

Simulation of cluster growth in pores with diffusion interaction

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We consider local effects of cluster growth in pores which are connected by diffusion interaction. Nucleation is mainly governed by the conditions (supersaturation) inside the cavity, whereas the growth of clusters results from the diffusion of free particles between the pores.

A multivariate master equation of the problem is formulated, deterministic equations (reaction–diffusion equations) for the space- and time dependent cluster distribution are derived and solved by means of computer simulations.

1. Introduction

In systems where diffusion processes proceed much faster than the process of cluster formation and growth (e.g. in gases, simple liquids), finite size effects due to the conservation of the total particle number result only 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 discussed previously (see, e.g. ref. [1], and references therein).

A rather different situation is given in systems where cluster growth does not follow the borderline cases of reaction or diffusion limited growth. This situation is realized, e.g. in gels or in ceolites, being a network of cavities, communicating through slightly smaller orifices [2].

The diameter of such cells ranges between 5 and 80 nm; 10^2 to 10^4 particles are included in one cell [3]. The tunnels between the cavities allow diffusion of free particles [2], but caused by the small diffusion coefficients long range order relaxations are mostly impossible, resulting in a spatially inhomogeneous system. Here *local* effects, say the *local* supersaturation, play the important role [11].

The first stage of the phase transition, nucleation, in such small cavities is mainly governed by the conditions (supersaturation) in the cell [4–6], whereas the further growth of clusters results from the diffusion of free particles from neighboring cavities [7].

The box model, introduced in the next section gives us a quite simple model to include the space dependence of the phase transition.

2. Model of interacting boxes

We discuss a system 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 via nucleation and cluster growth, leading to a cluster distribution $n(t)$ and a distribution of free particles $N(t)$ which both depend on time and space; therefore we introduce the state vectors:

$$\begin{aligned} n(t) &= \{n_1(t), n_2(t), \dots, n_i(t), \dots, n_z(t)\}, \\ N(t) &= \{N_1(t), N_2(t), \dots, N_i(t), \dots, N_z(t)\}. \end{aligned} \quad (1)$$

The index is the box number. We have assumed (cf. ref. [4]) that, at the very most, in every box only one cluster of size n is formed, which cannot leave the cavity through the small orifices. By creating the first supercritical cluster, the supersaturation in such a small cavity drops so much that the nucleation period is concluded.

Further, we assume that free particles can diffuse between neighboring cavities. Because of this diffusion interaction $N_j + n_j \neq \text{constant}$ yields for very box, but there are relevant situations where the total particle number in all boxes stays fixed.

3. Stochastic description of nucleation and diffusion – the multivariate master equation

In the framework of a stochastic description we discuss the probability $P(N, \mathbf{n}, t)$, to find a given space- and time dependent distribution of free particles and clusters in the box system. The change of $P(N, \mathbf{n}, t)$ is given by the multivariate master equation [8]:

$$\begin{aligned} & \frac{\partial P(N, \mathbf{n}, t)}{\partial t} \\ &= \sum_{\substack{i,j \\ (i \neq j)}} \{w_D P(N_i + 1, N_j - 1, N^*, \mathbf{n}, t) \\ & - w_D P(N, \mathbf{n}, t)\} \\ & + \sum_i \{w_R^+ P(N_i - 1, n_i + 1, N^*, \mathbf{n}^*, t) \\ & + w_R^- P(N_i + 1, n_i - 1, N^*, \mathbf{n}^*, t) \\ & - [w_R^+ + w_R^-] P(N, \mathbf{n}, t)\}. \end{aligned} \quad (2)$$

The values N^*, \mathbf{n}^* denote those elements of the vectors (1) which have not changed, the changed elements are explicitly written down.

The first term of eq. (2) expresses the change of free particles due to diffusion processes to/from neighboring boxes with a transition rate $w_D(N_i)$ between the boxes i and j . It yields $w_D = 0$ for non-adjacent boxes. The second term of eq. (2) considers the changes of the free and bound particles. It is assumed that the clusters grow and shrink only due to one-particle steps.

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, introduced in eq. (2), in a former proved form [9]:

$$\begin{aligned} w_R^-(N_j) &\equiv w(N_j - 1, n_j + 1 | N_j, n_j) \\ &= \alpha n_j^{2/3} N_j / V^*, \end{aligned} \quad (3)$$

$$\begin{aligned} w_R^+(N_j) &\equiv w(N_j + 1, n_j - 1 | N_j, n_j) \\ &= \alpha n_j^{2/3} N_0(n_j) / V^*. \end{aligned} \quad (4)$$

The transition probability of cluster growth (3) depends on the cluster surface and the density of free particles inside the box. The parameter α 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 (4) depends on the equilibrium concentration of free particles above the curved cluster surface, $N_0(n_j)/V^*$:

$$N_0(n_j)/V^* = c_{\text{eq}}(T) \exp(2B/3k_B T n_j^{1/3}) \quad (5)$$

$c_{\text{eq}}(T)$ is the saturation concentration and B is a constant related to the surface tension.

The transition probabilities of diffusion of free particles, introduced in eq. (2), are chosen (cf. refs. [7,9]) as:

$$w_D^-(N_j) \equiv w(N_j - 1 | N_j) = \sum_m D_{jm} N_j / V^*, \quad (6)$$

$$\begin{aligned} w_D^+(N_j) &\equiv w(N_j + 1 | N_j) = \sum_m D_{mj} N_m / V^* \\ &= \sum_m w_D^-(N_m). \end{aligned} \quad (7)$$

D_{ij} is the coupling constant between the boxes. It yields:

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

$$D_{ij} = 0 \text{ for non-adjointing boxes.} \quad (8)$$

The coupling constant is related to Fick's diffusion coefficient D_F via $D_{ij} = D_F/l^2$, where l is the characteristic length of the system, e.g. the box diameter.

We use further the abbreviations:

$$a(n_j) = \alpha n_j^{2/3} / V^*; \quad d_{ij} = D_{ij} / V^* \quad (9)$$

and for d_{ij} not explicitly depending on space, also $d_{ij} = d$. It depends on the ratio of the two kinetic prefactors $a(n_j)$ and d_{ij} 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 (1) can be derived from $P(N, \mathbf{n}, t)$ by calculating the mean values. Using the usual formalism [8] we obtain

$$\langle \dot{N}_j \rangle = -\langle \dot{n}_j \rangle + \sum_m d_{jm} \langle N_m - N_j \rangle, \quad (10)$$

$$\begin{aligned} \langle \dot{n}_j \rangle &= \langle w_R^-(N_j) - w_R^+(N_j) \rangle \\ &= \langle a(n_j) \{N_j - N_0(n_j)\} \rangle. \end{aligned} \quad (11)$$

Eqs. (10) and (11) mean a coupled system of reaction–diffusion equations for $j = 1, \dots, z$. The stationary solutions for conserved and non-conserved particle numbers are discussed in ref. [7].

Turning to a continuous description of space, that means $\langle n_j \rangle = n(r)$ and $\langle N_j \rangle = N(r)$, and introducing the radius of the assumed spherical cluster by $R^3(r) = n(r) / (4\pi c_\alpha / 3)$, we get from eqs. (10) and (11) finally (cf. ref. [7])

$$\begin{aligned} \dot{R}(r, t) &= \alpha \frac{c_{\text{eq}}(T) d_0}{(4\pi c_\alpha / 3)^{1/3}} \\ &\times \left\{ \frac{1}{R_{\text{cr}}(r, t)} - \frac{1}{R(r, t)} \right\}, \end{aligned} \quad (12)$$

where R_{cr} is the critical radius, introduced by

$$R_{\text{cr}}(r, t) = d_0 / \ln \{ N(r, t) / c_{\text{eq}} V^* \}, \quad (13)$$

$d_0 = 2\sigma / c_\alpha k_B T$ being the capillary length, σ the surface tension and c_α the density of the cluster,

Eq. (13) formally agrees with the known deterministic kinetics of gaseous systems [9]. But now the cluster size, $R(r)$, and the critical radius,

$R_{\text{cr}}(r)$, both depend on the space coordinate. That means, we have no global value of R_{cr} , which acts as a selection parameter for all clusters – but only a local selection. Since, via the local density of free particles, $R_{\text{cr}}(r, t)$ depends on both the time scales of reaction and of diffusion, (expressed by α and d), it is governed by the local conditions if $R(r)$ is larger or smaller than the critical radius $R_{\text{cr}}(r)$ at the same point, if the cluster can grow further or not. According to whether α or d dominates, we expect a quite different behaviour of the critical radius.

6. Numerical simulations and discussion

In order to evaluate the time- and space-dependent cluster distribution of the box system numerically, we discuss a linear system of boxes forming a ring; that means the total number of particles is conserved. The simulation was carried out for a ring of 50 boxes, each with 100 particles initially. The box volume is chosen to be $1.63 \times 10^{-23} \text{ m}^3$, that means a sphere diameter of 30 nm.

We assume now, that during the first time step a random nucleation process occurs, which is governed only by the conditions (supersaturation, defined by $y_0 = N_j / c_{\text{eq}} V^*$) inside the box. In our simulation the initial supersaturation was equal to 5. Choosing, e.g., the thermodynamic properties of ethanol for 290 K, an initial critical cluster size of 15 particles (critical radius $R_{\text{cr}} = 0.697 \text{ nm}$) is estimated from eq. (13).

The nucleation process results in an initial cluster distribution around the initial critical cluster size, where the clusters are randomly distributed in the boxes (see fig. 1, obtained from the stochastic simulation of nucleation).

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 via diffusion exists between the boxes; 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 coupled reaction–diffusion eqs. (10) and (11).

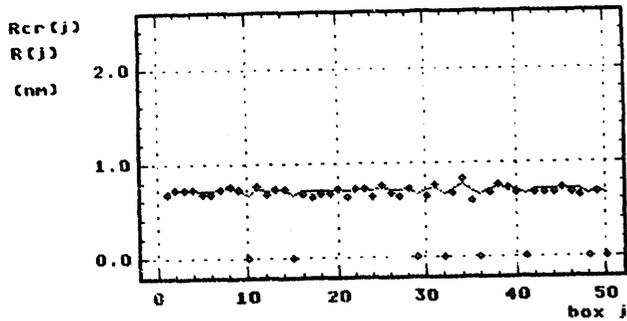


Fig. 1. Cluster radius $R(j)$ (dots) and critical radius $R_{cr}(j)$ (line) versus box number j after the nucleation period (no diffusion between the boxes).

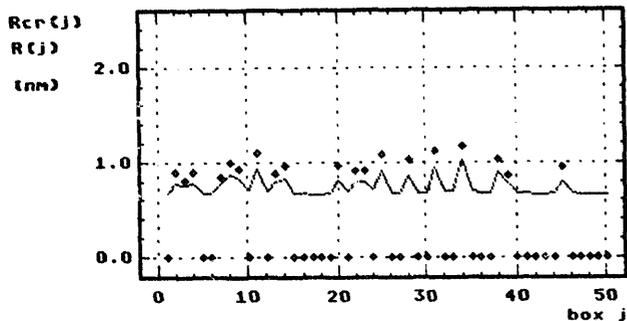


Fig. 2. Cluster radius $R(j)$ (dots) and critical radius $R_{cr}(j)$ (line) versus box number j after $t=5$ time steps (d/a) (including diffusion interaction between the boxes).

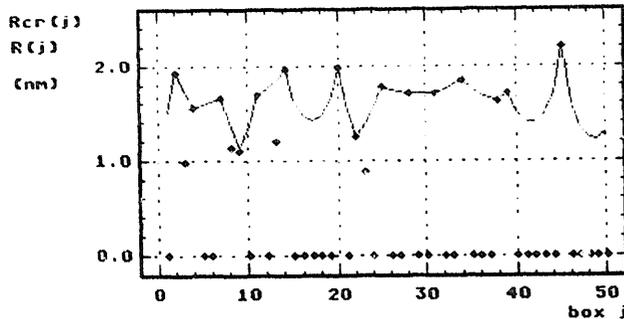


Fig. 3. The same as fig. 2 after $t=100$ time steps.

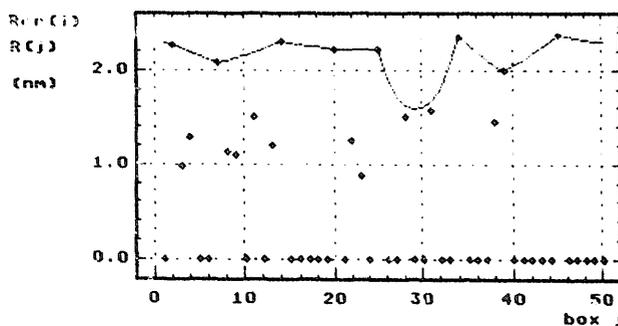


Fig. 4. The same as fig. 2 after $t=1000$ time steps.

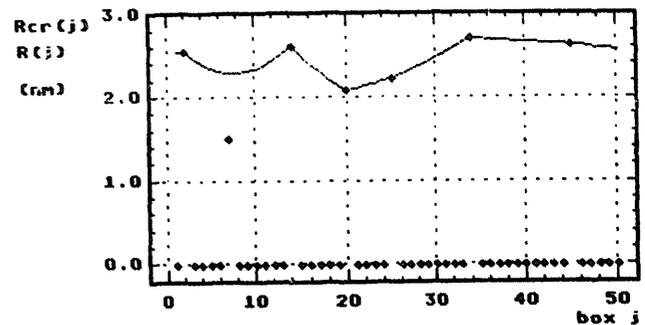


Fig. 5. The same as fig. 2 after $t=3000$ time steps.

Figs. 2–5 present different time steps of the evolution of the space- and time dependent cluster size distribution in terms of the cluster radius and the critical radius of the different boxes. Although the simulation was carried out only for an one-dimensional chain of boxes, the results fit qualitatively the behavior of growing crystals in gels [11] in the middle time stages.

The computer simulations lead to the following conclusions:

- (i) Slightly subcritical clusters are able to grow to a supercritical size, if the diffusion from the neighbouring boxes is large enough.
- (ii) The growth of clusters over large time intervals depends strongly on the cluster distribution in the surrounding (local competition effect). A consideration of the space dependence shows, that in general the initially largest cluster will *not* surely be superior to the others.
- (iii) In the late stage of cluster growth the radii of all growing clusters have the values of their local critical radius.
- (iv) Because of $R(r) \approx R_{cr}(r)$, we have practically a competition between the different critical radii. But the winner is not always determined by the largest $R_{cr}(r)$, 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.

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References

- [1] H. Ulbricht, J. Schmelzer, R. Mahnke and F. Schweitzer, *Thermodynamics of Finite Systems and the Kinetics of First-Order Phase Transitions* (Teubner, Leipzig, 1988).
- [2] R. Rächel, R.L. Steere and E.F. Erbe, *J. Chromatogr.* 166 (1978) 563.
- [3] J. Dumas, J. Gauthier, J. Serughetti and J.F. Quinson, *J. Mater. Sci. Lett.* 4 (1985) 1089.
- [4] P. Andrezza, F. Lefauchaux and B. Mutaftschiev, *J. Cryst. Growth* 92 (1988) 415.
- [5] F. Schweitzer and L. Schimansky-Geier, *J. Colloid Interface Sci.* 119 (1987) 67.
- [6] J. Schmelzer and F. Schweitzer, *Z. Phys. Chem. (Leipzig)* 271 (1990) 565.
- [7] F. Schweitzer, in: *Nucleation-Clusters-Fractals*, Eds. F. Schweitzer and H. Ulbricht (Rostock, 1991) p. 33-47.
- [8] C.W. Gardiner, *Handbook of Stochastic Methods*, (Springer, Berlin, 1984).
- [9] F. Schweitzer, L. Schimansky-Geier, W. Ebeling and H. Ulbricht, *Physica A* 150 (1988) 261; 153 (1988) 573.
- [10] H. Malchow and L. Schimansky-Geier, *Noise and Diffusion in Bistable Nonequilibrium Systems* (Teubner, Leipzig, 1985).
- [11] F. Lefauchaux, M.C. Robert, Y. Bernhard and S. Gits, *Cryst. Res. & Technol.* 19 (1984) 1541.