On the Kinetics of Nucleation: Stochastic Description and Fokker-Planck Equation

1. Introduction

We consider a metastable system (e.g. a supersaturated vapour), where the thermodynamic constraints (e.g. temperature, pressure, system size, density) are chosen in a way that a first order phase transition is possible to undergo in the system.

If impurities (e.g. dust, ions, other particles) are absent the phase transition occurs a certain region of the value of the supersaturation which gives a measure for the metastability of the system. The mechanism of this phase transition is described by a homogenous nucleation process. In the homogenous system (e.g. vapour) small clusters (e.g. droplets) are created spontaneously, which can grow to a macroscopic size under certain conditions.

The theoretical description of this process is held at different levels. A general method with respect to the basic processes of the phase transition is the formalism of master equations [1, 2, 3]. The evolution of the clusters is assumed there to be a Markovian birth, and death process with certain transition probabilities. This way of description is close connected with computer simulation experiments when the same basic reactions are used. In this case the clusters are descretely characterized. For a continuous description of the ensemble of the clusters a cluster distribution function is introduced and the master equation can be converted into a Fokker-Planck equation, which gives the time dependence of this distribution function.

When the diffusion of the system is eliminated, we get from the Fokker-Planck equation a Liouville equation which describes the deterministic evolution of the system. With such a deterministic equation the competition process of the cluster ensemble can be well explained for the late stage of the phase transition (Ostwald ripening). This is a typical behaviour of systems with limited particle numbers.

But to describe the first stage of the phase transition a stochastic method is necessary to use. It explains the establishment of the cluster distribution as well as transitions between the stable states of the system.

In this paper we derive starting with the basic master equation the equations for the mean values and the Fokker-Planck equation. By means of this equation we discuss the deterministic kinetics of the system.

2. The stochastic basic processes of homogeneous nucleation

We consider a closed and finite system with N free particles being an ideal gas mixture. We fix the thermodynamic constraints

\[ N = \text{const}, \quad V = \text{const}, \quad T = \text{const} \]

in such a way that the pressure of the supposed ideal vapour

\[ p = \frac{N}{V} k_B T \]

is larger than the equilibrium pressure \( p_\infty (T) \) for the saturated vapour at a planar liquid interface. We define a supersaturation of the initial state as follows

\[ \gamma_0 = \frac{p}{p_\infty} = \frac{N k_B T}{p_\infty V} \]

(3)

The supersaturation gives a measure for the metastability of the system. \( \gamma_0 \) has to reach at least a critical value to insert a nucleation process, as further discussed (see e.g. /4, 5/). This fact is assumed to be realized here.

We suppose further, that the nucleation process, the formation of droplets from the vapour, can be described by the following kinetic mechanism:

\[ \begin{array}{c}
A_0 \rightarrow A_1 \quad \text{with} \quad \frac{w^+}{w^-} \frac{A_0}{A_1}
\end{array} \]

(4)

\( \xi \) is the number of particles bound in the droplet \( \xi \leq N \).

It is assumed here that the growth and shrinkage of the droplet takes place only by the attachment or the evaporation of a free particle (monomer). The given reactions occur with the transition probabilities per unit time \( w^+ \) and \( w^- \). In the given kinetic model (4) interactions between the clusters with \( \xi \geq 2 \) like coagulation processes or collisions between two or more clusters are not taken into account. The probabilities of these events should be negligible in comparison with the probabilities of the reactions (4).

By means of the kinetics (1) a cluster distribution \( N \) should be established:

\[ \begin{array}{c}
N = [N_0 N_1 \ldots N_\xi \ldots N_N]
\end{array} \]

(5)

That means at a given time \( t \) there exist \( N_0 \) free particles (monomers) \( N_1 \) dimers \ldots etc. in the system.

Because of the conservation of the overall particle number (1) the relation holds:

\[ N = \sum_{\xi} N_{\xi} = \text{const} \]

(6)

For the maximum number of clusters with \( \xi \) particles the following inequation holds:

\[ 0 \leq N_{\xi} \leq \frac{N}{\xi} \quad \xi = 1, \ldots, N \]

(7)

The evolution of the cluster distribution by means of (4) is assumed to be a Markovian birth and death process and can be described with a master equation. We define

\[ P(N, t) = P(N_0, t) \]

as the probability to find a cluster distribution \( N \) (5) at the time \( t \). Then the time dependence of \( P(N, t) \) is given by the following master equation \( \partial / \partial t \):

\[ \frac{\partial P(N, t)}{\partial t} = \sum_{N'} \left[ w(N|N') P(N', t) - w(N'|N) P(N, t) \right] \]

(8)

\( N' \) specifies those cluster distributions which are attainable from the assumed distribution \( N \) via the reactions (4).
The quantities \( w(N/N') \) are the transition probabilities per unit time for the transition form \( N' \) to \( N \). In agreement with former investigations we define them as follows (1, 7):

\[
w(N_1 - 1 \ldots N - 1 N_{1\ldots \ell} \ldots N_N) = w(N_1 N_{1\ldots \ell} \ldots N_N) = \propto \ell^{3/2} N \ell^{-1} N_1
\]

(9.1)

\[
w(N_1 + 1 \ldots N + 1 N_{1\ldots \ell} \ldots N_N) = w(N_1 N_{1\ldots \ell} \ldots N_N) = \propto \ell^{3/2} N \ell^{-1} \exp \left( \frac{1}{\kappa_B T} (\ell - \ell^*) \right)
\]

(9.2)

In (9.1) we assume that the probability of an attachment of a monomer to a cluster of the size \( \ell \) increases with the surface of the cluster (\( \propto \ell^{3/2} \)) and with the number of clusters of size \( \ell \). \( N_{\ell} \) and with the density of the monomers: \( N_{1\ldots \ell} / V \). The probability of the growth process of clusters of different sizes \( \ell = 1, \ldots, N \) are correlated since the number of particles is conserved (9).

Note, that for \( \ell = 1 \) the number of monomers changes from \( N_1 \) to \( (N_1 - 2) \) by creating a dimer. The transition probability in this case reads:

\[
w_1^1(N_1) = \propto \frac{N_1(N_1 - 1)}{V}
\]

(10)

The transition probability of the evaporation of a monomer from a cluster of the size \( \ell \) is also determined by the surface of the cluster and by the number of clusters of size \( \ell \). \( \lambda_1 = h^2 \pi \alpha \kappa_B T \) is the de Broglie wave length of a free particle with the mass \( m \). \( \lambda \) is a potential function, which includes volume and surface effects as follows:

\[
l = -A + B \ell^{3/2}
\]

(11)

Note, that \( f_1 = 0 \). \( A \) and \( B \) are constants given by /4/:

\[
A = -\kappa_B T \ln \frac{\rho_0}{\kappa_B T} \ell_1^2 B = \frac{4\pi n_c}{3} \ell^{3/2} - \frac{2}{3} \sigma
\]

(12)

\( \sigma \) is a constant with respect to the special properties of the droplet like the liquid density \( n_c \) [particles/m\(^3\)], the surface tension \( \sigma \) and the temperature \( T \).

Again, the transition probability (9.2) is modified for the evaporation of a dimer, because this transition changes \( N_1 \) and \( N_2 \) to \( (N_1 - 2) \) and \( (N_2 - 1) \). Due to the kinetic mechanism (4) the transition probabilities for all other processes different from (9) are assumed to be zero.

3. Derivation of equations for the mean values

A further discussion of the master equation (8) is not necessary here, because we are interested in the calculation of the mean values of the numbers of clusters \( N_1 \).

The mean number of clusters of size \( \ell \) we receive from the first moment of \( P(N, t) \):

\[
\langle N(\ell) \rangle = \sum_{N_1} N_1 P(N_1, \ldots, N_{1\ldots \ell}, N_{N\ell + 1})
\]

(13)

For the time dependent change of \( N_\ell \) this equation can be written as follows /8/:

\[
\frac{\partial}{\partial t} \langle N(\ell) \rangle = \sum_\ell A_\ell N_\ell \langle w_j(N_\ell) \rangle
\]

(14)

\( A_\ell \) \( N_\ell \) gives the value of the change of \( N_\ell \) for the basic reaction \( j \), expressed by the mean value of the transition probability \( w_j(N_\ell) \).

We obtain from (14) the following system of equations for the time evolution of the mean values /1/:

\[
\frac{\partial}{\partial t} \langle N_\ell(N_{1\ldots \ell+1}) = -w_\ell(N_\ell) + w_{\ell+1}(N_{1\ldots \ell}, N_\ell) - w_{\ell-1}(N_{1\ldots \ell-1}, N_\ell) \rangle
\]

(15)

\[
\frac{\partial}{\partial t} \langle N_\ell(N_{1\ldots \ell-1}) = w_{\ell-1}(N_{1\ldots \ell-1}, N_\ell) - w_{\ell-2}(N_{1\ldots \ell-2}, N_\ell) + \sum_{\ell'} \langle w_{\ell'}(N_\ell N_{\ell'}, N_{1\ldots \ell'}) \rangle
\]

(15)

with \( w_\ell = w_{\ell+1} = w_{\ell-2} = 0 \).

Summing all numbers of clusters with \( \ell \geq 2 \) it holds with (15.1):

\[
\frac{\partial}{\partial t} \left( \sum_{\ell=2}^{N} \langle N_\ell \rangle \right) = \langle w_{\ell+1}(N_\ell) - w_{\ell-2}(N_\ell) \rangle
\]

(16)

This equation means that the number of clusters (\( \ell \geq 2 \)) can only be changed by the creation or evaporation of dimers. If we exclude these processes, the whole number of clusters (\( \ell \geq 2 \)) is constant. Obviously it follows for the whole number of particles in the considered case:

\[
\frac{\partial}{\partial t} \left( \langle N_1 \rangle + \sum_{\ell=2}^{N} \langle N_\ell \rangle \right) = 0
\]

(17)

The actual pressure of the system is given by the sum of the partial pressures of all clusters and monomers:

\[
p(t) = \sum_{\ell=1}^{N} \frac{\langle N_\ell \rangle}{\kappa_B T} \frac{1}{V}
\]

(18)

If we introduced an actual supersaturation \( y(t) \) in analogy to the definition of the initial supersaturation \( y_0(3) \):

\[
y(t) = \frac{p(t)}{p_\infty} = \sum_{\ell=1}^{N} \frac{\langle N_\ell \rangle}{\kappa_B T} \frac{1}{\rho_0 V}
\]

(19)

then it follows from (15.2) and (16) for the time dependent change of the actual supersaturation:

\[
\frac{\partial}{\partial t} y(t) = -\kappa_B T \sum_{\ell=1}^{N} \langle w_{\ell+1}(N_{1\ldots \ell+1}, N_\ell) \rangle
\]

(20)

4. The Fokker-Planck equation

To derive the Fokker-Planck equation (FPE) for the mean values we treat \( N_\ell \) as a continuous function of \( \ell \) and make use of a Kramers-Moyal expansion \( \partial \ell / \partial t \). Starting with (13.1) we introduce a Taylor expansion for the transition probabilities:

\[
w_{\ell+1}(N_{1\ldots \ell+1}) = w_{\ell}(N_{1\ldots \ell}) + \frac{\partial}{\partial \ell} w_{\ell}(\ell + 1 - \ell) \]

\[
+ \frac{1}{2} \left( \frac{\partial^2}{\partial \ell^2} w_{\ell}(\ell + 1 - \ell) \right)^2 + \ldots
\]

(21)

\[
w_{\ell-1}(N_{1\ldots \ell-1}) = w_{\ell}(N_{1\ldots \ell}) + \frac{\partial}{\partial \ell} w_{\ell}(\ell - 1 - \ell) \]

\[
+ \frac{1}{2} \left( \frac{\partial^2}{\partial \ell^2} w_{\ell}(\ell - 1 - \ell) \right)^2 + \ldots
\]

(21)

Neglecting terms of higher than the second derivative we get from (15.1):

\[
\frac{\partial}{\partial t} \langle N_\ell \rangle = -\frac{\partial}{\partial \ell} \left( \langle w_{\ell}(N_\ell) - w_{\ell}(N_{\ell-1}) \rangle \right)
\]

\[
+ \frac{1}{2} \left( \frac{\partial^2}{\partial \ell^2} \langle w_{\ell}(N_\ell) + w_{\ell}(N_{\ell-1}) \rangle \right) \]

(22)

Using the transition probabilities (9) with the approximation \( \langle N_\ell N_{\ell'} \rangle \approx \langle N_\ell \rangle \langle N_{\ell'} \rangle \) we receive the following FPE:
\[
\begin{align*}
\frac{\partial}{\partial t} \langle N_{p} \rangle &= -\frac{1}{\hat{E}} a \langle \hat{E} \rangle \langle N_{p} \rangle \left( \frac{N_{p}}{V} - \frac{V}{x_{r}^3} \exp \left[ \frac{\hat{E} - \hat{E}_{r}}{k_{B}T} \right] \right) \\
&+ \frac{1}{2} \frac{\partial^2}{\partial \hat{E}^2} a \langle \hat{E} \rangle \langle N_{p} \rangle \left( \frac{N_{p}}{V} + \frac{V}{x_{r}^3} \exp \left[ \frac{\hat{E} - \hat{E}_{r}}{k_{B}T} \right] \right)
\end{align*}
\] (23)

As the restrictive condition of the FPE (23) equation (17) considers the case \( \hat{E} = 1 \). Equation (23) can be transformed further more. We write for the argument of the exponential function

\[
\hat{E} - \hat{E}_{r} = -A + B \left( \hat{E} - (\hat{E} - 1)^{1/2} \right) = -A + \frac{2}{3} B \hat{E}^{1/3}
\]

Make use of a power expansion we can write for the first term of the r.h.s. of (23):

\[
a \langle \hat{E} \rangle^{1/3} \langle N_{p} \rangle \left( \frac{N_{p}}{V} - \frac{V}{x_{r}^3} \exp \left[ \frac{A - \hat{E}_{r}}{k_{B}T} \right] \right)
\]

\[
= a \langle \hat{E} \rangle^{1/3} \langle N_{p} \rangle \left( \frac{N_{p}}{V} + \frac{V}{x_{r}^3} \exp \left[ \frac{A - \hat{E}_{r}}{k_{B}T} \right] \right)
\]

Instead of a discrete description of the clusters by means of the number \( \hat{E} \) we introduce now the cluster radius as a continuous variable:

\[
\langle \hat{E} \rangle = \frac{4}{3} \pi c_{p} r_{c}^{3}
\]

(25.1)

c_{p} is the particle density in the cluster and is assumed to be constant. With respect to the constant B (12) it holds:

\[
\frac{2}{3} \frac{B}{k_{B}T} \langle \hat{E} \rangle^{1/3} c_{p} = \frac{d_{0}}{r_{e}}
\]

(25.3)

where \( d_{0} = 2 \pi c_{p} k_{B} T \) is the capillary length. Note, that the continuous change of \( r_{c} \) with increasing \( \hat{E} \) is correct only for large clusters. The introduction of \( r_{c} \) results in a continuous cluster distribution \( N(r_{c}, t) \) instead of the discrete cluster distribution \( N \) (5). The smallest value of \( r_{c} \) is given by the radius of the free particles \( r_{e} \). We define a cluster density distribution:

\[
n(r_{c}, t) = \frac{\langle N(r_{c}, t) \rangle}{V} \cdot \frac{\langle N(r_{e}, t) \rangle \otimes \langle N_{p} \rangle}{\langle N(r_{e}, t) \rangle \otimes \langle N_{p} \rangle}
\]

(26)

With (25.1) and (26) the restrictive condition (17) gets the form:

\[
\left( \frac{4}{3} \pi c_{p} \right)^{1/3} \cdot 3 \int_{0}^{r_{e}} \frac{1}{r_{c}} n(r_{c}, t) dr_{c} \approx \frac{N}{V} = \text{const.}
\]

(27)

Ih means of the cluster radius \( r_{c} \) and the cluster density distribution \( n(r_{c}, t) \) we find for the FPE (23)

\[
\begin{align*}
\frac{\partial}{\partial t} n(r_{c}, t) &= -\frac{\partial}{\partial r_{c}} a \left( \frac{4}{3} \pi c_{p} \right)^{1/3} \frac{d_{0}}{x_{r}^3} n(r_{c}, t) \\
&+ \frac{1}{2} \frac{\partial^2}{\partial \hat{E}^2} a \langle \hat{E} \rangle n(r_{c}, t) \\
&+ \frac{1}{2} \frac{\partial^2}{\partial \hat{E}^2} a \langle \hat{E} \rangle n(r_{c}, t) \\
&+ \frac{1}{2} \frac{\partial^2}{\partial \hat{E}^2} a \langle \hat{E} \rangle n(r_{c}, t) \\
&\cdot n(r_{c}, t) \langle \hat{E} \rangle^{1/3} \exp \left( -\frac{A}{k_{B}T} + \frac{d_{0}}{x_{r}^3} \right)
\end{align*}
\] (28)

Another form of writing (28) is given in (29)

\[
\begin{align*}
\frac{\partial}{\partial t} n(r_{c}, t) &= -\frac{\partial}{\partial r_{c}} \left( v(r_{c}, n(r_{c}, t)) - \frac{\partial}{\partial r_{c}} a(r_{c}) n(r_{c}, t) \right)
\end{align*}
\] (29)

with the quantities:

\[
v(r_{c}) = \frac{a}{3} \left( \frac{4}{3} \pi c_{p} \right)^{1/3} d_{0} \left( \frac{1}{r_{e}} - \frac{1}{r_{c}} \right)
\]

(30)

and

\[
a(r_{c}) = \frac{a}{6} \left( \frac{4}{3} \pi c_{p} \right)^{1/3} \cdot \frac{1}{r_{e}} n(r_{e}, t) + \frac{P_{\infty}}{k_{B}T} \exp \left( \frac{d_{0}}{r_{c}} \right)
\]

(31)

In (30) a new variable is introduced:

\[
\frac{1}{r_{c}} d_{0} \left( \frac{n(r_{e}, t)k_{B}T}{P_{\infty}} \right)^{-1}
\]

(32)

\( r_{e} \) is the critical radius. It results from (28) with A from (12). We explain the meaning of \( r_{e} \) in the next section. We devide two characteristic terms in the FPE of the form (29): the drift term \( v(r_{c}, n(r_{c}, t)) \) and the diffusion term \( a(r_{c}) n(r_{e}, t) \). The drift term describes the deterministic behaviour of the system while the diffusion term is related to the nondeterministic behaviour due to the consideration of fluctuations in the system. \( v(r_{c}) \) is interpreted to be the mean velocity of the deterministic cluster growth and shrinkage, as explained in the following section, \( a(r_{c}) \) represents a diffusion parameter. The stationary solution \( n(r_{c}, t) \) is obtained from the condition:

\[
\frac{\partial}{\partial t} n(r_{c}, t) = 0
\]

We find:

\[
v(r_{c}) + \frac{\partial}{\partial r_{c}} a(r_{c}) n(r_{c}, t) = \frac{a(r_{c})}{k_{B}T} \frac{\partial}{\partial r_{c}} n(r_{c}, t)
\]

(33)

It follows from (33), that the kinetic coefficients \( v(r_{c}) \) and \( a(r_{c}) \) don't stipulate independently from each other. If we use the stationary solution in the form

\[
n(r_{c}, t) = \exp \left( -\frac{\Delta F_{c}}{k_{B}T} \right)
\]

(34)

with \( \Delta F_{c} \) being the change of the free energy due to the establishment of the cluster of size \( r_{c} \) then (33) results in:

\[
v(r_{c}) + \frac{\partial}{\partial r_{c}} a(r_{c}) n(r_{c}, t) = \frac{a(r_{c})}{k_{B}T} \frac{\partial}{\partial r_{c}} n(r_{c}, t)
\]

(35)

By means of (33), (34) or (35) the kinetic coefficients \( v(r_{c}) \) and \( a(r_{c}) \) or the stationary solution \( n(r_{c}, t) \) or the free energy \( \Delta F_{c} \) are able to be calculated. We have determined the stationary solution in a former discussion of the free energy (1) :

\[
n(r_{c}) = \frac{1}{x_{r}^3} \exp \left( \frac{4}{3} \pi c_{p} r_{c}^{3} \right) - \frac{1}{x_{r}^3} \left( \frac{4}{3} \pi c_{p} r_{e}^{3} \right)
\]

(36)

Use of (33) leads to the close form of the FPE (29):

\[
\frac{\partial}{\partial t} n(r_{c}, t) = \frac{\partial}{\partial r_{c}} \left( a(r_{c}) n(r_{c}, t) - \frac{\partial}{\partial r_{c}} a(r_{c}) n(r_{c}, t) \right)
\]

(37)

Note, that the FPE (29) respectively (37) is a good approximation only in the range of large \( r_{c} \) where a quasi-continuous change of \( r_{c} \) with \( r_{c} \) is fulfilled. To describe the formation of clusters with small radii, the formalism of master equations has to be prefered.

5. The deterministic behaviour of the system

Neglecting the diffusion term \( a(r_{c}) n(r_{c}, t) \) in (29) which considers the fluctuations in the system we obtain only the drift term \( v(r_{c}) n(r_{c}, t) \) which allows to predict the
дeterministic evolution of the system. In the deterministic case we receive from (39) the following Liouville equation /1/:

$$\frac{\partial}{\partial t} n(r, t) = - \frac{\partial}{\partial r} \left[ \alpha \frac{4 \pi}{3} a_s \right]^{1/3} \frac{1}{a_s^{1/3}} \frac{1}{r_c^{1/3}} n(r, t) \quad r_c > r_0$$

(38)

If we don’t take into account the formation or disappearance of clusters, (38) can be written as a continuous equation:

$$\frac{\partial}{\partial t} n(r, t) + \nabla \cdot (n(r, t) \cdot \nabla) = 0$$

(39)

In general the formation, disappearance of clusters has to be considered in additional terms on the r.h.s. of (39) in analogy to (16).

Comparing (30) with (38) we find the equation for the time dependent change of the cluster radius

$$\frac{\partial}{\partial t} r_c = \left[ \frac{4 \pi}{3} a_s \right]^{1/3} \frac{1}{a_s^{1/3}} \frac{1}{r_c^{1/3}} r_c > r_0$$

(40)

Equation (40) gives the mean velocity of the growth and shrinkage of one cluster with the radius $r_c$ in agreement with the kinetic coefficient $v(r_c)$ (30).

The mean velocity of cluster growth can be alternated. It is held:

$$v(r_c) \geq 0,$$ \text{if} $r_c \leq r_c^{cr}$

(41)

That means, the critical radius $r_c^{cr}$ (32) acts as a selection value. If we discuss the evolution of the cluster ensemble as a competitive process between the clusters /10/ the clusters are only able to evolve when their radius is larger than the critical radius. Clusters with a radius smaller than the critical one shrink and disappear again.

Because the density of the free particles $n(r, t)$ is coupled with the development of the other clusters by the condition (37) the critical radius possesses an information on the recent stage of the phase transition. If only free particles exist in the system at the initial time $t_0$ the smallest value of $r_c$ in agreement with former investigations /11/ is given by:

$$r_c(t_0) = d_0 \left( \ln \frac{N}{v_k T} \right)^{-1} = d_0 \left( \ln \frac{1}{v_0} \right)^{-1}$$

(42)

$r_c(t_0)$ increases during the phase transition, because the density of the free particles is decreasing. During the first stage of stochastic formation of small clusters $r_c$ changes only in a small range of order, the free particles are the majority of all clusters. By a stochastic formation of overcritical clusters a growth process inserts for these clusters, where the number of free particles decreases rapidly, $r_c$ increases faster with time. During the last stage of the phase transition, the so called Ostwald ripening, $r_c$ increases little with time again, because most of the free particles are in bound states. The selection process occurs slowly.

The deterministic growth equation (40) well estimates the development of the system for the stages of cluster growth and Ostwald ripening /12, 13/.

Zusammenfassung

Résumé
La présente étude traite théoriquement l'écriture des processus de phase transition dans des systèmes supersaturés par la théorie du développement des clusters. La densité de la matière est liée à l'évolution des clusters par les conditions (37). L'existence des clusters de taille critique possède des informations sur l'état récent de la transition de phase. Si seuls des clusters existent au départ $t_0$, la valeur critique $r_c$ n'est donnée que par:

$$r_c(t_0) = d_0 \left( \ln \frac{N}{v_k T} \right)^{-1} = d_0 \left( \ln \frac{1}{v_0} \right)^{-1}$$

(42)

$r_c(t_0)$ augmente pendant la transition de phase, car la densité des particules libres diminue. Pendant la première phase de formation des clusters de taille critique $r_c$ change seulement dans un petit intervalle de taille, les clusters sont la majorité de tous les clusters. Une formation aléatoire de clusters critiques engendre un processus de croissance qui insère pour ces clusters, où le nombre de particules libres diminue rapidement, $r_c$ augmente plus rapidement avec le temps. Pendant la dernière phase de la transition de phase, le phénomène d'ostwald ripening, $r_c$ augmente peu avec le temps, car la majorité des particules libres sont dans des états liés. Le processus de sélection se produit lentement.

La formule de croissance déterministe (40) est une bonne estimation de l'évolution du système pour les phases de croissance des clusters et ostwald ripening /12, 13/.

Summary
This paper deals with the theoretical description of a phase transition in supersaturated systems by means of cluster formation (nucleation) and growth of clusters. Starting with general stochastic methods first a master equation is formulated which describes the establishment of a cluster distribution. The transition probabilities per unit time consider the basic processes of the phase transition.

By means of these transition probabilities equations for the mean values of the number of clusters are derived. The actual supersaturation of the system is calculated. A Fokker-Planck on the mean values equation is also derived explicitly, where the kinetic coefficients are calculated from the transition probabilities. This Fokker-Planck equation is widely discussed, the stationary solution is given too.

By discussion of the drift term of the Fokker-Planck equation the deterministic behaviour of the system is explained. The critical radius is calculated and discussed.
Résumé
L'étude présente est consacrée à la description théorique d'une transition de phase en systèmes suraturés par voie de formation de clusters (nucléation) et de croissance de clusters.
En partant de méthodes stochastiques générales, on établit d'abord une équation principale qui décrit le développement de la répartition des clusters. Les probabilités de transition par unité de temps tiennent compte des processus élémentaires de la transition de phase.
En se basant sur ces probabilités de transition, l'auteur dérive des équations de valeurs moyennes pour le nombre des clusters. On calcule la sursaturation actuelle du système. On dérive également d'une manière explicite une équation de Fokker-Planck, les coefficients cinétiques étant calculés à partir des probabilités de transition. Cette équation de Fokker-Planck est discutée en détail, la solution stationnaire est indiquée.
En discutant le terme de dérive de l'équation de Fokker-Planck, on explique le comportement déterministe du système. On calcule et discute le rayon critique.

Literatur

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