STOCHASTICS OF NUCLEATION IN ISOLATED GASES INCLUDING CARRIER MOLECULES

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A stochastic theory is presented for nucleation and growth of clusters in an isolated binary system, consisting of a vapour and a neutral carrier gas. We consider a discrete cluster distribution for which the entropy and the equilibrium probability distribution are derived. Due to the cluster formation the latent heat of condensation is released which effects an increase of the temperature. The influence of the carrier gas on the temperature increase is discussed. The isothermal nucleation process is derived as a limit case of the given description.

The cluster growth and shrinkage occurs by the attachment/evaporation of free particles. The transition probabilities reflect that the clusters of different sizes cannot evolve independently due to the dependence of the temperature and the number of free particles on the whole cluster distribution. The discussions shows, that for lower fractions of the carrier gas the transition probability of evaporation increases and the probability to find supercritical clusters is reduced. The supersaturation is dropped faster compared with the isothermal limit, which leads to quantitative changes in the kinetics of phase transition.

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 super-saturated 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 on the decrease of free particles. In particular, in a supersaturated vapour the formation and growth of different clusters is coupled by the vapor pressure and one finds a scenario of the phase transition where three stages can be distinguished.

This scenario has been discussed both from a deterministic point of view [5, 7] and in a stochastic context considering fluctuations [6, 7]. The advantage of the stochastic approach is a complete description of the nucleation period as well as the growth of the supercritical clusters and the late stage of Ostwald ripening by a uniform theory. Deterministic theories cannot explain the cross-over of the limitation nucleation barrier, which is an intrinsic stochastic process [8].

In previous papers [3–7] the condition of a constant temperature was assumed; this is realized only under certain constraints. In reality due to the attachment of free particles to the clusters the latent heat is released which increases the temperature of the system. Therefore it is more realistic to discuss nucleation and growth, e.g., under adiabatic constraints where the temperature is not constant, as has been done recently [9, 10].

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 effects an increase of the temperature. We will show that the isothermal nucleation process can be derived as a special case from this general point of view. Another limit case derived here corresponds to the nucleation of a pure vapour under isoenergetic conditions. Both cases will be compared with respect to the consequences for the nucleation process.

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 similar 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:

$$U = \text{const.}, \qquad V = \text{const.}, \qquad N = \text{const.} \tag{2.1}$$

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 "0". 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:

$$N = N_0 + N_v .$$ (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 (see fig. 1). This distribution is described by the vector N:

$$N = \{N_0, N_1 N_2 \ldots N_n \ldots N_{N_v}\} .$$ (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:

$$N_v = \sum_{n=1}^{N_v} n n_n = \text{const} .$$ (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
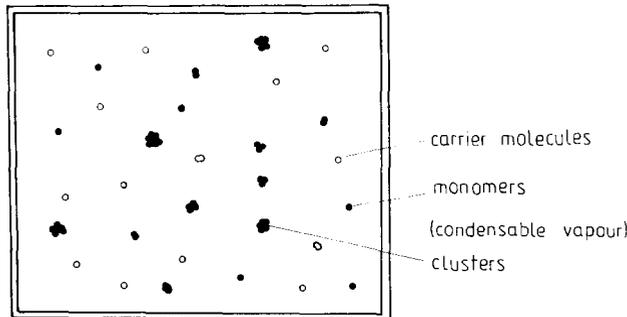

Fig. 1. Sketch of the considered system: We investigate a binary vapour consisting of a carrier gas and a condensable vapour where a cluster distribution has been established. The system is isolated, the system volume and the total particle number are fixed.

clusters it follows from eq. (2.4):

$$0 \leq N_n \leq N_v / n \ . \tag{2.5}$$

2.2. Equilibrium probability distribution

From a statistic point of view every possible distribution N is found with a certain probability for a given time, defined by

$$P(N, t) = P(N_0, N_1 N_2 \ldots N_n \ldots N_{N_v}, t) \ . \tag{2.6}$$

In a stochastic theory the formation and growth of clusters can be described by the change of $P(N, t)$ in time. Let us study first the equilibrium probability distribution $P^0(N)$. In thermodynamic equilibrium the probability $P^0(N)$ to find a certain distribution of clusters in the bath of the particles of the carrier gas is defined by the following relation [6, 16]:

$$P^0(N) = \int_{C(N)} \rho^0(q_1 \ldots p_N) \, dq_1 \ldots dp_N \ . \tag{2.7}$$

Here $\rho^0(q_1 \ldots p_N)$ means the equilibrium probability distribution for the N particles in the spatial and momentum coordinates of all particles. For a fixed total energy U the microscopic partical configuration is given by the microcanonical ensemble, which means [18]:

$$\rho^0(q_1 \ldots p_N) =$$

$$\begin{cases} \exp\left(-\dfrac{S(U, V, N)}{k_B}\right) = \text{const.} \, , & \text{for } U - \delta U \leq H \leq U + \delta U \, , \\ 0 \, , & \text{else} \, . \end{cases} \tag{2.8}$$

H is the Hamiltonian of the N particles system and δU the thickness of the energy shell. $S(U, V, N)$ in eq. (2.8) is the entropy of the N particles system which is known to be [15]

$$S(U, V, N) = k_B \ln \int d\Omega \, , \qquad d\Omega = dq_1 \ldots dq_N \, dp_1 \ldots dp_N \ . \tag{2.9}$$

The equilibrium probability distribution $P^0(N)$ (eq. (2.7)) is defined by an integration over a subspace $C(N)$ of the assumed cluster distribution. Inserting eq. (2.8) we find from eq. (2.7)

$$P^0(N) = \exp\left(-\frac{S(U, V, N)}{k_{\mathrm{B}}}\right) \int\limits_{C(N)} \mathrm{d}q_1 \dots \mathrm{d}p_N \,. \tag{2.10}$$

In agreement with eq. (2.9) we introduce now the entropy of the particle configuration N by

$$S(U, V, N) = k_{\mathrm{B}} \ln \int\limits_{C(N)} \mathrm{d}\Omega \tag{2.11}$$

and find the equilibrium probability distribution $P^0(N)$ finally in the form

$$P^0(N_0, N_1 \dots N_{N_v}) = \exp\left\{\frac{S(U, V, N_0, N_1 \dots N_{N_v}) - S(U, V, N)}{k_{\mathrm{B}}}\right\}, \tag{2.12}$$

where $S(U, V, N) = $ const. acts as a normalization [27].

3. Thermodynamic investigations

3.1. Free energy of the cluster distribution

In order to evaluate the equilibrium probability for the concrete system we have to calculate first the entropy $S(U, V, N)$ of the cluster distribution.

For our derivation we start with the free energy $F(T, V, N)$ for the considered cluster distribution 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 entropy is obtained by means of the relation

$$S(T, V, N) = -\left.\frac{\partial F(T, V, N)}{\partial T}\right|_{V,N} \,. \tag{3.1}$$

The free energy of the cluster distribution has been derived in a previous paper [6, 16] assuming isothermal conditions and an ideal mixture of clusters and free particles. 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:

$$F(T, V, N) = \sum_{n=1}^{N_v} N_n\left\{f_n + k_{\mathrm{B}}T\left(\ln \frac{N_n}{V} \lambda_n^3 - 1\right)\right\} + N_0 k_{\mathrm{B}} T\left(\ln \frac{N_0}{V} \lambda_0^3 - 1\right)$$

$$= F_v + F_0 \,, \qquad T, V, N = \text{const.} \,, \tag{3.2}$$

where λ_n is the de Broglie wavelength,

$$\lambda_n = h(2\pi m_n k_B T)^{-1/2} ,$$ (3.3)

f_n is a potential term characterizing the energy of the cluster of size n. In a first approximation similar to the theory of atomic nuclei which includes only volume and surface effects we choose [19]:

$$f_n = -A(T)n + B(T)n^{2/3} .$$ (3.4)

The first term of eq. (3.4) corresponds to the binding energy in the cluster, the second term to the surface energy.

In comparison with thermodynamic results the following expression for A was derived [20]:

$$A(T) = -k_B T \ln \frac{p'(T)}{k_B T} \lambda_1^3 .$$ (3.5)

$p'(T)$ is the equilibrium vapour pressure of the condensable vapour at the given temperature. The surface energy is proportional to the surface area and to the surface tension σ. Assuming a spherical cluster it yields for the constant B [20]:

$$B(T) = 4\pi \left(\frac{4\pi}{3} c_\alpha \right)^{-2/3} \sigma .$$ (3.6)

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 with respect to the curvature.

We note that the ansatz (3.4) for f_n is valid only for large clusters, where a real surface can be distinguished from the inner part of the clusters. It fails mainly for small clusters. In particular for monomers $f_1 = 0$ must be satisfied. We use here the ansatz for f_n for $n \geq 2$, mentioning that a proper estimation of f_n in the range of small n must be obtained from a microscopic theory [21].

The free energy (eq. (3.2)) includes the contributions of the pressure p and the Gibbs free enthalpy: $F = G - pV$. For the pressure follows:

$$p = \frac{k_B T}{V} \left(N_0 + \sum_{n=1}^{N_v} N_n \right) ,$$ (3.7)

while the Gibbs potential G is given by

$$G = \sum_{n=1}^{N_v} \mu_n N_n + \mu_0 N_0$$

with

$$\mu_n = f_n + k_B T \ln \frac{N_n}{V} \lambda_n^3 \qquad (3.8)$$

being the chemical potential of a cluster of size n and

$$\mu_0 = k_B T \ln \frac{N_0}{V} \lambda_0^3 \qquad (3.9)$$

the chemical potential of the particles of the carrier gas.

3.2. Entropy and equilibrium cluster distribution

By means of the free energy (eq. (3.2)) the entropy of the cluster distribution N can be derived from eq. (3.1). It results

$$
\begin{aligned}
S(T, V, N) &= k_B \sum_{n=1}^{N_v} N_n \left\{ \frac{5}{2} - \frac{1}{k_B} \frac{\partial f_n}{\partial T} - \ln \frac{N_n}{V} \lambda_n^3 \right\} + N_0 k_B \left(\frac{5}{2} - \ln \frac{N_0}{V} \lambda_0^3 \right) \\
&= S_v + S_0 , \qquad (3.10)
\end{aligned}
$$

where S_v stands for the contribution of the cluster distribution and S_0 results from the carrier gas. We note that the entropy in eq. (3.10) depends on the variables T, V, N, while for the calculation of $P^0(N)$ (eq. (2.12)) the function $S = S(U, V, N)$ is needed. Therefore, a proper dependence of the temperature T on the parameters of the system must be found [22].

Using the relation $U = F + TS$ the total internal energy U can be calculated by

$$U = \sum_{n=1}^{N_v} N_n \left\{ \tfrac{3}{2} k_B T + f_n + T \frac{\partial f_n}{\partial T} \right\} + \tfrac{3}{2} N_0 k_B T = \text{const} . \qquad (3.11)$$

From eq. (3.11) the dependence of the temperature on the parameters U and V and the actual cluster distribution results as follows:

$$T(U, V, N) = \frac{U - \displaystyle\sum_{n=1}^{N_v} N_n f_n}{\tfrac{3}{2} k_B \left(N_0 + \displaystyle\sum_{n=1}^{N_v} N_n \right) - \displaystyle\sum_{n=1}^{N_v} N_n \frac{\partial f_n}{\partial T}} . \qquad (3.12)$$

With respect to [23]

$$p'(T) = p'(T_0) \exp\left\{ \frac{q}{k_B} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\} , \qquad T_0 = \text{const.} , \qquad (3.13)$$

q being the particle evaporation heat, we find for the derivative $\partial f_n / \partial T$:

$$T \frac{\partial f_n}{\partial T} = \tfrac{5}{2} k_B T n - (A - q)n + \left[\frac{T}{\sigma} \frac{\partial \sigma}{\partial T} + \frac{2}{3} \frac{T}{c_\alpha} \frac{\partial c_\alpha}{\partial T} \right] B n^{2/3} . \tag{3.14}$$

The terms $(\partial \sigma / \partial T)$ and $(\partial c_\alpha / \partial T)$ are small compared with the others, therefore these expressions are neglected in the following. After insertion of eq. (3.14) the temperature of the system is obtained as [22]

$$T(U, V, N) = \frac{U + \sum_{n=2}^{N_v} N_n (qn - B n^{2/3})}{\tfrac{3}{2} k_B \left(N_0 + \sum_{n=1}^{N_v} N_n \right) + \tfrac{5}{2} k_B \sum_{n=2}^{N_v} n N_n} . \tag{3.15}$$

Eq. (3.15) indicates the change of the temperature of the system resulting from the cluster formation. But this influence strongly depends on the fraction of the carrier gas as will be discussed in section 3.3.

Inserting the expression $T(U, V, N)$ (eq. (3.15)) into that of the entropy $S(T, V, N)$ (eq. (3.10)) we arrive finally at the correct function $S(U, V, N)$ to calculate the equilibrium probability distribution $P^0(N)$. Now we are able to determine the equilibrium cluster distribution N^0 from the extremum condition:

$$\frac{\partial P^0(N)}{\partial N_n} \bigg|_{T = T_{eq}} = \frac{\partial S(U, V, N)}{\partial N_n} \bigg|_{T = T_{eq}} = 0 , \qquad n = 2, \ldots, N_v , \tag{3.16}$$

where T_{eq} is the equilibrium temperature in the system. We obtain

$$\left(\frac{N_n}{V} \lambda_n^3 \right) = \left(\frac{N_1^0}{V} \lambda_1^3 \right)^n \exp\left(-\frac{1}{k_B} \frac{\partial f_n}{\partial T} - \frac{3}{2} (n - 1) \right) ,$$

$$T = T_{eq} , \quad n = 2, \ldots, N_v , \tag{3.17}$$

with $N_1^0 = N_v - \sum_{n=2}^{N_v} n N_n^0$. Additionally, $T_{eq} = T(N^0)$ is related to the equilibrium cluster distribution by eq. (3.15). Due to these conditions eq. (3.17) is a nonlinear system of equations which has to be solved simultaneously.

Using the notation of the chemical potential μ_n (eq. (3.8)), the equilibrium solution (3.17) can be written in the form

$$\frac{\partial \mu_n}{\partial T} \bigg|_{T = T_{eq}} = n \frac{\partial \mu_1}{\partial T} \bigg|_{T = T_{eq}} , \qquad n = 2, \ldots, N_v . \tag{3.18}$$

An integration of eq. (3.18) leads to the known form of a mass action law [21].

3.3. Two limit cases

The thermodynamic investigations allow us to derive two limit cases. Because of the relation $U = F + TS$ it yields for an isolated system with the constraints (2.1):

$$dU = dF + d(TS) = 0 .$$ (3.19)

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

$$dS = dS_v + dS_0 .$$ (3.20)

We can now discuss the limit cases:

(i) $N_0 \gg N_v$: In this case the temperature (eq. (3.15)) can be approximated by

$$T \approx T_0 = 2U/3k_B N_0 = \text{const} .$$ (3.21)

That means the latent heat which is released during the condensation process will be transmitted to the carrier gas. It plays the role of the heat bath. Therefore we have isothermal conditions. It results from eq. (3.19) that the change of the entropy in the isothermal limit can be expressed by $dS = -(1/T) dF$ and the equilibrium probability distribution (eq. (2.12)) is now given by

$$P^0(N) \sim \exp\left\{ -\frac{F(T, V, N)}{k_B T} \right\} , \qquad T = \text{const} .$$ (3.22)

(ii) $N_0 \to 0$: 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. (3.10): $S_0 \to 0$ in the limit $N_0 \to 0$. Therefore, we obtain from eq. (3.20) $dS = dS_v$ leading to

$$P^0(N) \sim \exp\left\{ \frac{S_v(U, V, N)}{k_B} \right\} , \qquad N_0 \to 0 .$$ (3.23)

Thus the nucleation process in the considered binary vapour reduces in the limit cases given above either to an isothermal nucleation process in a one-component vapour (i) or to an isoenergetic nucleation process in a one-component vapour (ii). The real process of the phase transition via nucleation and cluster growth takes place between these limit cases. That is the

reason why we have to consider in general the influence of the carrier gas and the change of the temperature in the system.

4. Kinetics of the phase transition in isolated systems

4.1. 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 development of the distribution $N = \{N_0, N_1 \cdots N_{N_s}\}$. 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 of the condensable vapour. In terms of chemical kinetics this process can be represented by the stochastic reactions

$$A_n + A_1 \underset{w^-}{\overset{w^+}{\rightleftharpoons}} A_{n+1} \, . \tag{4.1}$$

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 (4.1) [24].

(iii) The kinetics of nucleation is assumed a Markovian discrete process. The dynamics of the probability $P(N, t)$ to find a certain cluster distribution N at time t obeys a master equation:

$$\frac{\partial P(N, t)}{\partial t} = \sum_{N'} \{ w(N|N')P(N', t) - w(N'|N)P(N, t) \} \, . \tag{4.2}$$

The quantities $w(N'|N)$ are the transition probabilities per unit time for the transition from N to N'. N' specifies those distributions which are attainable from the asssumed distribution N via the reactions (4.1).

The stationary solution of the master equation requires that $\partial P(N, t)/\partial t = 0$. From this condition we find $\Sigma_{N'} J(N|N') = 0$ with $J(N|N') = w(N|N')P(N', t) - w(N'|N)P(N, t)$ being the probability flux between the states N' and N. Since the system is not pumped the equilibrium condition is given by the more restricted condition of detailed balance. It means $J(N|N') = 0$ resulting in:

$$w(N|N')P^0(N') = w(N'|N)P^0(N) \, . \tag{4.3}$$

Inserting eq. (2.12) into eq. (4.3) we arrive at:

$$w(N|N') = w(N'|N) \exp\left\{ \frac{S(U, V, N) - S(U, V, N')}{k_B} \right\}.$$ (4.4)

We find that the transition probabilities $w(N|N')$ and $w(N'|N)$ are in a strong relation due to the knowledge of the equilibrium probability $P^0(N)$. Therefore only a kinetic assumption for one of the transition probabilities is needed. The transition probability for the opposite process can be determined by means of eq. (4.4).

4.2. Transition probabilities

To determine the transition probabilities for the attachment or the evaporation of monomers to/from clusters we assume in agreement with previous papers [6, 16] 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:

$$w(N'|N) = w(N_0, N_1 - 1 \ldots N_n - 1\, N_{n+1} + 1 \ldots N_{N_v} |$$
$$N_0, N_1 \ldots N_n N_{n+1} \ldots N_{N_v})$$
$$= w_n^+ (N_1 N_n) = \alpha(T) n^{2/3} N_n N_1 / V,$$
$$N_1 = N_v - \sum_{n=2}^{N_v} n N_n.$$ (4.5)

We note first 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.

This means consequently for the master equation (4.2) that the probability $P(N, t)$ does not factorize and the stochastic description will not reduce to a number of independent linear random walk processes, as has been discussed in refs. [12–14].

The parameter α 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 α can be derived only from microscopic considerations of the event of attachment.

Assume in a first approximation that the kinetic energy of the free particles incorporated into the cluster is larger compared with a certain energy barrier

ΔE at the surface which must be overcome: $\Delta E \ll k_B T$. In this case we may choose

$$\alpha(T) = \alpha_0 k_B T ,\tag{4.6}$$

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: $\alpha_0 = D_0 c_\alpha / 2\sigma$. D_0 is the diffusion coefficient, assumed to be nearly constant. Here arbitrarily $\alpha_0 = 1$ is chosen.

The transition probability per unit time for the evaporation of one particle from a cluster of size n can be obtained from eq. (4.4). 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 $S(U, V, N) - S(U, V, N')$ and a final transformation: $N \to N''$, $N' \to N$ we obtain the transition probability of evaporation:

$$
\begin{aligned}
w(N''|N) &= w(N_1, N_1 + 1 \dots N_{n-1} + 1\, N_n - 1 \dots N_{N_v}|\\
&\qquad N_1 \dots N_{n-1} N_n \dots N_{N_v})\\
&\equiv w_n(N_n)\\
&= \alpha_0 n^{2/3} N_n p'(T_0) \exp\left[\frac{q}{k_B}\left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{2}{3}\frac{B}{k_B T}\, n^{-1/3} \right].
\end{aligned}\tag{4.7}
$$

This transition probability is proportional to the surface area and the number of clusters of size n again. In the isothermal limit ($T = T_0$) it agrees with the probability of evaporation derived previously [6, 10], and w_n depends only on the conditions of the considered cluster.

For the isoenergetic system the change of the temperature marks an important distinction. Since $T = T(U, V, N)$ depends on the whole cluster distribution the transition probability of evaporation depends implicitly on the cluster distribution, too.

Let us further conclude the distinctions of the transition probabilities compared with the isothermal case. In dependence on the fraction of the carrier gas the temperature should increase during the condensation process due to the latent heat released. Therefore, the kinetic energy of the free particles increases too. But the transition probability of attachment will not increase at all, because the density of free particles reduces due to the formation and growth of clusters.

On the other hand, the transition probability of evaporation strongly depends on the temperature via the saturation pressure $p'(T)$ of the condensable vapour (eq. (3.13)). Mainly in the limit of a vanishing influence of the carrier gas, w^- rapidly grows up with an increasing temperature and most of the clusters have to evaporate again.

This should lead to a modification of the scenario of the phase transition which will be discussed in section 5.3. 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. For a nucleation process limited by finite heat conduction we refer the reader to ref. [10].

5. Discussion

5.1. Evolution of a single cluster

In order to explain the given results we discuss the transition probabilities for the evolution of a single cluster. For this simple case the transition probabilities (eqs. (4.5), (4.7)) reduce to

$$
w_n^+ = \alpha_0 n^{2/3} \frac{N_1}{V} k_B T , \qquad N_1 = N_v - n , \tag{5.1}
$$

$$
w_n^- = \alpha_0 n^{2/3} p'(T_0) \exp\left\{ \frac{q}{k_B} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{2}{3} \frac{B}{k_B T} n^{-1/3} \right\} , \tag{5.2}
$$

where the temperature T (eq. (3.15)) is now given by

$$
T = \frac{U + qn - Bn^{2/3}}{\frac{3}{2} k_B N_v (1 + N_0/N_v) + k_B (n + \frac{3}{2})} . \tag{5.3}
$$

As has been discussed in section 3.3 the ratio N_0/N_v determines whether we have isothermal or isoenergetic conditions for the cluster formation. First we want to define some reference values. The temperature of the initial system, where no cluster exists, can be introduced as follows:

$$
T^* = \frac{2U}{3k_B N_v (1 + N_0/N_v)} . \tag{5.4}
$$

Further, we introduce the partial supersaturation of the free particles of the condensable vapour, which is given by the ratio of the partial pressure p_1 compared with the saturation pressure for the actual temperature:

$$
y_1 = \frac{p_1}{p'(T)} = \frac{N_1 k_B T}{p'(T) V} = \frac{(N_v - n) k_B T}{p'(T) V} . \tag{5.5}
$$

The initial partial supersaturation y_1^* shall be defined by

$$y_1^* = \frac{N_v k_B T^*}{p'(T^*)V} .$$

(5.6)

In order to discuss comparable situations for the cluster formation we assume now that the initial temperature T^* and the initial density of free particles are the same for different ratios $A = N_0/N_v$, that is the probability of attachment w^+ is initially the same for the considered cases.

Fig. 2 presents the change of the temperature with an increasing cluster size for different fractions A of the carrier gas. As discussed before, a larger ratio of N_0/N_v leads to nearly isothermal conditions for the cluster formation.

Fig. 3 shows the dependence of the partial supersaturation on the cluster size. We find that y_1 is dropped much more faster in the limit of a vanishing rate of the carrier gas. While in the isothermal limit y_1 is reduced only by the decrease of free particles during the cluster growth, in the pure one-component vapour the increase of T additionally leads to a strong increase of the equilibrium pressure of the system and, therefore, to a stronger dropping effect. The decrease of y_1, caused by the increase of the temperature, should be interpreted as an additional depletion effect which acts in the same direction as the depletion of free particles by the cluster growth. This is in agreement with recent thermodynamic investigations of the nucleation process under adiabatic conditions [9, 10].

With respect to the discussion of y_1 and T we present in fig. 4A and B the transition probabilities for the attachment and evaporation of free particles to/from the single cluster, assuming again the same initial partial supersaturation for different values of $A = N_0/N_v$.
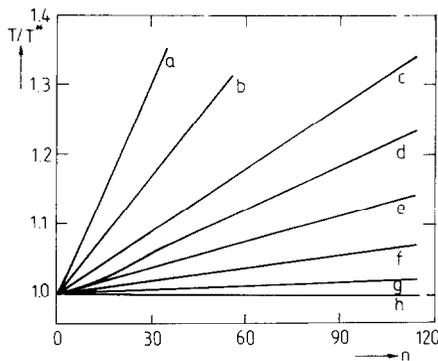

Fig. 2. Temperature T (eq. (5.3)) divided by $T^* = $ const (eq. (5.4)) in dependence on the cluster size n. Parameter: fraction $A = N_0/N_v$: (a) $A = 5$, (b) $A = 10$, (c) $A = 20$, (d) $A = 30$, (e) $A = 50$, (f) $A = 100$, (g) $A = 300$, (h) isothermal $T = T^*$. System volume $V = 1.7 \times 10^{-23}$ m^3, $N_v = 150$, $T^* = 280$ K $= $ const. The specific properties of the vapour are obtained from ethanol.
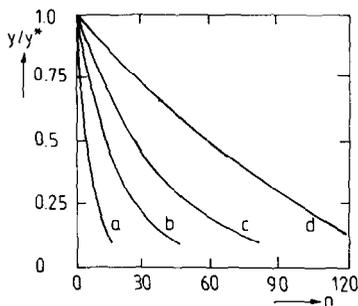
Fig. 3. Supersaturation y_1 (eq. (5.5)) divided by y_1^* (eq. (5.6)) in dependence on the cluster size n. Parameter: fraction $A = N_0/N_v$: (a) $A = 5$, (b) $A = 20$, (c) $A = 50$, (d) $A = 200$. For the system parameters see fig. 2.

Compared with fig. 4A the transition probability w^+ increases in fig. 4B more rapidly with n because of the increase of the temperature. Its decrease afterwards is caused by the depletion of the free particles of the condensable vapour. The transition probability w^- also strongly depends on the increase of the temperature via the equilibrium pressure.

It is shown that depending on the values of the initial supersaturation y_1^* and the rate of temperature increase two points of intersection between w^+ and w^- exist. The condition $w_n^+ = w_{n+1}^-$ gives the equilibrium condition for the single cluster, resulting from the condition of detailed balance and the extremum condition of the equilibrium probability distribution of the single cluster. The point of intersection for the smaller value of n determines the critical (instable) cluster size, while the point of intersection for the larger value of n gives the
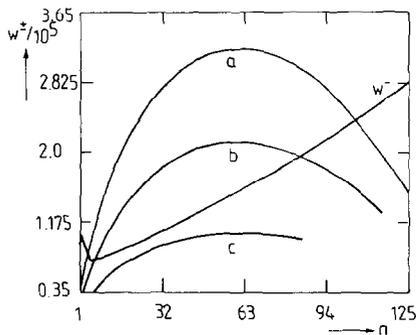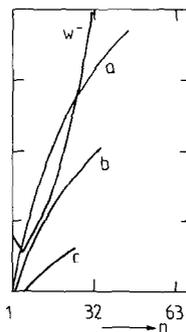
Fig. 4. Transition probabilities w_n^+ (eq. (5.1)) and w_n^- (eq. (5.2)) in dependence on the cluster size n. Fig. 4A: $A = N_0/N_v = 200$; fig. 4B: $A = N_0/N_v = 20$. Parameter: initial supersaturation y_1^* (eq. (5.6)). w_n^+ is presented for (a) $y_1^* = 12$, (b) $y_1^* = 8$, (c) $y_1^* = 4$. w_n^- does not depend on y_1^*. For the system parameters see fig. 2.

stable equilibrium cluster size [20, 25]. The existence of a stable equilibrium between the cluster and the surrounding vapour results from the depletion of the free particles in the finite system and from the increase of the equilibrium vapour pressure. This has been discussed in previous papers both from a thermodynamic and kinetic point of view [9, 25, 26].

In order to obtain a supercritical cluster w^+ must exceed w^- for a certain range of the cluster size n. Figs. 4A, B and 5 demonstrate that the critical cluster size increases and the stable cluster size decreases for a decreasing ratio $A = N_0/N_v$. That means, the space of supercritical cluster sizes $n_{cr} \leq n \leq n_{st}$ becomes smaller when an increase of the temperature takes place. Fig. 5 allows to find for a given initial supersaturation a critical ratio A_{cr} for the existence of a supercritical cluster in the finite system. For lower values of the supersaturation this critical ratio becomes larger.

5.2. Deterministic cluster growth

It is possible to derive from the master equation a Fokker–Planck equation for the mean values of the cluster distribution, as has been carried out in previous papers for the isothermal case [6, 16]. Here we want to discuss only the deterministic velocity of cluster growth and shrinkage being a part of the drift term of the Fokker–Planck equation. Neglecting higher correlations this deterministic velocity is defined by

$$V_n = \mathrm{d}\langle n \rangle / \mathrm{d}t = \langle w_n^+ - w_n^- \rangle . \tag{5.7}$$

Inserting the transition probabilities (eqs. (5.1), (5.2)) we find

$$\frac{\mathrm{d}\langle n \rangle}{\mathrm{d}t} = \alpha_0 \langle n \rangle^{2/3} p'(T) \left[\frac{\langle N_1 \rangle k_B T}{p'(T)V} - \exp\left(\frac{2}{3} \frac{B}{k_B T} \langle n \rangle^{-1/3} \right) \right] . \tag{5.8}$$
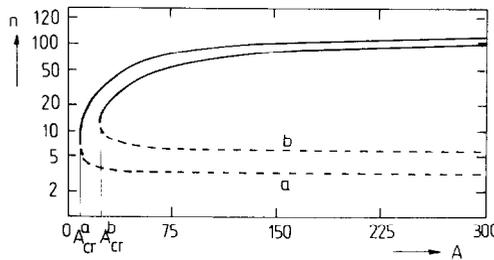

Fig. 5. Stable cluster size n_{st} (solid line) and critical cluster size n_{cr} (dashed line) in dependence on the fraction $A = N_0/N_v$. Parameter: initial supersaturation y_1^* (eq. 5.6): (a) $y_1^* = 12$, (b) $y_1^* = 8$. From the calculations we obtain critical values of A, where the critical and the stable cluster sizes coincide: (a) $A_{cr} = 8$, (b) $A_{cr} = 22$. For $A < A_{cr}(y_1^*)$ no supercritical cluster exists. For the system parameters see Fig. 2.

Use of power expansions in eq. (5.8) leads to determinsitic kinetics in the form

$$\frac{d\langle n \rangle^{1/3}}{dt} = \alpha_0 p'(T) \frac{2}{3} \frac{B}{k_B T} \left[\frac{1}{\langle n_{cr} \rangle^{1/3}} - \frac{1}{\langle n \rangle^{1/3}} \right], \tag{5.9}$$

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

$$\langle n_{cr} \rangle^{1/3} = \frac{2}{3} \frac{B}{k_B T} \left(\ln \frac{\langle N_1 \rangle k_B T}{p'(T) V} \right)^{-1} = \frac{2}{3} \frac{B}{k_B T} (\ln y_1)^{-1}. \tag{5.10}$$

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. In the initial state where no cluster exists $\langle n_{cr} \rangle$ has its smallest value given by

$$n_{cr}^{1/3}(t = 0) = \frac{2}{3} \frac{B}{k_B T^*} \left(\ln \frac{N_v k_B T^*}{p'(T^*) V} \right)^{-1} = \frac{2}{3} \frac{B}{k_B T^*} (\ln y_1^*)^{-1}. \tag{5.11}$$

It should increase during the nucleation process caused by the depletion of the vapour and additionally by the increase of the temperature, leading to a decrease of the supersaturation y_1. The time dependence of the critical cluster size can be expressed by the differential equation

$$\frac{d\langle n_{cr} \rangle^{1/3}}{dt} = -\frac{\langle n_{cr} \rangle^{1/3}}{\ln y_1} \left[\frac{1}{\langle N_1 \rangle} \frac{d\langle N_1 \rangle}{dt} + \frac{1}{T} \frac{dT}{dt} \left\{ \ln y_1 - \frac{q}{k_B T} + 1 \right\} \right]. \tag{5.12}$$

The time dependence of the free particles of the condensable vapour (N_1) and of the temperature must be specified in dependence on the evolution of the cluster distribution, because both, N_1 and T, depend on it. Since in the limit of a vanishing fraction of the carrier gas an increase of the temperature effects an additional depletion, n_{cr} should increase faster compared with the isothermal case.

5.3. Conclusions

For the whole process of nucleation and growth of clusters in the considered system we suppose a scenario of three stages which should qualitatively agree with previous results of computer simulations in isothermal–isochoric gases [6, 7]:

(i) A short period of predominant formation of undercritical clusters leading to a metastable cluster distribution.

(ii) The stochastic growth of some of the undercritical clusters to an overcritical size after a certain time lag, leading to a period of favoured cluster growth, where the supersaturation is decreasing.

(iii) A longer period of so-called Ostwald ripening, where the number of clusters and the number of bound particles are nearly constant. One of the larger clusters survives in a competition process [25], its growth to the final size occurs by a re-evaporation of the smaller clusters.

How will this scenario be modified if a decrease of the fraction of the carrier gas effects a transition from the isothermal to the isoenergetic nucleation?

(i) The first period will become much shorter because the partial supersaturation is dropped faster compared with the isothermal case. Due to this effect less clusters will reach an overcritical size.

(ii) The period of favoured cluster growth will be shortened caused by the fast reduction of the supersaturation.

(iii) The period of Ostwald ripening will be shortened too because less supercritical clusters have been formed and the stable cluster size decreases with a lower fraction of the carrier gas.

We can summarize the influence of the carrier gas molecules as follows:

– Lower fractions of the carrier gas lead to an increase of the temperature during the phase transition. Therefore less supercritical clusters will be formed and the supersaturation reduces more considerably.

– The stable cluster size depends on the temperature and therefore it can be adjusted by means of the fraction of the carrier gas.

– The formation of supercritical clusters depend both on the supersaturation and on the fraction of the carrier gas (cf. e.g. fig. 5). For a given initial supersaturation a critical fraction of the carrier gas exists where no supercritical cluster can be found. We suppose that a remove of the carrier gas from the system will prevent the nucleation process.

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