

A STOCHASTIC APPROACH TO NUCLEATION IN FINITE SYSTEMS: THEORY AND COMPUTER SIMULATIONS

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A stochastic theory is presented for nucleation and growth of clusters in a finite system. We consider a discrete cluster distribution for which the free energy and the equilibrium probability distribution are derived. The cluster growth and shrinkage occurs by the attachment/evaporation of free particles. The transition probabilities reflect that clusters of different sizes cannot evolve independently due to the limitation of the total particle number and the finite system size.

Computer simulations demonstrate the time dependence of various significant properties of the system: e.g. cluster distribution, supersaturation, critical cluster size. We discuss three stages of the phase transition in finite systems: a short period of predominant nucleation, a period of growth of supercritical clusters and a period of Ostwald ripening.

A Fokker–Planck equation for the mean cluster distribution is derived and solved by means of computer simulations. The evolution of the mean cluster distribution can be described by two time scales which are determined by simulation experiments.

1. Introduction

This paper deals with the description of nucleation and growth of clusters in a low supersaturated vapour. In contrast to the classical nucleation theory we consider a finite system with a limited total particle number.

Earlier investigations on a description of the nucleation process^{1–3}) presume an independent formation and growth of clusters. This assumption is valid only for infinite systems where the vapour state does not change due to the formation of clusters. In finite systems the limitation of the total particle number and the fixed system size lead to a depletion of the vapour. Therefore the formation and growth of different clusters is coupled by the vapour

pressure and we find a scenario of the phase transition where three stages can be distinguished.

This scenario can be derived generally also from a deterministic description based on thermodynamic investigations⁴⁻⁶). Indeed a thermodynamic analysis of a heterogenous finite system⁷) allows the prediction of the critical and stable cluster size^{8,9}) and will provide us with information on critical thermodynamic constraints for the phase transition¹⁰). But a detailed investigation on nucleation and growth of clusters in finite systems caused by fluctuations has been still in request.

We propose a stochastic description for the formation of clusters which restricts itself to a mesoscopic time scale. 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 similar to the classical droplet model. That means it can be characterized by a macroscopic density and surface tension.

In the considered case the simulation of the phase transition is started from an initial state of only free particles. The free energy of this state is much larger than that in the final equilibrium state; that means the system exists initially in a non-equilibrium state and will relax into the equilibrium state after crossing over an energy barrier. This nucleation barrier is known already from thermodynamic investigations^{1,8,9}) and separates the metastable and the stable state of the system. The cross-over of this barrier is an intrinsic stochastic process which can be explained only by consideration of the fluctuations in the system. In a deterministic sense undercritical clusters have to diminish again as will be shown in terms of a deterministic growth equation in section 5.

2. Description of the cluster distribution

2.1. Model of the finite system

In the following we consider a closed and finite system with a fixed system volume V and a fixed total particle number N in the gaseous state:

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

As is known from experiments on condensation in a vapour¹), in general a carrier gas is used to transport the latent heat which will be released during the condensation process. This carrier gas should be uncondensable for the given constraints. Therefore the total particle number is divided into the particle number of the carrier gas (N_0) and the particle number of the condensable

vapour (N_m) both being constant,

$$N = N_0 + N_m . \quad (2.2)$$

Due to interactions between the particles of the condensable vapour a number of particles is bound in clusters and a discrete distribution of clusters and free particles in the gas exists:

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

N denotes the discrete cluster distribution where N_1 is the number of free particles of the condensable vapour (monomers), N_2 the number of bound states with two particles (dimers) and so on. Because of the limited number of particles the following holds:

$$N_m = \sum_{n=1}^N nN_n = \text{const.} \quad (2.4)$$

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

$$0 \leq N_n \leq N_m/n . \quad (2.5)$$

We can now discuss the two limiting cases:

i) For $N_0 = 0$ we have isoenergetic conditions. The inner energy of the system should be constant because no condensation heat is transported to the background by means of the carrier gas.

ii) If $N_0 \gg N_m$, the latent heat of condensation will be completely brought back in a short time and we have isothermal conditions.

We restrict ourselves here to the second case of the isothermal nucleation process. The influence of the carrier gas on the phase transition will be considered elsewhere. So we fix the thermodynamic constraints now as follows:

$$N = N_m = \text{const.}, \quad V = \text{const.}, \quad T = \text{const.}, \quad (2.6)$$

with N now being the particle number of the condensable vapour. The thermodynamic constraints (2.6) are chosen in such a way that the pressure p_0 of a supposed perfect vapour consisting of free particles only is much larger than the equilibrium pressure $p'(T)$ at the same temperature:

$$p_0 = Nk_B T/V > p'(T) . \quad (2.7)$$

This allows us to introduce the initial supersaturation of a vapour with only free particles by $y_0 = p_0/p'$. It is an appropriate parameter to represent the thermodynamic constraints. We note here the existence of critical thermodynamic conditions to form supercritical clusters in finite systems, e.g. a critical total particle number, a critical system size, a critical temperature and a critical initial supersaturation¹⁰).

2.2. Free energy of the cluster distribution

We now derive the canonical partition function $Z(T, V, N)$ for the system with the assumed discrete cluster distribution N (eq. (2.3.)). In general $Z(T, V, N)$ can be calculated by¹¹)

$$Z(T, V, N) = \int_{c(N)} \exp\left\{-\frac{1}{k_B T} H(q_1 \cdots q_N, p_1 \cdots p_N)\right\} dq_1 \cdots dp_N. \quad (2.8)$$

$H(q_1 \cdots p_N)$ is the Hamiltonian of the N -particle system, where q_n are the space coordinates and p_n are the momentum coordinates of the free and bound particles ($n = 1, \dots, N$). The integration is carried out for the subspace of the assumed particle configuration N : $C(N) = C(N_1 \cdots N_N)$.

Supposing an ideal mixture of the clusters and free particles we get from eq. (2.8) with the correct normalization¹²)

$$Z(T, V, N) = \prod_{n=1}^N \frac{1}{n^{3N_n} N_n!} \int \exp\left\{-\frac{H_n}{k_B T}\right\} dQ_1 \cdots dQ_n dP_1 \cdots dP_n. \quad (2.9)$$

Q_n and P_n are now the space coordinates and momentum coordinates of clusters of size n . H_n is the Hamiltonian of a cluster with n particles and the mass m_n :

$$H_n = \frac{p_n^2}{2m_n} + f_n. \quad (2.10)$$

f_n denotes a potential contribution which depends only on the size n of a cluster. Because of the assumed ideal mixture no contributions arise from the interactions between clusters and monomers.

The free energy of a certain cluster distribution is defined as usually:

$$F(T, V, N_1 \cdots N_N) = -k_B T \ln Z(T, V, N_1 \cdots N_N). \quad (2.11)$$

After integration of eq. (2.9) with respect to eq. (2.10) we get for the free energy¹²⁾

$$F(T, V, N_1 \cdots N_N) = \sum_{n=1}^N N_n \left\{ f_n + k_B T \left(\ln \frac{N_n}{V} \lambda_n^3 - 1 \right) \right\}. \quad (2.12)$$

$\lambda_n = n / (2\pi m_n k_B T)^{1/2}$ is the de Broglie wavelength. To determine the potential term f_n we choose a first approximation similar to the theory of atomic nuclei which includes only volume and surface effects:

$$f_n = -An + Bn^{2/3}. \quad (2.13)$$

The first term of eq. (2.13) corresponds to the binding energy in the cluster, but the second term to the surface energy.

The constant A is the binding energy of a particle in the cluster. It can be estimated by the molar evaporation heat H_v : $A = H_v / N_A$. Another but quite equal expression for A was derived in comparison with thermodynamic results¹⁰⁾:

$$A = -k_B T \ln \frac{p'(T)}{k_B T} \lambda_1^3. \quad (2.14)$$

The surface energy is proportional to the surface area and the surface tension σ . Assuming a spherical cluster it yields for the constant B ¹⁰⁾:

$$B = 4\pi \left(\frac{4\pi}{3} c_\alpha \right)^{-2/3} \sigma. \quad (2.15)$$

c_α is the particle density in the cluster. Due to the classical droplet model presumed here the surface tension σ and the particle density are assumed to be constant.

The ansatz (2.13) for f_n is valid only for large clusters, where a real surface can be divided from the inner part of the cluster. On the other hand, it yields

$$\begin{aligned} f_1 &= 0, & \text{for monomers,} \\ f_2 &= -a, & \text{dimer binding energy.} \end{aligned} \quad (2.16)$$

The dimer binding energy has to be known from experiments. A possible form of f_n in the range of small values of n which satisfies the conditions (2.16) is proposed as follows:

$$f_n = -\frac{a}{2} n(n-1). \quad (2.17)$$

A Padé approximation as a possible interpolation of the expressions for $\partial f_n / \partial n$ in the range of small and large clusters was derived in ref. 13.

The free energy (eq. 2.12) includes the contribution of the pressure p and the Gibbs free enthalpy: $F = G - pV$. For the pressure follows:

$$p = \frac{k_B T}{V} \sum_{n=1}^N N_n, \quad (2.18)$$

while the Gibbs potential G is given by $G = \sum_{n=1}^N \mu_n N_n$ with

$$\mu_n = f_n + k_B T \ln \frac{N_n}{V} \lambda_n^3 \quad (2.19)$$

being the chemical potential of a cluster of size n .

3. Kinetics of the phase transition in finite systems

3.1. Kinetic assumptions and master equation

Nucleation process means the formation of clusters and their growth and shrinkage. The cluster evolution is represented by the time dependent development of the distribution $N = \{N_1, \dots, N_N\}$.

In order to discuss this evolution we suppose the following assumptions:

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



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

ii) Interactions between clusters, like coagulations 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).

Every possible configuration N of particles in clusters is found only with a certain probability defined by

$$P(N, t) = P(N_1, N_2, N_3 \cdots N_N, t).$$

Due to the interactions assumed in eq. (3.1) $P(N, t)$ changes with time. This

can be described by a master equation. Since N is a vector of discrete states the master equation has the form

$$\frac{\partial P(N, t)}{\partial t} = \sum_{N'} \{w(N|N')P(N', t) - w(N'|N)P(N, t)\}. \quad (3.2)$$

The quantities $w(N'|N)$ are the transition probabilities per time unit for the transition from N to N' . N' specifies those distributions which are attainable from the assumed distribution N via the reaction (3.1).

3.2. Equilibrium probability distribution

The stationary solution of the master equation requires that $\partial P(N, t)/\partial t = 0$. From this condition we find $\sum_{N'} J(N|N') = 0$ with $J(N|N') = w(N|N')P(N', t) - w(N'|N)P(N, t)$ being the probability flux between N' and N . For finite systems the equilibrium condition is given by the more restrictive condition of detailed balance. It means $J(N|N') = 0$ resulting in

$$w(N|N')P^0(N') = w(N'|N)P^0(N). \quad (3.3)$$

$P^0(N)$ is the equilibrium probability distribution in the space of all possible particle configurations. In the following it is derived from microscopic considerations.

Let $u(q_1 \cdots q_N p_1 \cdots p_N)$ be the probability distribution for the N particles in the phase space of the space and momentum coordinates of all particles. In thermodynamic equilibrium the following relation is valid:

$$u^0(q_1 \cdots p_N) = \frac{1}{Z(T, V, N)} \exp\left\{-\frac{1}{k_B T} H(q_1 \cdots q_N p_1 \cdots p_N)\right\}. \quad (3.4)$$

$H(q_1 \cdots p_N)$ is the Hamiltonian of the N particles as used already in eq. (2.8). $Z(T, V, N)$ is the canonical partition function of the N particles in an atomic picture. For the given constraints $Z(T, V, N)$ depends on the total particle number N and the thermodynamic constraints only and gives the normalization. We now define the probability of the equilibrium distribution $P^0(N)$ by an integral of $u^0(q_1 \cdots p_N)$ over the subspace $C(N)$:

$$P^0(N) = \int_{C(N)} u^0(q_1 \cdots p_N) dq_1 \cdots dp_N. \quad (3.5)$$

Use of eqs. (2.8) and (3.4) allows us to introduce the canonical partition function for the assumed cluster distribution $Z(T, V, N)$ into eq. (3.5). We

receive finally with respect to eq. (2.11) the probability of the equilibrium distribution in the form

$$P^0(N) = \frac{Z(T, V, N)}{Z(T, V, N)} = \frac{1}{Z(T, V, N)} \exp\left\{-\frac{1}{k_B T} F(T, V, N_1 \cdots N_N)\right\}. \tag{3.6}$$

The equilibrium cluster distribution can be found from the minimum condition $\partial P^0(N)/\partial N_n = 0$. We find

$$\left(\frac{N_n^0}{V} \lambda_n^3\right) = \left(\frac{N_n^0}{V} \lambda_1^3\right)^n \exp\left\{-\frac{f_n}{k_B T}\right\}, \quad n = 2, \dots, N, \tag{3.7}$$

where $N_1 = N - \sum_{n=2}^N nN_n$.

Due to this boundary condition eq. (3.7) is a system of equations which have to be solved simultaneously. Using the denotation of the chemical potential μ_n (eq. 2.19) the equilibrium solution can be written in the form of a mass action law¹¹): $\mu_n^0 = n\mu_1^0$.

3.3. Transition probabilities

For a discussion of the stochastic evolution of the cluster distribution we need now proper transition probabilities to describe the attachment or evaporation of monomers to/from clusters. With respect to the condition of detailed balance in the final equilibrium state only one kinetic assumption is used which considers the reaction (3.1). The transition probability for the opposite process can be determined by means of the free energy as follows:

$$w(N|N') = w(N'|N) \exp\left\{\frac{1}{k_B T} [F(T, V, N') - F(T, V, N)]\right\}. \tag{3.9}$$

We assume that the probability of the attachment of a monomer to a cluster of size n increases with the surface of the cluster and with the density of free particles and the number of clusters of size n . In this way we get for the special process of attachment:

$$\begin{aligned} w(N'|N) &= w(N_1 - 1 \cdots N_n - 1 N_{n+1} + 1 \cdots N_N | N_1 \cdots N_n N_{n+1} \cdots N_N) \\ &\equiv w_n^+(N_1 N_n) = \alpha n^{2/3} N_n N_1 / V, \quad N_1 = N - \sum_{n=2}^N nN_n. \end{aligned} \tag{3.10}$$

α is a constant which scales the time. In this paper α is set equal to one. In

general for the value of the parameter α one has to consider the specific properties of the surface, like surface tension, composition of the surface and the sticking coefficient.

Previous investigations on a stochastic description of the nucleation process¹⁴⁻¹⁶) presume an independent formation and growth of clusters. In the case of isobaric constraints the description is reduced to a linear random walk process for the size of a single cluster. But in isochoric finite systems the probability $P(N, t)$ does not factorize because the total number of particles is conserved and the growth of clusters of different sizes are correlated by the vapour pressure.

We note that in the case of creating a dimer the transition probability differs slightly. In this case it reads

$$w(N_1 - 2 N_2 + 1 \cdots N_N | N_1 N_2 \cdots N_N) \equiv w_1^+(N_1) = \alpha N_1(N_1 - 1)/V. \tag{3.11}$$

The transition probability per time unit for the evaporation of one particle from a cluster of size n is received from eq. (3.9) in the form

$$\begin{aligned} w(N' | N) &= w(N_1 + 1 \cdots N_{n-1} + 1 N_n - 1 \cdots N_N | N_1 \cdots N_{n-1} N_n \cdots N_N) \\ &\equiv w_n^-(N_n) = \alpha n^{2/3} N_n \left(\frac{n-1}{n}\right)^{13/6} \frac{1}{\lambda_1^3} \exp\left\{\frac{1}{k_B T} (f_n - f_{n-1})\right\}. \end{aligned} \tag{3.12}$$

The transition probability of evaporation is proportional to the surface area and the number of clusters of size n again. Neglecting the term $(n-1/n)^{13/6}$ which is nearly equal to one and using the ansatz for f_n (eq. 2.13) valid for large clusters, the transition probability (eq. 3.12) can be written in the form

$$w_n^-(N_n) = \alpha n^{2/3} N_n \frac{p'(T)}{k_B T} \exp\left\{\frac{2}{3} \frac{B}{k_B T} n^{-1/3}\right\}. \tag{3.13}$$

Let us note that the transition probability of evaporation in our model is not determined by the whole cluster distribution as is the case for the transition probability of attachment. It depends only on the conditions of the cluster itself.

3.4. Results of computer simulations

We now investigate the stochastic evolution of the cluster distribution in the finite system by means of computer simulations. In order to solve the master equation we use the stochastic dynamics technique^{17,18}).

In order to simulate the whole process of formation and growth of clusters

we choose a constant overall particle number $N = 150$. The thermodynamic constraints are represented in terms of the initial supersaturation $y_0 = Nk_B T/p'(T)V$. With respect to the constant value of N an increase of y_0 means a decrease of the temperature T or a decrease of the system volume V .

The specific properties of the vapour and the liquid phase are obtained for ethanol. For a temperature $T = 290$ K the constants A (eq. 2.14) and B (eq. 2.15) representing these properties are held as: $A = 19.08k_B T$ and $B = 5.32k_B T$.

The stochastic simulation starts with the restriction that in the initial state only free particles exist in the system. The first possible reaction is the formation of a dimer. This dimer has a certain lifetime which is determined randomly with respect to the transition probabilities. For the second reaction three possibilities exist: the dimer grows up to a trimer, or the dimer splits, or a second dimer will be created. One of these reactions is randomly chosen corresponding to the values of the possible transition probabilities. With the obtained new particle configuration the evolution of the cluster distribution will be continued.

The results of the stochastic cluster evolution are presented in fig. 1 obtained from a single computer run. It gives five snapshots of the particle configuration for different moments. Figs. 2 and 3 shall accompany the discussion of the phase transition. They present the time dependent evolution of the total number of clusters ($n \geq 2$) and of the total number of bound particles in clusters, respectively.

We can distinguish between three different stages of the phase transition in finite systems:

(i) First a period of predominant formation of undercritical clusters occurs where a distribution of free particles, dimers, trimers have been established in a very short time (after about 500 reactive collisions) (compare fig. 1a). Both the number of clusters and the number of bound particles in clusters increase rapidly.

(ii) After a certain time lag some of these small clusters begin to grow up stochastically to a supercritical size (compare fig. 1b, c). In this period a favoured cluster growth is obtained. The nucleation period has been finished and the number of clusters is already decreasing. The number of bound particles increases again.

(iii) In the last but longest period the number of clusters and the number of bound particles are nearly constant, but fluctuate because always new dimers are created or disappear. During this period one of the larger clusters grows to its final stable state. This cluster succeeds in a competition process, that means its further growth occurs at the expense of the smaller clusters which have to disappear. This process is also called "Ostwald ripening" characterized by the

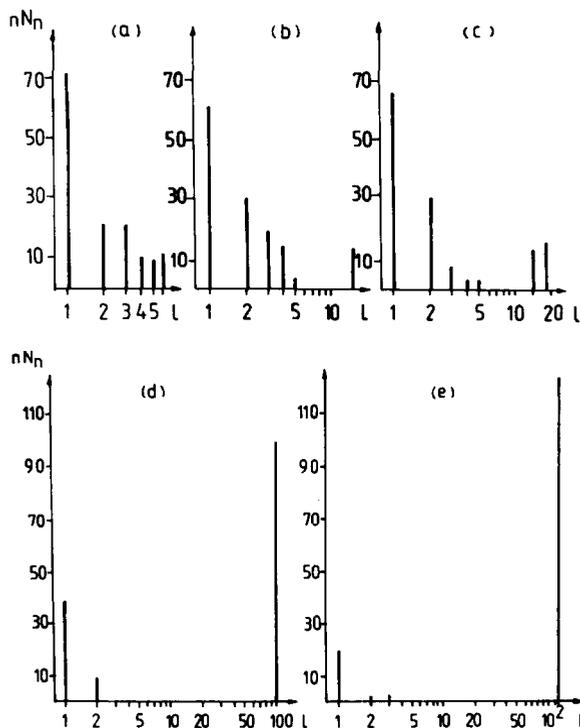


Fig. 1. Stochastic evolution of the cluster distribution. Presented is the number nN_n versus cluster size n for different time moments (in time units). R gives the number of reactive collisions during the given time t , y denotes the recent supersaturation in the system. Initial supersaturation $y_0 = 12.5$.

- (a) $R = 5 \times 10^2$, $t = 0.368$, $y = 8.35$;
- (b) $R = 1 \times 10^3$, $t = 0.719$, $y = 8.15$;
- (c) $R = 2 \times 10^3$, $t = 1.472$, $y = 7.30$;
- (d) $R = 5 \times 10^3$, $t = 6.750$, $y = 3.17$;
- (e) $R = 1 \times 10^4$, $t = 27.250$, $y = 2.17$.

restoration of the already bound particles from smaller to larger clusters caused by the re-evaporation of the small clusters (compare fig. 1d, e).

The final state (fig. 1e) is given by one large cluster surrounded by a distribution mainly of free particles and small clusters. This state is in accordance with the thermodynamic equilibrium of the two coexisting phases. The stable cluster size is determined by the thermodynamic constraints of the finite system only.

We note again that the process of formation of critical clusters – (i) – can be understood only by consideration of fluctuations in the system, while the growth of supercritical clusters and the Ostwald ripening period can be described by deterministic equations^{3,4}).

The time dependence of the supersaturation in the system presented in fig. 4

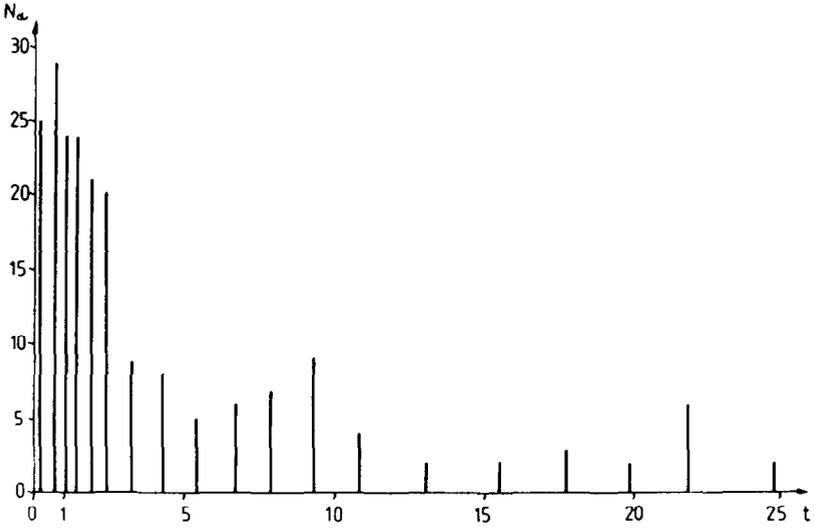


Fig. 2. Stochastic evolution of the number of clusters $N_\alpha = \sum_{n=2}^N N_n$ versus time (in time units). Initial supersaturation $y_0 = 12.5$.

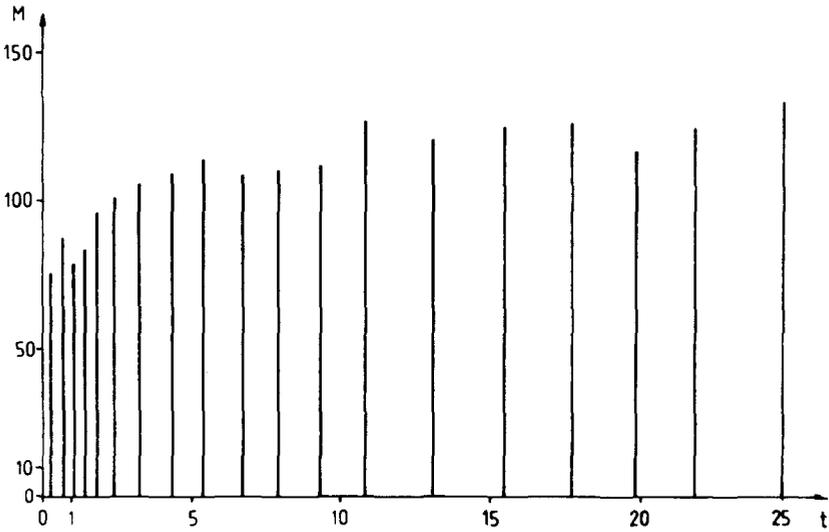


Fig. 3. Stochastic evolution of the number of bound particles in clusters $M = \sum_{n=2}^N nN_n$ versus time (in time units). Initial supersaturation $y_0 = 12.5$.

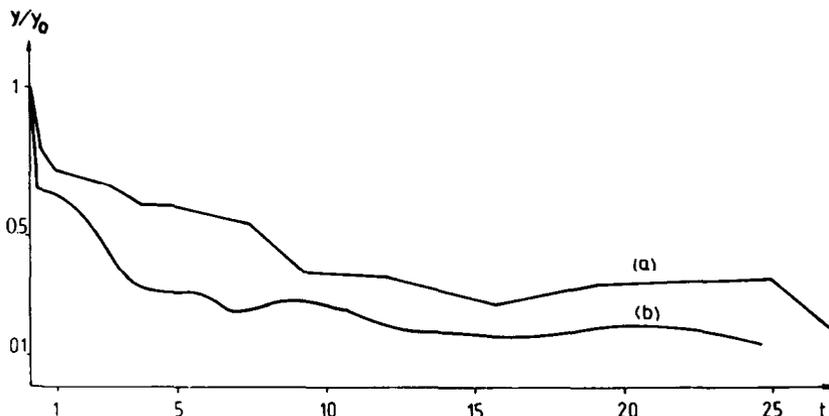


Fig. 4. Stochastic evolution of the reduced supersaturation $y(t)/y_0$ versus time (in time units). Initial supersaturation: (a) $y_0 = 7.5$; (b) $y_0 = 12.5$.

confirms the given results. The actual supersaturation $y(t)$ gives a measure of the distance from the equilibrium state. It starts with the value of the initial supersaturation y_0 and is reduced first in a very short time due to the nucleation process and then it decreases because of the depletion of the vapour when the overcritical clusters grow. In the last period the pressure in the system is nearly constant and changes stochastically. We note that the larger initial supersaturation decreases more rapidly.

4. Evolution of the mean cluster distribution

4.1. Fokker-Planck equation

In order to get a deeper insight into the time dependence of the phase transition in finite systems, we complete the given results of the stochastic evolution with a discussion of the mean cluster distribution.

The mean number of clusters is received from the first moment of the probability $P(N, t)$:

$$\langle N_n(t) \rangle = \sum_{\{N_i\}} N_n P(N_1 \cdots N_n \cdots N_N, t). \tag{4.1}$$

$\{N_i\}$ means every possible cluster distribution which fulfills the restrictive condition $N = \text{const}$.

By means of the master equation (3.2) the time dependence of the mean values $\langle N_n(t) \rangle$ can be expressed in the following form¹⁸:

$$\frac{d}{dt} \langle N_n(t) \rangle = \sum_j \Delta_j N_n \langle w_j(N' | N) \rangle. \tag{4.2}$$

$\Delta_j N_n$ gives the value of the change of N_n for every possible stochastic reaction j where the N_n participate. $\langle w_j(N'|N) \rangle$ denotes the averaged value of the related transition probability for the reaction j . Using the transition probabilities (3.10), (3.12) we obtain from eq. (4.2) the following system of equations:

$$\begin{aligned} \frac{d}{dt} \langle N_n \rangle &= \langle -w_n^- - w_n^+ + w_{n+1}^- + w_{n-1}^+ \rangle, \quad n = 2, \dots, N, \\ \frac{d}{dt} \langle N_1 \rangle &= \langle -2w_1^+ + 2w_2^- - \sum_{j=2}^N (w_j^+ - w_{j+1}^-) \rangle \\ &= -\langle w_1^+ - w_2^- + \sum_{j=1}^N (w_j^+ - w_{j+1}^-) \rangle. \end{aligned} \quad (4.3)$$

Now we make use of a Taylor expansion for the transition probabilities w_{n+1}^- and w_{n-1}^+ . Neglecting terms of higher than the second derivative we get the following differential equation:

$$\begin{aligned} \frac{d}{dt} \langle N_n(t) \rangle &= -\frac{\partial}{\partial n} \langle w_n^+(N_1 N_n) - w_n^-(N_n) \rangle \\ &\quad + \frac{1}{2} \frac{\partial^2}{\partial n^2} \langle w_n^+(N_1 N_n) + w_n^-(N_n) \rangle. \end{aligned} \quad (4.4)$$

Using the transition probabilities (3.10), (3.13) with the approximation $\langle N_1 N_n \rangle \approx \langle N_1 \rangle \langle N_n \rangle$ we find the following Fokker-Planck equation:

$$\frac{d}{dt} \langle N_n(t) \rangle = -\frac{\partial}{\partial n} \left[v_n \langle N_n(t) \rangle - \frac{\partial}{\partial n} (a_n \langle N_n(t) \rangle) \right] \quad (4.5)$$

with the quantities:

$$v_n = \alpha \langle n \rangle^{2/3} \left[\frac{\langle N_1 \rangle}{V} - \frac{p'}{k_B T} \exp \left\{ \frac{2}{3} \frac{B}{k_B T} \langle n \rangle^{-1/3} \right\} \right] \quad (4.6)$$

and

$$a_n = \frac{\alpha}{2} \langle n \rangle^{2/3} \left[\frac{\langle N_1 \rangle}{V} + \frac{p'}{k_B T} \exp \left\{ \frac{2}{3} \frac{B}{k_B T} \langle n \rangle^{-1/3} \right\} \right]. \quad (4.7)$$

The time dependent change of the mean number of clusters is now described in terms of a differential equation. The change of the mean number of free

particles must be considered with respect to the conservation of the overall particle number N :

$$\frac{d}{dt} \langle N_1(t) \rangle = - \frac{d}{dt} \sum_{n=2}^N \langle nN_n(t) \rangle . \tag{4.8}$$

The quantity v_n (eq. 4.6) is interpreted as the mean velocity of the deterministic cluster growth and shrinkage and will be discussed later. a_n (eq. 4.7) is a diffusion parameter indicating the measure of the fluctuations.

The time dependent evolution of the mean cluster distribution is sketched in fig. 5. For the initial state which consists of only free particles $\langle N_n(t=0) \rangle$ is a delta function in the state $n = 1$. The further evolution of $\langle N_n(t) \rangle$ can be described by means of two time scales^{19,20}:

i) In a shorter, quasistationary time scale the initial delta function relaxes into a Poissonian distribution around the nearest stable state. This state is given by the vapour phase being a metastable one. The metastable cluster distribution consisting of only free particles and small clusters exists in the supersaturated state over a certain time.

ii) During a larger, stationary time scale overcritical fluctuations become important. The metastable state is left and the mean cluster distribution will be broadened. Near the second stable state (drop) another maximum of the distribution is built up. Thus the phase transition occurs in the stationary time scale, which means stochastic behaviour.

At the end of the phase transition we find instead of the metastable unimodal mean cluster distribution a bimodal distribution which describes the coexistence of a stable cluster and the vapour by means of two maxima of $\langle N_n(t) \rangle$. The final state is asymptotically reached. In this case the maxima of $\langle N_n(t) \rangle$ coincide with the thermodynamic stable states of the deterministic picture, while the minimum is related to the instable state.

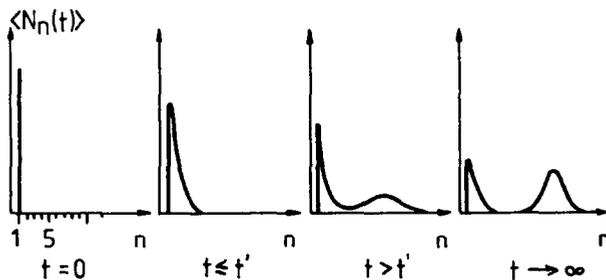


Fig. 5. Sketch of the mean cluster distribution for different moments. t' denotes the mean first passage time to reach a state where over-critical clusters ($n > n_{cr}$) exist.

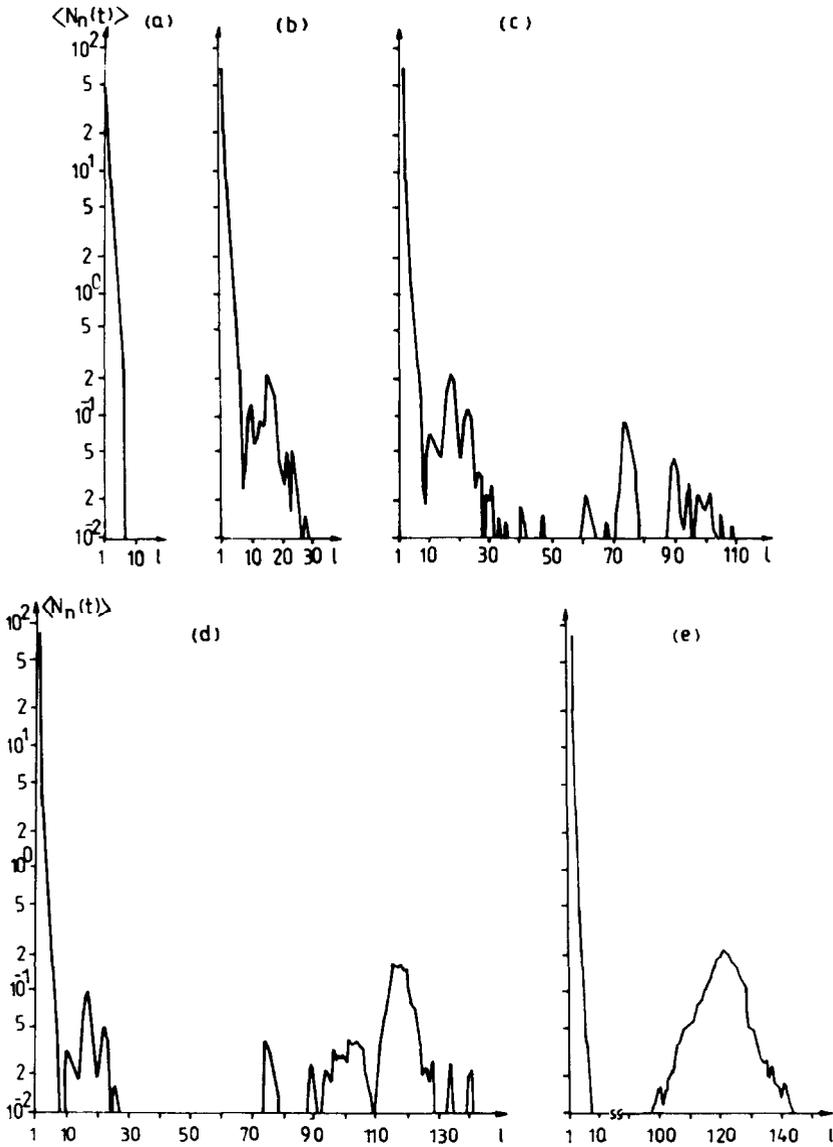


Fig. 6. Frequency of finding clusters with size n during a given time t (in time units) for a single run. R denotes the number of reactive collisions during the given time.

(a) $R = 5.0 \times 10^2$, $t = 0.368$;

(b) $R = 2.5 \times 10^3$, $t = 1.931$;

(c) $R = 5.0 \times 10^3$, $t = 6.752$;

(d) $R = 1.0 \times 10^4$, $t = 27.250$;

(e) $R = 3.2 \times 10^4$, $t = 129.371$.

Initial supersaturation $y_0 = 12.5$; vapour: ethanol, $N = 150$, $T = 290$ K.

The discussion of the mean cluster distribution is illustrated by means of computer simulations. Fig. 6 presents the simulation of the distribution obtained only from a single run. Averaging over a big number of independent runs this frequency distribution converges into the probability distribution. In fig. 6a it is to be seen that for less than 0.5 time units the metastable state is not left. Later on the frequency of finding larger clusters gains importance. During the phase transition a broad cluster distribution is obtained. When the stable cluster size is reached the frequency is confined near the second stable state and for large times we find a clear bimodal cluster distribution. The fluctuations of the stable cluster size can be found easy from fig. 6c.

4.2. Simulations of the mean first passage times

It has been shown that the phase transition can be described by means of two time scales. In order to characterize these time scales the concept of mean first passage time can be used.

The mean time of first passage into the critical state gives a measure for the quasistationary time scale. It approximates the lifetime of the metastable cluster distribution.

With the formation of the first critical cluster the probability of the phase transition increases. The minimum time to establish the bimodal mean cluster distribution can be characterized by the mean time of first passage into the stable state. Therefore it is a measure for the stationary time scale when the phase transition occurs.

Table I gives some values for the mean times of first passage into the critical and the stable state averaged over 20 independent computer runs. With an increasing initial supersaturation the transition times are shorter, but they fluctuate very strongly.

Analytic results for the mean first passage time are obtained only in the case of an one-dimensional random walk process, see ref. 21.

TABLE I
 Mean first passage time (in time units) from the initial state into the critical state (τ_{cr}) and into the stable state (τ_{st}) averaged over 20 runs. y_0 denotes the initial supersaturation, n_{cr} and n_{st} are the critical and the stable cluster sizes for the given thermodynamic constraints, φ denotes the standard deviation; vapour: ethanol, $N = 150$, $T = 290$ K.

y_0	n_{cr}	n_{st}	$\tau_{cr} \pm \varphi_{cr}$	$\tau_{st} \pm \varphi_{st}$
7.5	13	108	3.03 ± 2.64	21.24 ± 11.96
10.0	10	119	0.81 ± 0.43	11.30 ± 3.02
12.5	7	125	0.29 ± 0.18	9.23 ± 1.62

4.3. Deterministic cluster growth

The Fokker–Planck equation (4.5) allows a discussion of the deterministic cluster evolution in the limiting case of vanishing fluctuations. In this case the formation of new clusters or the disappearing of clusters is not taken into account and the deterministic kinetics can be written in the form of a continuity equation:

$$\langle N_n(t) \rangle + \text{div} \langle N_n(t) \dot{n} \rangle = 0. \quad (4.9)$$

\dot{n} denotes the deterministic velocity for the growth or shrinkage of the cluster of size n as already given in eq. (4.6). Use of power expansions in eq. (4.6) leads to the deterministic kinetics in the form:

$$\frac{d}{dt} \langle n \rangle^{1/3} = \alpha \frac{2}{3} \frac{B}{k_B T} \frac{p'}{k_B T} \left[\frac{1}{\langle n_{cr} \rangle^{1/3}} - \frac{1}{\langle n \rangle^{1/3}} \right], \quad (4.10)$$

where $\langle n_{cr} \rangle$ is the critical cluster size given by²²

$$\langle n_{cr}(t) \rangle^{1/3} = \frac{2}{3} \frac{B}{k_B T} \left(\ln \frac{\langle N_1(t) \rangle k_B T}{p' V} \right)^{-1}. \quad (4.11)$$

The critical cluster size acts as a selection value. Only clusters with an overcritical size are able to grow, undercritical clusters have to disappear again. The mean critical cluster size depends on time because the number of free particles $\langle N_1 \rangle$ reduces with the formation and growth of clusters. That is the reason why the critical cluster size possesses information on the recent state of the phase transition. Fig. 7 presents the time dependence of the critical cluster

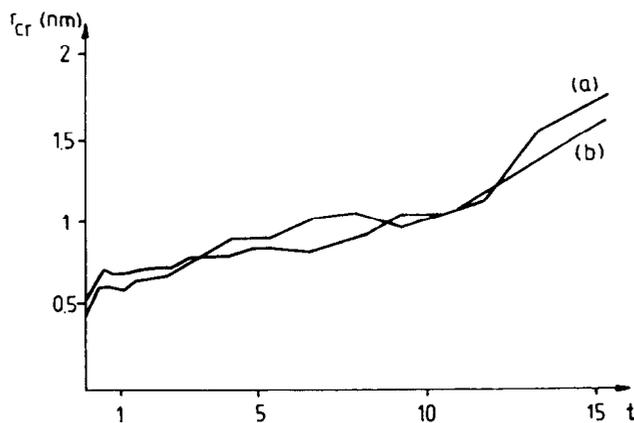


Fig. 7. Stochastic evolution of the critical cluster size (in nm) versus time (in time units). Initial supersaturation: (a) $y_0 = 7.5$; (b) $y_0 = 12.5$; vapour: ethanol, $N = 150$, $T = 290$ K.

size for the earlier stages of the phase transition as has been obtained from the stochastic simulations. In the initial state of only free particles n_{cr} has its smallest value given by²²⁾:

$$\langle n_{cr}(t=0) \rangle^{1/3} = \frac{2}{3} \frac{B}{k_B T} (\ln y_0)^{-1}. \quad (4.12)$$

It increases during the phase transition caused by the depletion of the vapour. The largest value (not shown in fig. 7) is reached if the pressure in the system is given by the saturation pressure. The time dependence of the critical cluster size is a typical finite system effect.

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