

A STOCHASTIC APPROACH TO NUCLEATION IN ISOLATED SYSTEMS

Axel Budde, Frank Schweitzer, Reinhard Mahnke

1. INTRODUCTION

Since the end of the twenties many efforts have been done in order to develop a complete theory of the formation and growth of clusters in supersaturated systems /1-2/. We remember the classical nucleation theory /3-4/ which is valid for a description of nucleation in an infinite system under isothermal constraints. A limitation of the total particle number leads to a dependence of formation and growth of clusters, because of a decrease of free particles. In particular, in a supersaturated vapour the formation and growth of different clusters is coupled by the vapour pressure and one finds a scenario of the phase transition where three stages can be distinguished /5-7/ (see also the accompanying paper /28/).

The present paper deals with the description of nucleation and growth of clusters in an isolated binary system, consisting of a vapour and a neutral carrier gas. Due to the cluster formation the latent heat of condensation is released which leads to an increase of the temperature. We will show here that the isothermal nucleation process can be derived as a special case from this general point of view. The other limiting case discussed here in more detail corresponds to the nucleation of a pure vapour under isobaric conditions. For this case results of computer simulations are presented.

For the formation of clusters we use again a stochastic description which restricts itself to a mesoscopic time scale /6,11,16/. That means a scale where the microscopic processes are not considered in detail but reflected by small changes of the macroscopic parameters of the system (e.g. pressure, temperature). The cluster itself is described similarly to the classical droplet model /1/. That means it can be characterized by a macroscopic density and surface tension.

2. THE GENERAL MODEL

2.1. MODEL OF THE ISOLATED SYSTEM

In the following we consider a closed and finite isolated system. That means a fixed total internal energy U , a fixed system volume V and a fixed total particle number N :

$$U = \text{const.}, \quad V = \text{const.}, \quad N = \text{const.} \quad (2.1)$$

The constraints are chosen in such a way that the system exists in a gaseous state. This gas consists of two components: a condensable vapour specified by the index "v" and a carrier gas denoted by the index "c". It is known from experiments on vapour condensation that the carrier gas is used to take over the latent heat which is released during the condensation process. The carrier gas should be uncondensable under the given constraints. The total particle number N therefore is divided into the particle numbers of the two components, both being constant:

$$N = N_c + N_v \quad (2.2)$$

Due to interactions between the particles a number of particles of the condensable vapour is bound in clusters and a discrete distribution of clusters and free particles in the gas exists. This distribution is described by the vector $N = (N_0, N_1, \dots)$:

$$N = \{ N_0, N_1, N_2, \dots, N_n, \dots, N_n \} \quad (2.3)$$

N_0 is the number of the free particles of the carrier gas, N_1 the number of free particles of the condensable vapour (monomers), N_2 the number of bound states of two particles (dimers) and so on.

Because of the limited number of particles it holds:

$$N_v = \sum n N_n = \text{const.} \quad (2.4)$$

n is the number of condensable particles bound in the cluster, the number of clusters consisting of n particles is denoted by N_n . For the maximum number of clusters it follows from eq. (2.4):

$$0 \leq N_n \leq N/n$$

$$(2.5)$$

2.2. THERMODYNAMIC INVESTIGATIONS

In order to evaluate the thermodynamic properties of the system we start with the free energy $F(T, V, N)$ for the considered cluster distribution N in the volume V and at the temperature T . We assume that T is a global parameter which depends on the present cluster distribution. The free energy of the cluster distribution has been derived in previous papers /8,16/ assuming isothermal conditions and an ideal mixture of clusters and free particles (canonical ensemble). It consists of two parts with respect to the carrier gas (F_0) and the condensable vapour, including the cluster distribution (F_v). We found for the free energy:

$$F(T, V, N) = \sum N_n \{ f_n + k_B T \ln(\lambda_n^{-3} N_n / V) - 1 \} + N_0 k_B T \ln(\lambda_0^{-3} N_0 / V) - 1 = F_v + F_0 \quad (2.6)$$

where λ_n is the de-Broglie wave length

$$\lambda_n = h(2\pi m_n k_B T)^{-1/2} \quad (2.7)$$

f_n is a potential term characterizing the energy of the cluster of size n , which will be specified afterwards.

By means of the free energy (eq.2.6) the entropy of the cluster distribution can be derived by:

$$S(T, V, N) = - \partial F(T, V, N) / \partial T \quad (2.8)$$

It results /6/

$$S(T, V, N) = k_B \sum N_n [S/2 - k_B^{-1} \partial f_n / \partial T - \ln(\lambda_n^{-3} N_n / V)] + k_B N_0 [S/2 - 2 \ln(\lambda_0^{-3} N_0 / V)] = S_v + S_0 \quad (2.9)$$

where S_v stands for the contribution of the cluster distribution and S_0 is connected with the carrier gas. Using the relation $U = F + TS$ the total internal energy U can be calculated by:

$$U(T, V, N) = \sum N_n \{ 3k_B T/2 + f_n - T \partial f_n / \partial T \} + 3k_B T N_0 / 2 \quad (2.10)$$

In order to get from eq.(2.10) the dependence of the temperature on the parameters U and V and the actual cluster distribution N we have to specify the potential energy term and its temperature dependence $f_n(T)$. After this specification the inversion of $U = U(T, V, N)$ (eq.2.10) gives the function $T = T(U, V, N)$, which has to be inserted into the expression for the entropy (eq.2.9) to get finally the state function $S = S(U, V, N)$.

3. KINETIC APPROACH

3.1. KINETIC ASSUMPTIONS

The nucleation process consists of the formation of clusters, their growth and shrinkage. The cluster evolution is represented by the time development of the distribution $N = \{N_0, N_1, \dots, N_n\}$. In order to discuss this evolution we make the following assumptions:

- (i) The growth and shrinkage of a cluster is due only to an attachment or evaporation of monomers of the condensable vapour. In terms of chemical kinetics this process can be represented by the stochastic reactions



w^+ and w^- are the transition probabilities per unit time for the stochastic reaction in the given direction. They will be specified later.

- (ii) Interactions between clusters, like coagulation or collisions between two or more clusters are not taken into account. Also a break of a cluster into pieces is not considered. The probabilities of these events should be negligible in comparison with the probabilities of the reactions (3.1) /24/.

3.2. MASTER EQUATION AND EQUILIBRIUM PROBABILITY DISTRIBUTION

From a statistic point of view every possible distribution of clusters \underline{N} is found with a certain probability at a given time, defined by

$$P(\underline{N}, t) = P(N_0, N_1, N_2, \dots, N_n, \dots, N_n, t) \quad (3.2)$$

In a stochastic theory the formation and growth of clusters can be described by the change of $P(\underline{N}, t)$ with time.

If the kinetics of nucleation is considered as a Markovian discrete process, the dynamics of the probability $P(\underline{N}, t)$ to find a certain cluster distribution \underline{N} at time t obeys a master equation:

$$\partial P(\underline{N}, t) / \partial t = \sum_{\underline{N}'} (w(\underline{N}' \rightarrow \underline{N}) P(\underline{N}', t) - w(\underline{N} \rightarrow \underline{N}') P(\underline{N}, t)) \quad (3.3)$$

The quantities $w(\underline{N}' \rightarrow \underline{N})$ are the transition probabilities per unit time for the transition from \underline{N}' to \underline{N} . \underline{N}' specifies those distributions which are attainable from the assumed distribution \underline{N} via the reactions (3.1).

The stationary solution of the master equation requires that $\partial P(\underline{N}, t) / \partial t = 0$. From this condition we find $\sum_{\underline{N}'} J(\underline{N}' \rightarrow \underline{N}) = 0$ with $J(\underline{N}' \rightarrow \underline{N}) = w(\underline{N}' \rightarrow \underline{N}) P(\underline{N}', t) - w(\underline{N} \rightarrow \underline{N}') P(\underline{N}, t)$ being the probability flux between the states \underline{N}' and \underline{N} .

Since the system is not pumped the equilibrium condition is given by the more restricted condition of detailed balance. It means $J(\underline{N}' \rightarrow \underline{N}) = 0$ resulting in:

$$w(\underline{N}' \rightarrow \underline{N}) P_0(\underline{N}') = w(\underline{N} \rightarrow \underline{N}') P_0(\underline{N}) \quad (3.4)$$

$P_0(\underline{N})$ is the equilibrium probability distribution in the space of all possible particle configurations. It has been derived from microscopic considerations /6/. As the final result we obtain

$$P_0(N_0, \underline{N}_1) = \exp \{ (S(U, V, N_0, N_1, \dots, N_n) - S(U, V, N)) / k_B \} \quad (3.5)$$

where $S(U, V, N_0, N_1, \dots, N_n)$ is the entropy of the assumed cluster distribution and $S(U, V, N)$ the entropy of the N particles system. It is a constant for the fixed thermodynamic

constraints (2.1) and acts as a normalization.

We note, that for the calculation of $P_0(\underline{N})$ the state function $S = S(U, V, \underline{N})$ is needed.

3.3. TWO LIMITING CASES

The thermodynamic investigations of section 2.2. allow us to derive two limit cases for the equilibrium probability distribution $P_0(\underline{N})$ /6/. Because of the thermodynamic relations it yields for isolated system with the constraints (2.1):

$$U = F + TS = \text{const} \quad (3.6)$$

Further, the entropy consists of two parts describing the contributions of the carrier gas and the condensable vapour:

$$S = S_V + S_0 \quad (3.7)$$

We can now discuss the limit cases /6/:

(1) $N_0 \gg N_1$: In this case the temperature can be approximated by

$$T \approx T_0 = 2U / 3k_B N_0 = \text{const} \quad (3.8)$$

That means the latent heat which is released during the condensation process will be transmitted to the carrier gas. It plays the role of a heat bath. Therefore we have isothermal conditions.

It results from eq. (3.6) that the change of the entropy in the isothermal limit can be expressed by $S = (U - F) / T$ and the equilibrium probability distribution (eq. 3.5) is now given by:

$$P_0(\underline{N}) \sim \exp \{ - F(T, V, \underline{N}) / k_B T \} \quad T = \text{const} \quad (3.9)$$

(ii) $N_0 \rightarrow 0$: If no carrier gas is present, the latent heat of the condensation process leads to an increase of the temperature of the system. It results from eq. (2.9) $S_0 \rightarrow 0$ in the limit $N_0 \rightarrow 0$. Therefore, we obtain from eq. (3.7) $S = S_V$ leading to

$$P_0(\underline{N}) \sim \exp \{ S_V(U, V, \underline{N}) / k_B \} \quad U = \text{const} \quad (3.10)$$

Thus the nucleation process in the considered binary vapour may be reduced in the limit cases given above either to an isothermal nucleation process in an one-component vapour (1) or to an isoenergetic nucleation process in an one-component vapour (ii). Since the first of these two limit cases has been widely discussed in previous papers /8,7,16/ we restrict ourselves in the following to the investigation of isoenergetic nucleation in an one-component vapour.

4. ISOENERGETIC NUCLEATION

4.1. THERMODYNAMIC INVESTIGATIONS

In order to solve the master equation (3.3) which describes the stochastic evolution of the cluster distribution now we need the proper transition probabilities for the assumed stochastic reactions (3.1). In the following we discuss the isoenergetic limit case. Inserting the equilibrium probability distribution $P_0(N)$ (eq.3.10) for this case into the condition of detailed balance (eq.3.4) we find the following relation between the transition probabilities $w(N \rightarrow N')$ and $w(N' \rightarrow N)$:

$$w(N \rightarrow N') = w(N' \rightarrow N) \exp\{(\sum_{i=1}^N U_i - \sum_{i=1}^{N'} U_i) / k_B T\} \quad (4.1)$$

By means of this condition only a kinetic assumption for one of the transition probabilities is needed. The transition probability for the opposite process can be obtained with provided the entropy $S(U, V, N_1, \dots, N_n)$ is known. This function $S(U, V, N)$ is determined in the following in more detail. In section 2.2. we found the general expression for the entropy (see eq.(2.9)). In the limit case of vanishing carrier gas $N_0 \rightarrow 0$ we get $S \approx S$

$$S(T, V, N) = k_B \ln \left[\frac{V^n}{2^n} \left(\frac{\lambda_n}{h} \right)^{3n} \left(\frac{2\pi m_n}{h^2} \right)^{3n/2} \right] \quad (4.2)$$

The negative binding energies $f_n(T)$ for each cluster size n have to be incorporated empirically into the thermodynamic theory. As a first approximation one could use a form similar to the Bethe-Weizsäcker-formula

$$f_n(T) = \mu_-(T) n + \sigma A_n \quad (4.3)$$

which includes volume and surface terms only. The surface of a spherical cluster containing n monomers is denoted by $A_n = 4\pi n^{2/3} = (c_m 4\pi/3)^{2/3} n^{2/3}$. c_m is the particle density of the liquid, σ is the surface tension both taken here as temperature independent, and $\mu_-(T)$ is the chemical potential of a monomer in the macroscopic fluid. In accordance with the classical droplet model the surface tension σ and the particle density c_m are assumed to be constant also with respect to the curvature.

By a comparison of eq. (4.3) with experimental data for cluster energies it becomes evident that the expression (4.3) is valid for large clusters only. Thus a corrected version of eq. (4.3) is desired. Taking into account the condition that free particles (monomers) have no binding energy

$$f_1(T) = 0 \quad (4.4)$$

we propose the following approximation for the potential energy

$$f_n(T) = \mu_-(T) n (1 - 1/n^\alpha) + \sigma A_n n^{2/3} (1 - 1/n^\beta) \quad (4.5)$$

This so-called Padé approximation for all cluster sizes has two parameters α and β to fit experimental data for small clusters ($n=2, \dots, 10$). We have carried out this for water clusters getting from eq.(4.5) for $T=293$ K the value $f_2=9.07 k_B T$ ($\alpha=1.1$ and $\beta=2.4$) in good agreement with the experimental result $f_2=9.27 k_B T$ /29/ for water dimers.

From thermodynamic investigations the following expression for the chemical potential $\mu_-(T)$ is known /20/:

$$\mu_-(T) = k_B T \ln(c_m(T) \lambda_1^3) \quad (4.6)$$

Using the Clausius-Clapeyron-equation for the temperature dependence of the equilibrium vapour pressure we find

$$c_m(T) = c_m(T_0) \exp\left\{ \frac{\Delta Q}{k_B} \left[\frac{1}{T_0} - \frac{1}{T} \right] \right\} \quad (4.7)$$

with the reference equilibrium concentration c_m at the tempera-

ture T_0 and the heat of evaporation ΔQ .

Starting from eq.(2.10) and using eqs.(4.5)-(4.7) we calculate the temperature via

$$T(U, V, N) = \frac{U - \sigma A_n + \Delta Q M_n}{k_B [(3/2)N_n + (5/2)M_n]} \quad (4.8)$$

with the abbreviations

$$N_n = \sum N_n \quad (n=1, \dots, N_v) \quad (4.9)$$

$$M_n = \sum N_n n (1-1/n^\sigma) \quad (n=2, \dots, N_v) \quad (4.10)$$

$$A_n = \sum N_n A_n (1-1/n^\sigma) \quad (n=2, \dots, N_v) \quad (4.11)$$

Eq.(4.8) describes the change of the temperature of the system resulting from the cluster formation for a fixed internal energy U and a fixed volume V . Let us note that the temperature in our approach is a global parameter. Therefore, the latent heat released or consumed during the attachment or evaporation of particles should be immediately distributed in the considered volume. Eq.(4.8) allows the calculation of the state function entropy based on eq.(4.2). The final result is given by:

$$S(U, V, N) / k_B = [(3/2)N_n + (5/2)M_n] \ln \frac{U - \sigma A_n + \Delta Q M_n}{k_B T_0 [(3/2)N_n + (5/2)M_n]} + (5/2)M_n \ln \frac{U - \sigma A_n + \Delta Q M_n}{k_B T_0 [(3/2)N_n + (5/2)M_n]} - \sum N_n \ln (A_n n^{-\sigma} / 2n / V) \quad (4.12)$$

4.2. TRANSITION PROBABILITIES

To determine the transition probabilities for the attachment or the evaporation of monomers to/from the clusters we assume in agreement with previous papers /6,16,8/ that the transition probability of the attachment of a monomer to a cluster of size n increases with the surface area of the cluster, with the number of clusters of size n and with the density of the free particles of the condensable vapour. In this way we get for the special process of attachment

$$w(N_1, N) = w(N_1-1, \dots, N_n-1, N_{n+1}+1, \dots, N_n, N_1, \dots, N_n) \\ \equiv w_n^+(N_1, N_n) = \alpha(T) A_n n^{\sigma-1} N_1 / V, \quad (4.13) \\ N_1 = N_v - \sum n N_n$$

We note, that the transition probabilities for the growth of clusters of different sizes are correlated, since the number of free particles depends on the whole cluster distribution. Therefore, the clusters do not evolve independently.

The parameter $\alpha(T)$ determines the time scale of the stochastic processes. One has to consider further the specific properties of the surface, like surface tension σ , composition of the surface and the sticking coefficient. A proper estimation of $\alpha(T)$ can be done only from microscopic considerations of the process of attachment.

We assume in a first approximation, that the kinetic energy of the free particles is large compared with the energy barrier ΔE at the surface which must be overwhelmed to incorporate the particles into the cluster ($\Delta E \ll k_B T$). In this case we may choose /8/:

$$\alpha(T) = \alpha_0 k_B T \quad (4.14)$$

where the proportionality constant α_0 reflects the conditions at the surface. A possible choice of α_0 has been proposed in refs. /22,25/ based on a comparison with deterministic growth equations: $\alpha_0 = D c_\infty / 2\sigma$. D is the diffusion coefficient assumed to be nearly constant.

The transition probability per unit time for the evaporation of one particle from a cluster of size n can be obtained from eq.(4.1). The calculation of the exponent is complicated because both the temperature and the number of free particles of the condensable vapour depend on the whole cluster distribution. After a careful evaluation of $S(U, V, N) - S(U, V, N')$ (eq.4.12) and a final transformation $N \rightarrow N'$, $N' \rightarrow N$ we obtain the transition probability of evaporation

$$w(N_n, N) = w(N_n+1, \dots, N_{n-1}+1, N_n-1, \dots, N_n, N_1, \dots, N_n)$$

$$\begin{aligned}
 &= W_n^{-1}(N_n) & (4.15) \\
 &= \alpha k_B T_0 A_1 n^2 / 3 N_0 (1-1/n)^{1/3} \exp[(\Delta Q/k_B T_0) - 1] \\
 & (T'/T)^{(\alpha n^2 + \beta n^2 / 2 - 1)} (T'/T_0)^{(\beta/2) \alpha n - \alpha n^2} \\
 & \exp[(5/2 - 1) \ln(\Delta_0^2 C_0) - \Delta Q/k_B T_0] [1/n^{\alpha-1} - 1/(n-1)^{\alpha-1}]
 \end{aligned}$$

with the temperatures T' and T given by

$$T'(U, V, \underline{N}') = \frac{U - \sigma A_{\alpha'} + \Delta Q M_{\alpha'}}{k_B [(3/2) N_{\alpha'} + (5/2) M_{\alpha}']} \quad (4.16)$$

with

$$N_{\alpha'} = N_{\alpha} + 1 \quad (4.17)$$

$$M_{\alpha'} = M_{\alpha} - [1 - (1/n^{\alpha-1}) + (1/(n-1)^{\alpha-1})] \quad (4.18)$$

$$A_{\alpha'} = A_{\alpha} - A_1 n^2 / 3 (1-1/n^{\alpha}) + A_1 (n-1)^2 / 3 (1-1/(n-1)^{\alpha}) \quad (4.19)$$

and eqs. (4.8, 4.9-4.11) for T, respectively. This transition probability is proportional to the surface area and the number of clusters of size n again. It strongly depends on the temperature. W' (eq. 4.16) rapidly grows up with an increasing temperature and most of the clusters have to evaporate again.

5. RESULTS OF COMPUTER SIMULATIONS FOR ISOENERGETIC NUCLEATION

5.1. NUMERICAL ANALYSIS OF THE ENTROPY FUNCTION

In order to investigate the landscape of the state function entropy (eq. 4.12) in the high dimensional space of independent variables (inner energy U, volume V, cluster distribution $N_1, N_2, \dots, N_n, \dots, N_n$) we fix the values of energy and volume and look for the extrema of the state function over the N-space. The maxima of S(U, V, \underline{N}) correspond to the equilibrium cluster distribution

$$N_i^0 = \{ N_1^0, N_2^0, \dots, N_n^0, \dots, N_n^0 \} \quad (5.1)$$

Taking into account the finiteness of the system (eq. 2.4)

$$N_i = \sum_{n=1}^{\infty} n N_n = N_i + \sum_{n=2}^{\infty} n N_n = \text{const} \quad (5.2)$$

the extrema of the entropy with respect to the number of clusters follow from

$$\mu_n = \partial S(T, V, \underline{N}) / \partial N_n = 0 \quad \text{for } n \geq 2 \quad (5.3)$$

Using the notation μ_n for the chemical potential the calculation of (eq. 5.3) leads to the so-called mass action law. This formal expression was obtained in /6/.

But here we use a different approach which is more convenient for systems with small integer numbers as we are dealing with: $N_1 = 1, 2, 3, \dots, N_n$. A numerical analysis of the high dimensional entropy gives the equilibrium values (eq. 5.1). Using the gradient method step by step we search in the cluster space N for the maxima of the entropy. We find two maxima of S which are divided by a saddle point. This is a typical situation for bistable systems. The metastable primary distribution $N_{n=1}$ consists of a number of small clusters, but in the final cluster distribution $N_{n=1}$ we find one big cluster accompanied by few small clusters. Between these distributions there exist a relative minimum (saddle point) which corresponds to the critical distribution $N_{n=c}$. The activation energy

$$E_A(U, V) = S(U, V, \underline{N}_{n=c}) - S(U, V, \underline{N}_{n=1}) \quad (5.4)$$

is a measure for the probability of a transition from $N_{n=1}$ to $N_{n=c}$.

Summarizing the parameters of the considered system

$$\begin{aligned}
 \text{Inner Energy:} & \quad U = 9.09765 \cdot 10^{-18} \text{ J} \\
 \text{Volume:} & \quad V = 1.9 \cdot 10^{-21} \text{ m}^3 \\
 \text{Particle number:} & \quad N_i = 15000
 \end{aligned} \quad (5.5)$$

and the data for liquid water /29/

Liquid density:	$\rho = 3.35 \cdot 10^28 \text{ m}^{-3}$
Surface tension:	$\sigma = 7.3 \cdot 10^{-2} \text{ kg/s}^2$
Diffusion coefficient:	$D = 10^{-9} \text{ m}^2/\text{s}$
Molar mass:	$M = 18 \text{ kg/kmol}$
Heat of evaporation:	$\Delta Q = 7.35 \cdot 10^{-20} \text{ J}$
Reference temperature:	$T_0 = 293 \text{ K}$
Equilibrium concentration:	$C_0 = 5.78 \cdot 10^{23} \text{ m}^{-3}$
Equilibrium concentration of vapour at T_0 :	

we get numerically the following equilibrium distributions (eq.5.1) for our system (eq.5.5)

$$N_{mwc} = \{ N_1=14901, N_2=34, N_3=6, N_4=2, N_5=1 \}$$

$$S(U, V, N_{mwc}) - S_{hom} = 48.4956 \text{ kJ} \quad (5.7)$$

and

$$N_{m^*} = \{ N_1=14811, N_2=20, N_3=1, N_4=1 \}$$

$$S(U, V, N_{m^*}) - S_{hom} = 85.9367 \text{ kJ} \quad (5.8)$$

with

$$S_{hom} / k_B = 277872.18 \quad (5.9)$$

as the value of the entropy for the initial homogeneous situation $N = \{ N_1=15000 \}$ at time $t = 0$.

In the following we discuss the results of the stochastic simulations of isoengetic nucleation in a water system (eq.5.6) of 15000 particles (eq.5.5). The calculations were done on the 16-bit computer ATARI 1040ST and one run requires about 40 hours of computer time. As the starting point we use an uniform homogeneous supersaturated situation of monomers an (gaseous state), that means we have at $t=0$:

- Particle distribution: $N_i = N_i = 15000$
- Supersaturation: $y = 12.65$ (5.10)
- Entropy: $S_{hom}/k_B = 277872.18$
- Free energy: $F_{hom}/k_B T_0 = -255372.18$
- Pressure: $P_{hom} = 31.92 \text{ kPa}$
- Temperature: $T_{hom} = T_0 = 293 \text{ K}$

According to the master equation (3.3) with the transition rates per unit time (eqs.4.13,4.15) the nucleation process is simulated. Not going into the details of the simulation procedure the kinetics of the phase transition is shown in Fig. 1, describing the frequencies N_n (here we use instead of N_n the quantity nN_n) over the clusters sizes n . The time evolution of the droplet ensemble is snapshotted at nine

different times (Fig. 1a-1). For these nine steps we present in (5.11) the cluster distributions, the values of the reduced entropy $\Delta S = S(U, V, N(t)) - S_{hom}$ and further quantities (see Sect. 5.2):

- a) $t = 0$ ns, 0 reactions
 $\Delta S/k_B = 0$, $\Delta F = 0$ J, $\Delta P = 0$ kPa, $N_m = 0$, $M_m = 0$, $A_m = 0$ nm²
 $T = 293 \text{ K}$, $y = 12.86$, $N_1 = 15000$ } (5.11)
- b) $t = 0.032$ ns, 33041 reactions
 $N = \{ N_1=14911, N_2=28, N_3=4, N_4=2, N_5=1 \}$
 $\Delta S/k_B = 48.36$, $\Delta F = -6.083$ J, $\Delta P = 0.5779 \text{ kPa}$
 $T = 299.36 \text{ K}$, $y = 8.427$, $N_m = 36$, $M_m = 89$, $A_m = 30.12 \text{ nm}^2$
- c) $t = 0.285$ ns, 297084 reactions
 $N = \{ N_1=14862, N_2=37, N_3=5, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 44.51$, $\Delta F = -10.889$ J, $\Delta P = 1.0413 \text{ kPa}$
 $T = 304.40 \text{ K}$, $y = 6.117$, $N_m = 50$, $M_m = 138$, $A_m = 44.47 \text{ nm}^2$
- d) $t = 0.325$ ns, 338860 reactions
 $N = \{ N_1=14881, N_2=39, N_3=5, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 47.11$, $\Delta F = -8.973$ J, $\Delta P = 0.8626 \text{ kPa}$
 $T = 302.41 \text{ K}$, $y = 6.944$, $N_m = 45$, $M_m = 119$, $A_m = 38.82 \text{ nm}^2$
- e) $t = 0.542$ ns, 565807 reactions
 $N = \{ N_1=14869, N_2=38, N_3=4, N_4=2, N_5=1 \}$
 $\Delta S/k_B = 46.91$, $\Delta F = -10.988$ J, $\Delta P = 1.069 \text{ kPa}$
 $T = 304.54 \text{ K}$, $y = 6.069$, $N_m = 46$, $M_m = 131$, $A_m = 40.51 \text{ nm}^2$
- f) $t = 0.701$ ns, 732837 reactions
 $N = \{ N_1=14871, N_2=29, N_3=5, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 48.54$, $\Delta F = -12.808$ J, $\Delta P = 1.263 \text{ kPa}$
 $T = 306.45 \text{ K}$, $y = 5.377$, $N_m = 38$, $M_m = 129$, $A_m = 36.44 \text{ nm}^2$
- g) $t = 0.788$ ns, 824575 reactions
 $N = \{ N_1=14860, N_2=30, N_3=5, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 54.47$, $\Delta F = -11.587$ J, $\Delta P = 1.1406 \text{ kPa}$
 $T = 305.16 \text{ K}$, $y = 5.840$, $N_m = 37$, $M_m = 120$, $A_m = 34.21 \text{ nm}^2$
- h) $t = 1.000$ ns, 1048963 reactions
 $N = \{ N_1=14837, N_2=21, N_3=4, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 67.32$, $\Delta F = -15.647$ J, $\Delta P = 1.5714 \text{ kPa}$
 $T = 309.42 \text{ K}$, $y = 4.451$, $N_m = 26$, $M_m = 123$, $A_m = 27.21 \text{ nm}^2$
- i) $t = 2.000$ ns, 2142908 reactions
 $N = \{ N_1=14796, N_2=18, N_3=3, N_4=1, N_5=1 \}$
 $\Delta S/k_B = 84.35$, $\Delta F = -32.754$ J, $\Delta P = 3.3191 \text{ kPa}$
 $T = 327.44 \text{ K}$, $y = 1.225$, $N_m = 22$, $M_m = 204$, $A_m = 29.86 \text{ nm}^2$

It is obvious that the isolated system relaxes into the thermodynamic equilibrium characterized by the maximum value of the entropy (Fig. 2). The results of a single run (Fig. 1, Fig. 2) and the mean value of ten runs (Fig. 3) demonstrate quite clearly the kinetics (Fig. 1) and thermodynamics (Fig. 2, Fig. 3) of the nucleation process in time. We note the agreement of the numerical and the theoretical equilibrium values for the primary distribution (eqs.5.11b, 5.7, Fig. 1b)

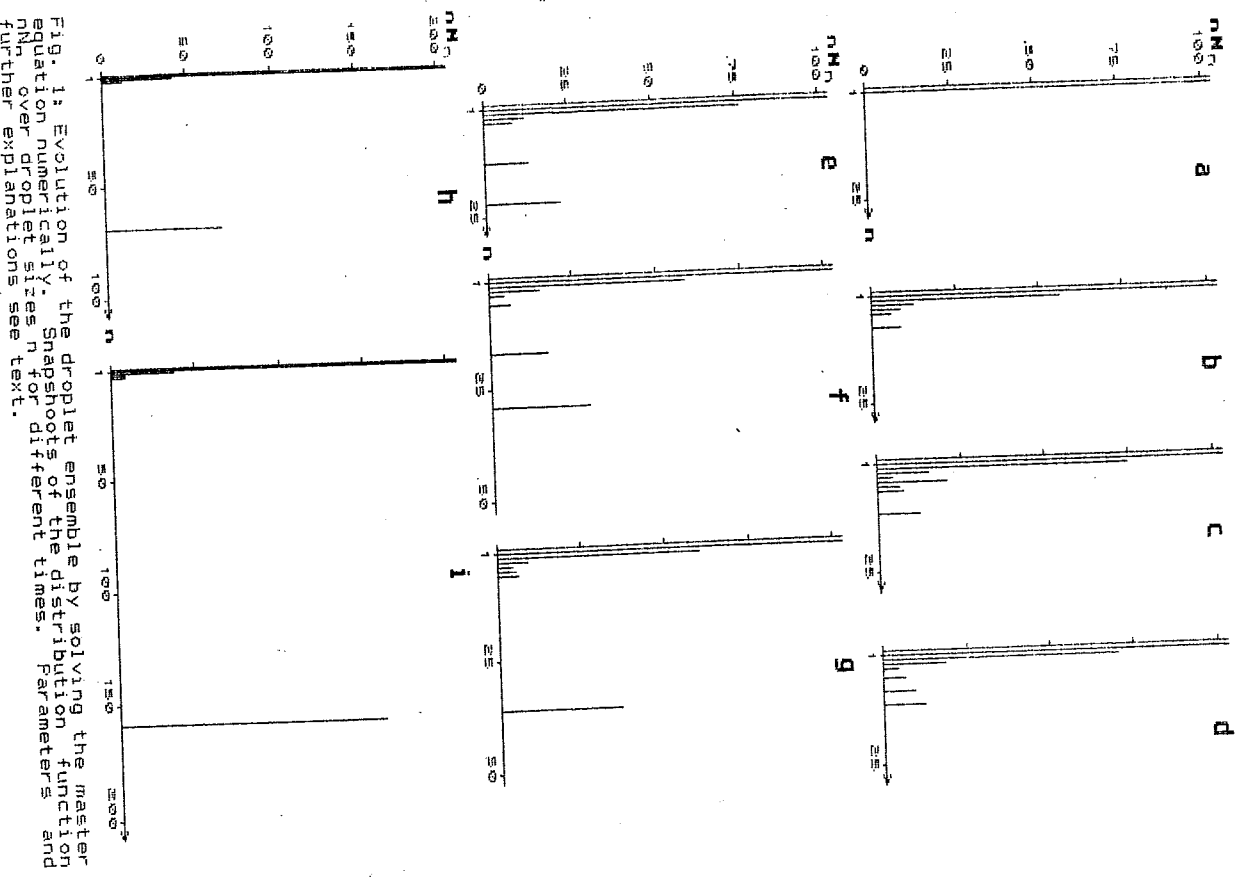


Fig. 1: Evolution of the droplet ensemble by solving the master equation numerically. Snapshots of the distribution function f_n over droplet sizes n for different times. Parameters and further explanations see text.

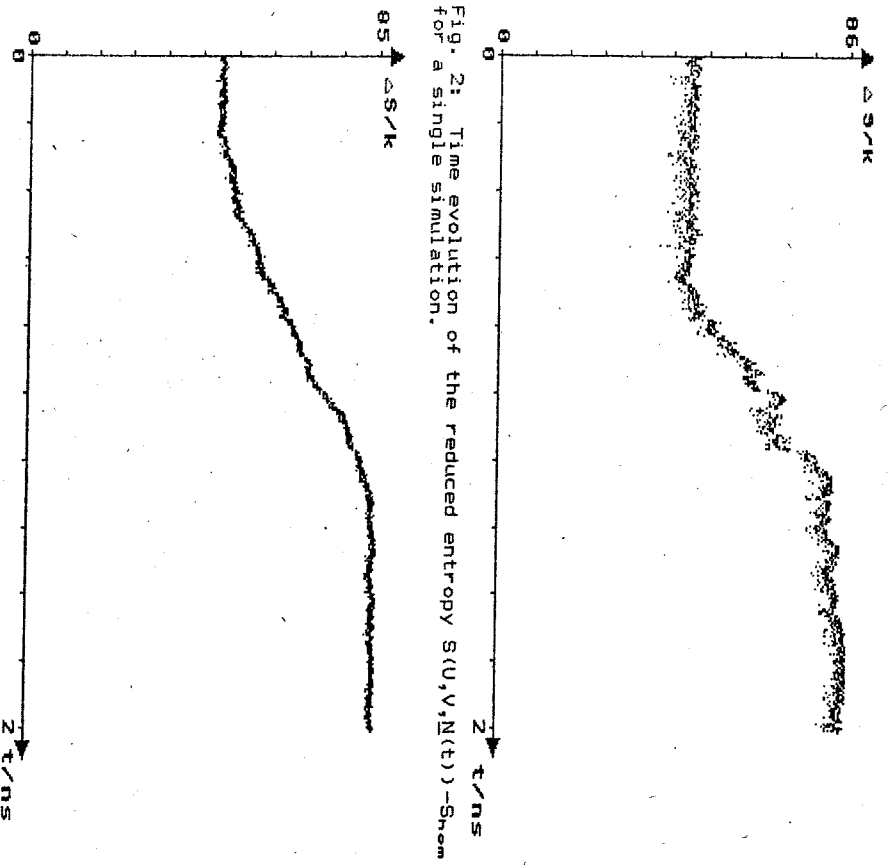


Fig. 2: Time evolution of the reduced entropy $S(U, V, N(t)) - S_0$ for a single simulation.

Fig. 3: Time evolution of the reduced entropy $S(U, V, N(t)) - S_0$ averaged over 10 stochastic simulations (runs) of the formation of water droplets.

and the final distribution (eqs. 5.11, 5.8, Fig. 11). We want to underline that the behavior of the state function entropy (eq. 4.12) over time (Fig. 2, Fig. 3) depends strongly on the correct expression of the potential energy $f_n(t)$ (eq. 4.5). In particular, applying the simple Bethe-Weizsäcker-formula (eq. 4.3) to all cluster sizes we get incorrect results and a wrong behaviour of the entropy. We come to the conclusion that

a careful analysis of the binding energies of clusters, especially of small nuclei, together with experimental data is necessary to understand the qualitative and quantitative features of the dynamical and thermodynamical properties of first-order phase transitions.

5.2. TIME EVOLUTION OF CHARACTERISTIC QUANTITIES

In the following pictures (Fig. 4-9) we present the time evolution of some characteristic quantities during the gas-liquid phase transition of water (isoenergetic nucleation). As already shown in Fig. 3 by the averaged entropy we have done 10 independent stochastic realisations solving the master equation. These mean values calculated as functions of the cluster distribution $N(t)$ and therefore of time are shown in Fig. 4-9. The temperature (eq. 4.8, Fig. 4) and the pressure (eq. 5.12, Fig. 5)

$$P(U, V, N) = k_B T / V \sum N_n \quad (5.12)$$

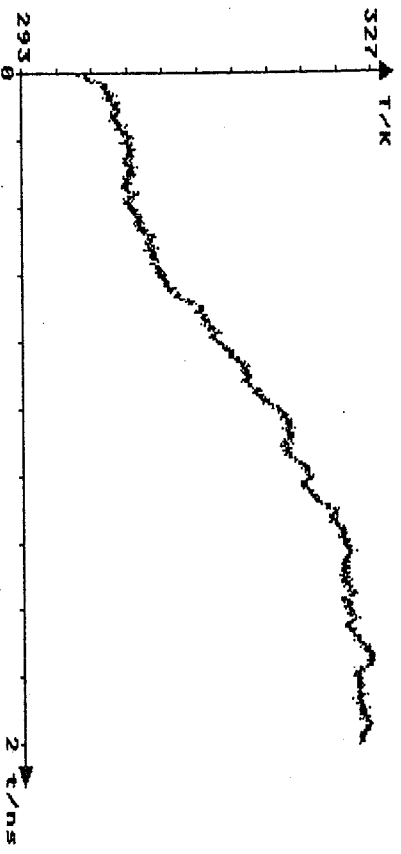


Fig. 4: The increase of the temperature in the system of condensable particles during the nucleation and growth of liquid water droplets.

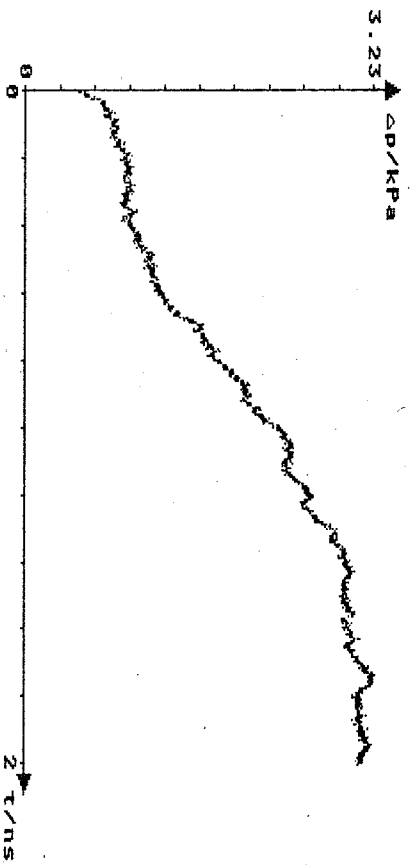


Fig. 5: The change of the temperature of the isolated system results the growth of the pressure $\Delta P = P(U, V, N(t)) - P_{hom}$ in the same time as the number of free particles is decreasing.

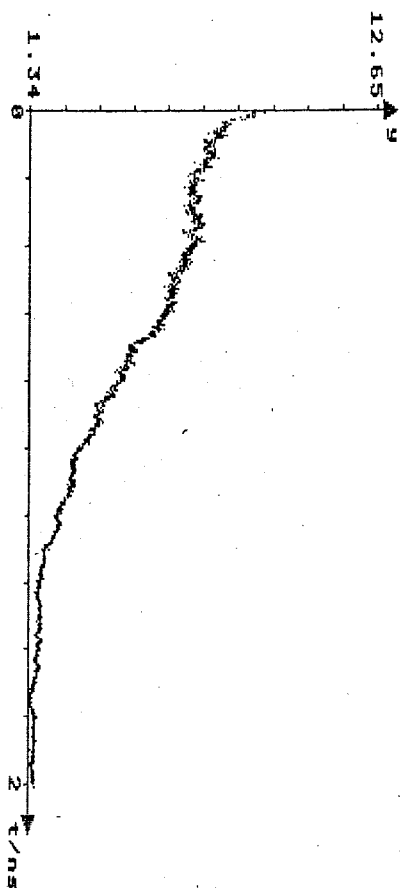


Fig. 6: The averaged time evolution of the supersaturation with respect to the temperature dependence of the equilibrium concentration of vapour.

are increasing. The supersaturation (eq. 5.13, Fig. 6)

$$y = (N_1/V - c_{eq}(T)) / c_{eq}(T) \quad (5.13)$$

starting with $y=12.65$ goes down to its equilibrium value.

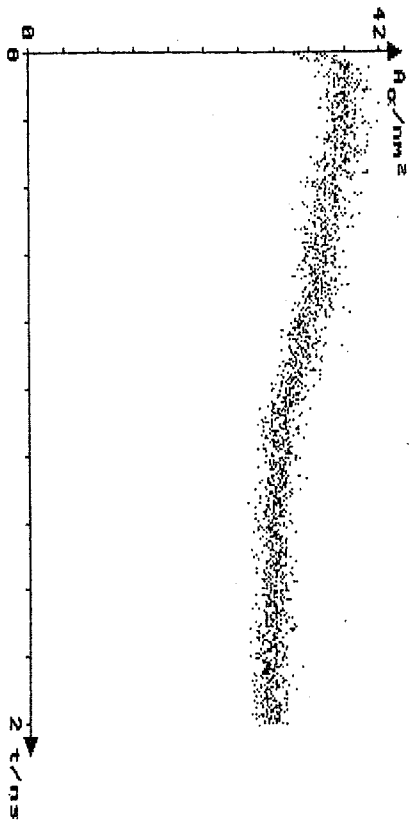


Fig. 7: The averaged time evolution of the overall surface area of all clusters (without monomers). The figure shows the fast growth of small clusters in the first stage of phase transition and the minimisation of the surface in the stage of Ostwald ripening.

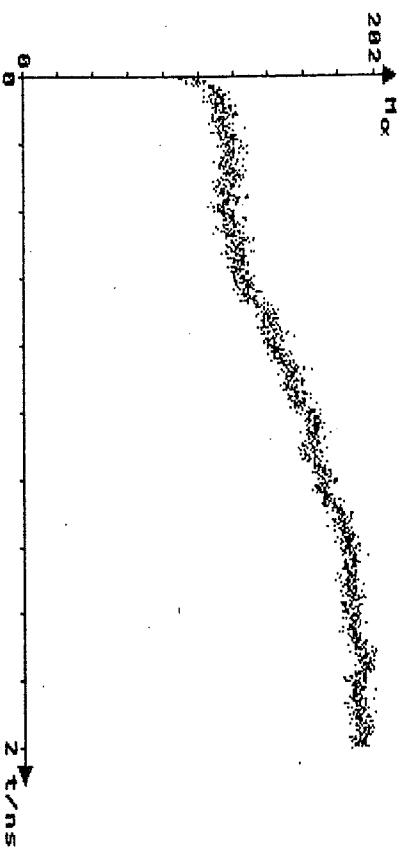


Fig. 8: The averaged time evolution of the overall number of bounded particles.

All these thermodynamic quantities and characteristics of the droplet ensemble, too, as the total surface of all drops $A_c = \sum A_n N_n$ (Fig. 7), the total number of bounded monomers $M_c = \sum n N_n$ (Fig. 8), the overall number of clusters $N_c = \sum N_n$

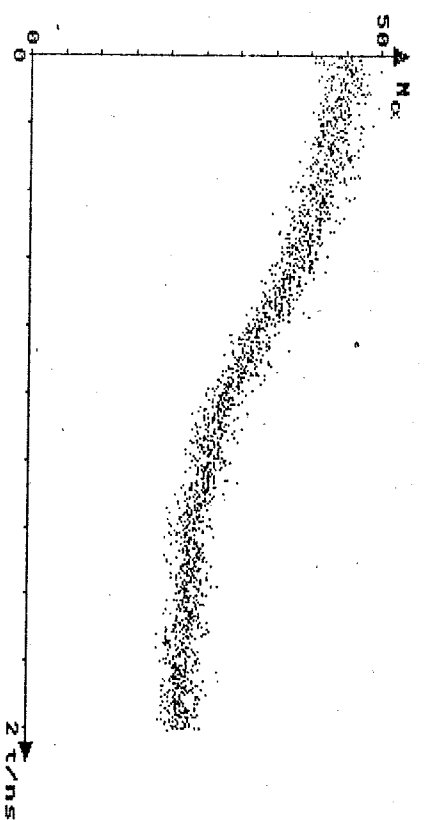


Fig. 9: The averaged time evolution of the number of all clusters (without monomers). The figure shows the fast formation of small clusters in the first stage of phase transition and their evaporation during the stage of Ostwald ripening.

(Fig. 9) make transparent the three stages of the transformation process: nucleation, growth and Ostwald ripening (The summation index n goes here from $n=2$ / dimers/ to $n=N_c$). During the first very short stage, in the supersaturated vapour small nuclei are formed by thermal fluctuations. If we take into account a depletion of the vapour in a finite system, that means the supersaturation decreases because of nucleation, at a certain value of supersaturation no more overcritical droplets are able to arise and the growth process of the established droplets is dominating. For a more decreased supersaturation the growth is converted to a long-time competition process of the droplets, that is the so called Ostwald ripening.

REFERENCES

- 1) A.C.Zettlemoyer. (Ed.), Nucleation, New York 1969, Nuclear-
tion Phenomena, Adv. Colloid Interface Sci. Z (1977)
- 2) J.D.Gunton, M.San Miguel, P.S. Sahni, (The Dynamics of
First-Order Phase Transitions), in: Phase Transitions and
Critical Phenomena (Eds: C.Domb, M.S.Green, J.L.Lebowitz)
vol. 8 London-New York 1983
- 3) M.Volmer, A.Weber, Z.phys.Chem 119 (1926) 277;
R.Becker, W.Döring, Ann.Phys. 24 (1935) 719
- 4) J.L.Frenkel, Kinetik Theory of Liquids, New York 1955
- 5) J.Schmelzer, H.Ulbricht, J.Colloid Interface Sci. 117
(1987) 325
- 6) F.Schweitzer, L.Schimansky-Geier, W.Ebeling, H.Ulbricht,
Physica A (1988), in press
- 7) H.Ulbricht, J.Schmelzer, R.Mahnke, F.Schweitzer; Thermo-
dynamics of Finite Systems and the Kinetics of First-Order
Phase Transitions, Teubner, Leipzig 1988
- 8) F.Schweitzer, L.Schimansky-Geier, W.Ebeling, H.Ulbricht,
Physica A 150 (1988) 261
- 9) J.Schmelzer, F.Schweitzer, Z.phys.Chem. (1988) in press
- 10) J.Schmelzer, H.Ulbricht, J.Colloid Interface Sci. (1988) in
press
- 11) C.W.Gardiner, Handbook of Stochastic Methods, Berlin-
Heidelberg-New York 1984
- 12) W.J.Shugard, H.Reiss, J.Chem.Phys. 65 (1976) 2827
- 13) H.Metiu, K.Kitahara, J.Ross, J.Chem.Phys. 64 (1976) 292
- 14) D.T.Gillespie, J.Chem.Phys. 74 (1981) 661
- 15) L.Schimansky-Geier, W.Ebeling, Ann.Phys.(Leipzig) 40 (1983)
10; W.Ebeling, L.Schimansky-Geier, Physica 98A (1979) 587
- 16) L.Schimansky-Geier, F.Schweitzer, W.Ebeling, H.Ulbricht;
in: Selforganization by Nonlinear Irreversible Processes
(Eds. W.Ebeling, H.Ulbricht) Berlin-Heidelberg-New York
1986, p.67
- 17) see e.g. R.H.Heist, H.Reiss, J.Chem.Phys., 59 (1973) 665
- 18) W.Becker, Theorie der Wärme, Berlin-Heidelberg-New York 1964
- 19) W.Ebeling, Sitzungsberichte der AdW der DDR ZZN (1981) 33
- 20) F.Schweitzer, L.Schimansky-Geier, J.Colloid Interface Sci.
119 (1987) 67
- 21) W.Ebeling, D.Kremp, W.Kraeft; Theory of Bound States,
Berlin 1976
- 22) A.Budde, R.Mahnke, Rostocker Physik. Manuskript. 10 (1987)
92
- 23) G.Kortüm, Einführung in die chemische Thermodynamik,
Göttingen 1963
- 24) W.H.Zureck, W.C.Schieve, in: Phase Transitions, vol.2.
Gordon and Breach 1981, p.31
- 25) H.Ulbricht, F.Schweitzer, R.Mahnke, in: Selforganization by
Nonlinear Irreversible Processes (Eds. W.Ebeling,
H.Ulbricht), Berlin-Heidelberg-New York 1986, p.27
- 26) J.Schmelzer, F.Schweitzer, Z.Phys.Chem.(Leipzig) 266 (1985)
943
- 27) Yu.L. Klimontovich: Statistical Physics, Moscow 1982, New
York 1985
- 28) J.Schmelzer, H.Ulbricht, Thermodynamics and the Scenario of
First-Order Phase Transitions, present volume
- 29) Water (Ed. F.Franks), vol. 1, New York London 1972

Authors:

Dr. Frank Schweitzer
Dr. Axel Budde
Dr. Reinhard Mahnke
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock
DDR - 2500