

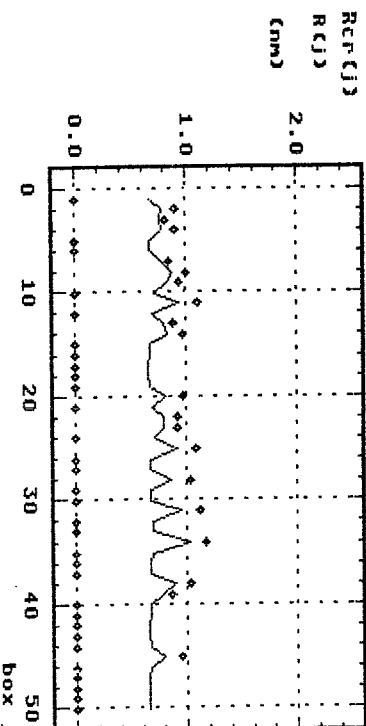


Fig. 2 b: ... for  $t = 5$  time steps

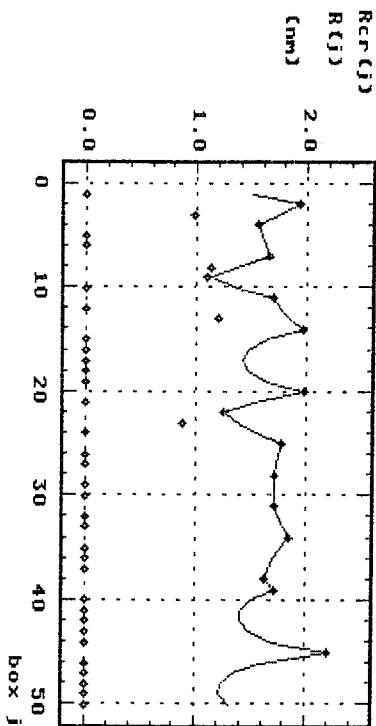


Fig. 2 c: ... for  $t = 100$  time steps

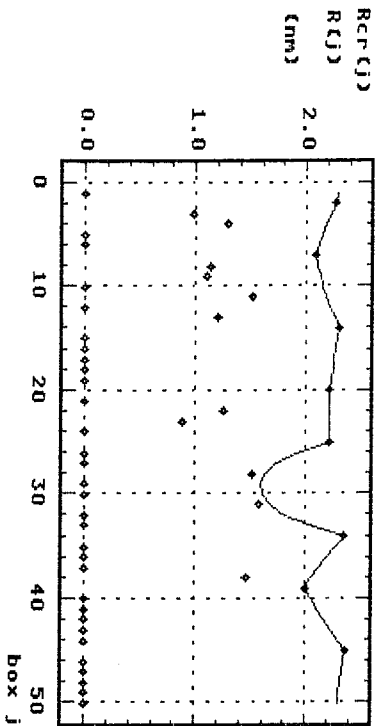


Fig. 2 d: ... for  $t = 1000$  time steps

(ii) The growth of clusters over large time intervals depends strongly on the cluster distribution in the surroundings (local competition effect). A consideration of the space dependence shows, that in general the initially largest cluster will not surely superior to the others (as to be seen e.g. in box 34 and 45, comparing time step 5 with time step 100).

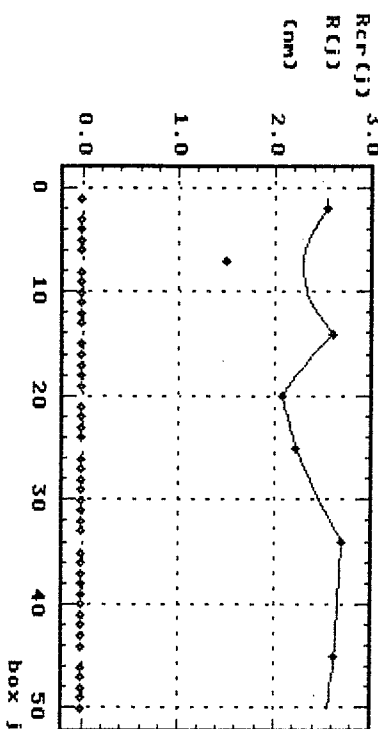


Fig. 2 e: ... for  $t = 3000$  time steps

(iii) The influence of local effects increases if the diffusion is much slower than the reaction. On the other hand, for fast diffusion the competition process between the clusters results "only" from a global depletion of free particles (Ostwald ripening) and the known results are obtained. As to be seen in Figs. 2c-e, in the late stage of cluster growth the radii of all growing clusters have the values of their local critical radius. The difference is positive, but rather small, this leads to a very small growth velocity and therefore to a very long stage of Ostwald ripening. Because of  $R(r) \approx Rcr(r)$ , we have practically a competition between the different critical radii. But the winner is, as before, not always determined by the largest  $Rcr(r)$ , it depends on the width and the gradient of the diffusion zone around the largest clusters. If such diffusion zones overlap, the included cluster shrinks rather fast.

For example, in Fig. 3 we see clearly two diffusion zones with the centres at the minima (box 14 and 34). The maxima are characterized by other clusters, which become subcritical. In the given example, at time step 4000 in box 20 a cluster is located, which has to disappear in order to "produce" free particles for the diffusion towards the gradient of free particles. At time step 6000, the width and the depth of the diffusion pots has been increased - and now the cluster in box 25 must disappear - and so on.

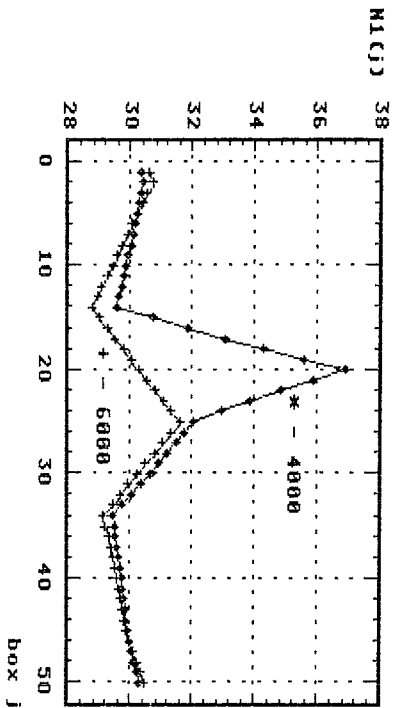


Fig. 3: Distribution of free particles vs. box number  $j$  for two different time steps

We can conclude that the box model presented in this paper allows us, indeed, the study of nucleation and cluster growth in systems where the space-dependence of diffusion processes are of relevance. The investigation of diffusion zones in the vicinity of clusters is as possible as the estimation of the time- and space-dependence of the cluster distribution in systems of small cavities.

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#### References

1. A.C.Zettlemoyer (Ed.), Nucleation, New York 1969, Nucleation Phenomena, Adv. Colloid Interface Sci. 2 (1977)
2. F.Schweitzer, L.Schimansky-Geier, W.Ebeling, H.Ulbricht, *Physica A* 150 (1988) 261-278, *A* 153 (1988) 573-591
3. H.Ulbricht, J.Schweitzer, R.Mahnke, F.Schweitzer; Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions, Teubner, Leipzig 1988

4. L.L. Hench, S.W. Freiman (Eds.); Advances in Nucleation and Crystallization in Glasses, Columbus OH 1971
5. J. Schweitzer, I. Gutzow, R. Pascova, *J. Crystal Growth* 104 (1990) 505-520
6. R. Rächel, F. Lefaucheux, A.C. Robert, *J. Chromatogr.* 166 (1978) 563
7. J. Dumas, J. Gauthier, J. Serughetti, J.F. Guinson, *J. Material Sci. Lett.* 4 (1985) 1089
8. F.Schweitzer, L.Schimansky-Geier, *J. Colloid Interface Sci.* 119 (1987) 67;
9. J. Schweitzer, *Z.phys.Chemie (Leipzig)* 271 (1990) 565-574
10. P.Andreaazza, F. Leufaucheux, B. Mutatschiew, *J. Crystal Growth* 92 (1988) 415-422
11. C.W.Gardiner, Handbook of Stochastic Methods, Berlin-Heidelberg-New York 1984
12. W. Ebeling, Strukturbildung bei irreversiblen Prozessen, Teubner, Leipzig 1976
13. H. Malchow, L. Schimansky-Geier; Noise and Diffusion in Bistable Nonequilibrium Systems, Teubner, Leipzig 1985
14. W. Ebeling, R. Feistel; Physik der Selbstorganisation und Evolution, Akademie-Verlag, Berlin 1982