ISSN 0323-4479 · Z. phys. Chemie · Leipzig · **271** (1990) 6 · S. 1113–1122

Sektion Physik der Humboldt-Universität zu Berlin and Universität Rostock

Stochastic Approach to Cluster Formation in Adiabatically Expanding Molecular Beams[1]

By W. Ebeling, F. Schweitzer, L. Schimansky-Geier[2] and H. Ulbricht[3]

With 4 Figures

(Received 19th February 1990)

Abstract

We investigate the formation of clusters in a rapidly expanding mixture of a condensable vapor and a carrier gas similar to the experimental situation of a molecular beam.

The system is divided into small disks which change their volume via a given time programm. The temperature of the disk results from the expansion law but changes additionally because of the latent heat released during the cluster formation.

The kinetics is described by a master equation. The transition probabilities obey the condition of detailed balance and reflect the attachment and detachment of single particles as well as coagulation and split of clusters.

The discussion presents an estimation of the onset of cluster formation in a gas of free particles and a possible scenario of the evolution of the cluster distribution into a frozen state.

1. Introduction

The investigations of cluster formation in expanding molecular beams started in the fifties with pioneering papers of BECKER and others [1]. In the last ten years this field has attracted considerable exerimental as well as theoretical attention [2–8]. Much of the work has been motivated by a strong interest in applications to surface technology, heterogeneous catalysis, and microelectronics. In spite of this high level of interest it is still true that the mechanism of cluster formation in many systems of practical importance is not well understood till now and a complete theory of cluster formation under changing conditions is still in request.

Subsequently to earlier studies of nucleation processes [9–12] this paper aims to present a model of the cluster formation in a conically expanding nozzle beam.

---

[1] Herrn Prof. Dr. h. c. ROBERT ROMPE zum 85. Geburtstag gewidmet.

[2] Prof. WERNER EBELING and Dr. LUTZ SCHIMANSKY-GEIER, Humboldt-Universität zu Berlin, Fachbereich Physik, B 04, Invalidenstraße 42, O - 1040 Berlin.

[3] Dr. FRANK SCHWEITZER and Prof. HEINZ ULBRICHT, Universität Rostock, Sektion Physik, Universitätsplatz 3, O - 2500 Rostock.

2. Model of the Expanding Molecular Beam

In the following we discuss a simple model of the experimental situation. Let us consider a chamber with a small nozzle of diameter $d = 2R_0$ (see Fig. 1 a). Inside the chamber a gas mixture, consisting of a carrier gas and a condensable vapour, exists under atmospheric pressure, outside the chamber we have nearly a vacuum.

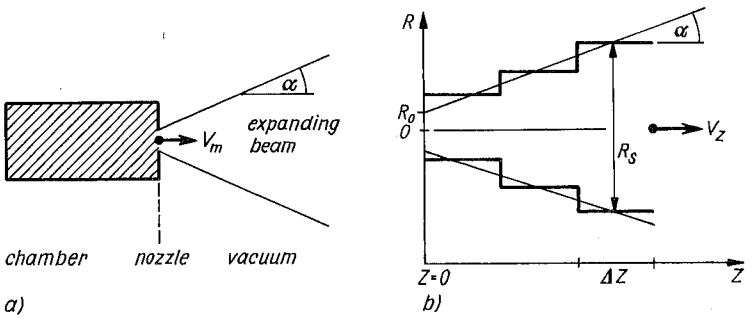

Fig. 1 a. Sketch of the adiabatic expansion from a molecular beam chamber

Fig. 1 b. Model to describe the conical expansion by means of small disks (thickness Δz, radius R_s)

The gas mixture expands in a conical form into the vacuum with a scattering angle α, which depends on the geometric form of the nozzle. The mean velocity v_m of the gas stream when just leaving the chamber is governed by the nozzle form too, further by the pressure and temperature gradients and the molar mass of the carrier gas. In the model considered here both values, α and v_m, are taken as adjustable parameters (e.g. $\alpha = 15°$, $v_m = 10^3$ m/s).

In order to describe the expanding gas mixture we propose the following model (see Fig. 1 b): The conus with the length $z = v_z t$, v being the velocity in the spatial dimension z, is divided into a number of small disks (indicated by s) with a length Δz. Assuming Δz very small, the volume V_z of each disk can be approximated by a cylindric form, that means $V_s = \pi R_s^2 \Delta z$. R_s is the Radius of the disk of number s, depending on time and the parameters α and V_z as follows:

$$R_s(t) = R_0 + v_z t \sin\alpha . \tag{2.1}$$

That means with $t = s\Delta t$

$$V_s(t) = \pi (R_0 + v_z s \Delta t \sin\alpha)^2 \Delta z \tag{2.2}$$

where Δt is time of delay for the gas particles in every disk, approximately given by $\Delta t = \Delta_z / v_z$.

Assuming in a first approximation, that the velocity v_z, which describes the motion of the disk in the spatial dimension z, is kept constant and equal to v_m, the mean velocity at the point $z = 0$.

To choose a proper value of Δz we assume that the relevant distance z for cluster formation after leaving the chamber is about 10 diameters d of the nozzle. Assuming $d = 1$ mm and dividing the volume of the relevant cone into 1 000 disks, it yields $\Delta z = 10^{-5}$ m and $\Delta t = 10^{-8}$ s for the time of delay.

Due to the conical expansion of the gas mixture a strong undercooling occurs, which leads to a

highly supersaturated state. The temperature difference $\Delta T = T_{s-1} - T_s$ between neighboring disks $(s-1, s)$ for a nearly free adiabatic expansion has an order of magnitude of 10^{-2} to 1 K and results from

$$T_s = T_{s-1}\,(V_{s-1}/V_s)^{\varkappa-1} \tag{2.3}$$

$\varkappa$ being the adiabatic exponent.

Averaging over the 1000 disks, this means a spatial cooling rate

$$\delta = (T_{1000} - T_0)/1\,000\,\Delta z \tag{2.4}$$

of about 10^4 K/m, and with respect to the velocity v_z we have an average temporal cooling rate

$$\dot{T} = (T_{1000} - T_0)/(1\,000\,\Delta t) = \delta v_z \tag{2.5}$$

of about 10^7 K/s.

Inside the disk volume V_s we assume a global thermal equilibrium. This is satisfied, since the frequency of collisions between the particles of the gas is about $10^{34}\ s^{-1}\ m^{-3}$, that means for a duration time $\Delta t = 10^{-8}$ s about 10^{14} collisions in every disk volume, rather enough to equalize local temperature and density inhomogenities. In spite of this fact, the thermodynamic state of the disk is rather far from equilibrium because of the high supersaturation.

3. Cluster Formation during Adiabatic Expansion

3.1. Thermodynamic Assumptions

Caused by the large supercooling the expanding gas mixture undergoes a supersaturated state, which makes a formation of supercritical clusters possible. Therefore, we must consider that the particles of the condensable vapour are distributed in clusters of different sizes. Introducing a discrete cluster distribution [9–12] in a given disk s:

$$\boldsymbol{N} = \{N_0, N_1, N_2, \ldots N_{n-1}, N_n \ldots\} \tag{3.1}$$

where N_0 is the number of particles of the carrier gas, N_1 is the number of free particles of the condensable vapour (monomers), N_2 the number of dimers, ..., N_n the number of clusters of size n, that means they consist of n particles.

In order to describe the evolution of the cluster distribution during the expansion of the gas mixture we make the following assumptions:

(i) The gas is expanding radially without changing the total number of particles per disk, N_s, given by:

$$N_s = N_v + N_0 = \text{const.} \tag{3.2}$$

N_v means the total number of particles of the condensable vapor, which are able to create clusters. Let us note, that the cluster distribution (3.1) here refers to one disk s in our model, that means, the N_n are all functions of the disk number too, althrough no

explicitely written here. With respect to $\boldsymbol{N}$ (3.1) it yields:

$$N_0 = \text{const.}, \; N_v = \sum_{n=1}^{N} n N_n = \text{const.} \tag{3.3}$$

For the maximum number of clusters of a given size n results:

$$0 \leq N_n \leq N_v/n \tag{3.4}$$

(ii) Since the expanding cloud of particles is adiabatically isolated from the surrounding, the internal energy U of the cluster distribution per disk volume V_s is constant for a definite total particle number N_s and a constant volume V_s. Assuming an ideal mixture of clusters of different kinds and free particles, the internal energy of the isolated system has been given previously [11, 12]:

$$U(T_s, V_s, \boldsymbol{N}) = \sum_{n=0}^{N} N_n \left\{ \frac{3}{2} k_B T_s + f_n - T_s \left. \frac{\partial f_n}{\partial T} \right|_{T=T_s} \right\} . \tag{3.5}$$

Here f_n is a potential term characterizing the free energy of a cluster of size n. It is specified later, for the moment we consider only its temperature dependence.

Caused by the heat isolation (ii) the actual temperature T_s in the volume V_s can be changed because of the latent heat released during the cluster formation. We assume that T_s for a given volume V_s is a global parameter. Its dependence on the cluster distribution $\boldsymbol{N}$ can be obtained by means of the conservation of energy (eq. (3.5.) as follows:

$$T_s(U, V_s, \boldsymbol{N}) = \frac{U - \sum_{n=0}^{N} N_n f_n}{\sum_{n=0}^{N} N_n \left\{ \frac{3}{2} k_B - \left. \frac{\partial f_n}{\partial T} \right|_{T=T_s} \right\}} . \tag{3.6}$$

We note here, that the change of T_s caused by the cluster formation strongly depends on the magnitude of the carrier gas ($n = 0$). It has been discussed [11], that for a large ratio of N_0/N_v the temperature increases only very little during the cluster formation.

Assuming an ideal gas mixture we may further express the actual pressure p_s in the volume element V_s as follows:

$$p_s(\boldsymbol{N}) = \sum_{n=0}^{N} N_n \frac{k_B T_s(\boldsymbol{N})}{V_s} . \tag{3.7}$$

The proper thermodynamic potential to describe the cluster distribution $\boldsymbol{N}$ with respect to a constant internal energy U, a given total particle number N and a fixed volume V_s is the entropy S. It has been given in previous works [11, 12]:

$$S_s(\boldsymbol{N}) = \sum N_n \left\{ - \frac{\partial f_n}{\partial T} - k_B \ln \frac{N_n}{V_s} \lambda_n{}^3 + \frac{5}{2} k_B \right\} . \tag{3.8}$$

Here λ_n is the de Broglie wavelength:

$$\lambda_n(T_s) = \lambda_1(T_s) n^{-1/2} = h(2\pi m_1 k_B T_s)^{-1/2} n^{-1/2} . \tag{3.9}$$

The value of the entropy depends on time because of $V_s(t)$ (eq. 2.2), $\boldsymbol{N}(t)$ and $T_s(t)$ (eq. 2.3).

3.2. Kinetic Assumptions

The cluster evolution during the gas expansion is presented by the time development of the distribution $N = \{N_0, N_1 \ldots N_{Nv}\}$. In order to discuss this evolution we suppose, that the cluster growth and shrinkage may be expressed by a stochastic reaction, which is denoted in terms of chemical kinetics [12]:

$$A_n + A_m \underset{w^-}{\overset{w^+}{\rightleftarrows}} A_{n+m}, \; n, m \geq 0, \tag{3.10}$$

A_n is a cluster of size n which "reacts" with another cluster of size m; w^+ and w^- are the transition probabilities per unit time of the stochastic reaction in the given direction. They will be specified afterwards.

The reaction equation (3.10) includes a variety of possible processes:

(i) For $m = 0$ we consider impects of clusters or particles of the condensable vapour with these of the carrier gas, which results in a temperature relaxation in the system.

(ii) For $m = 1$ the cluster growth and shrinkage is due only to an attachment or evaporation of monomers of the condensable vapour (cluster-particle interaction).

(iii) For $m \geq 2$ the cluster growth occurs by the incorporation of other clusters, that means coagulation – or, in the opposite direction, a break of a large cluster into pieces is considered (cluster-cluster interaction).

Interactions between more than two participates may be approximated by successive reactions of two of them, like:

$$A_K + A_m + A_n \rightleftarrows A_K + A_{m+n} \rightleftarrows A_{K+m+n} \tag{3.11}$$

3.3. Dynamic Model of the Cluster Formation during Expansion

The dynamics of our model is based on discrete time steps t.

(i) At the time t_0 we start with a given cluster distribution N in a volume $V_0 = \pi R_0^2 z$, the temperature is given by T_0, which is related to the internal energy U via eq. (3.5).

(ii) In the first time step the volume V_0 is expanded via eq. (2.2), the new value V_1 results in a new temperature T_1.

(iii) During the time of delay, Δt, the volume V_s is kept constant, but the cluster distribution N may change via the reactions (3.10). Because of the latent heat produced or consumed during cluster formation or splitting, the temperature T_s changes too via eq. (3.9).

(iv) After the time Δt we have a new cluster distribution N and a new temperature T_s, which mark the initial values for the next time step: It begins with a further expansion (ii). During the expansion the cluster distribution is kept constant again, but the temperature and the volume are changing. The dynamics continues with (iii).

The basic assumption of this dynamic approach means that the thermodynamic equalization with respect to the velocity distribution and the corresponding temperature during the expansion is reached in a much shorter time than the clusters need for a change of their composition. We believe that this condition is satisfied for a sufficiently wide range of experimental conditions.

This assumption allows us to separate in our theoretical description the act of expansion (with a constant cluster distribution) from the act of changing the cluster distribution (in a constant volume). The temperature will change in both of these different processes, and it depends on the concrete parameters, which process results in a more considerable change of T_s. This fact should depend remarkable on the ratio of the carrier gas N_0/N_v [11].

4. Stochastic Approach to the Cluster Formation

4.1. Master Equation and Equilibrium Probability Distribution

From a statistic point of view every possible cluster distribution $\boldsymbol{N}$ in a certain disk is found with a certain probability for a given time, defined by

$$P(\boldsymbol{N}, t) = P(N_0, N_1 N_2 \ldots N_n \ldots N_{Nv}, t). \tag{4.1}$$

If the kinetics is assumed as an Markovian discrete process, the dynamics of the probability $P(\boldsymbol{N}, t)$ obeys a master equation:

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

The quantities $w(\boldsymbol{N}' \mid \boldsymbol{N})$ are the transition probabilities per unit time for the transition from $\boldsymbol{N}$ to $\boldsymbol{N}'$. $\boldsymbol{N}'$ specifies those distributions which are attainable from the assumed distribution $\boldsymbol{N}$ via the reactions (3.10).

We make the assumption that the kinetics of phase transition can be described by the master equation (4.2) with transition probabilities, which are determined from a uniform point of view both for the nucleation and the coagulation processes and their opposite reactions.

The stationary solution of the master equation requires that $\partial P(\boldsymbol{N}, t)/\partial t = 0$. From this condition we find $\sum J(\boldsymbol{N} \mid \boldsymbol{N}') = 0$ with $J(\boldsymbol{N} \mid \boldsymbol{N}') = w(\boldsymbol{N} \mid \boldsymbol{N}')\ P^s(\boldsymbol{N}') - w(\boldsymbol{N}' \mid \boldsymbol{N})\ P^s(\boldsymbol{N})$ being the probability flux between the states $\boldsymbol{N}'$ and $\boldsymbol{N}$. The stationary solution P^s is the equilibrium solution P^0, since the system is not pumped [13]. It means $J(\boldsymbol{N} \mid \boldsymbol{N}') = 0$ resulting in

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

Here $P^0(\boldsymbol{N})$ is the equilibrium probability to find a certain cluster distribution. It can be derived from microscopic considerations [11, 12]. As the result we have found:

$$P^0(N_0, N_1 \ldots N_N) = \exp \frac{S(U, V_s, N_0, N_1 \ldots N_{N_v}) - S(U, V_s, N_s)}{k_B} \tag{4.4}$$

where $S(U, V_s, \boldsymbol{N})$ is the entropy of a certain cluster distribution in a given volume element V_s. $S(U, V_s, N_s)$ is the entropy of the N_s particles system. It is constant for a given V_s and stands for the normalization [14].

4.2. Transition Probabilities

Inserting the equilibrium probability distribution $P^0(\boldsymbol{N}) \alpha \exp(S(\boldsymbol{N})/k_B)$ where $S(\boldsymbol{N})$ is given by eq. (2.9), into the condition of detailed balance, eq. (4.3), we arrive at:

$$w(\boldsymbol{N} \mid \boldsymbol{N}') = w(\boldsymbol{N}' \mid \boldsymbol{N}) \exp \frac{S(\boldsymbol{N}) - S(\boldsymbol{N}')}{k_B}. \tag{4.5}$$

We find that the transition probabilities $w(\boldsymbol{N} \mid \boldsymbol{N}')$ and $w(\boldsymbol{N}' \mid \boldsymbol{N})$ are in a strong relation due to the knowledge of the entropy $S(\boldsymbol{N})$. 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. (4.5).

The assumption to determine the transition probabilities from the condition of detailed balance involves a chemical equilibrium between all kinds of clusters. Stable vortex-like solutions for the probability flux are forbidden in the final chemical equilibrium state.

For the assumed reactions (3.10) the distribution $\boldsymbol{N}$ and $\boldsymbol{N}'$ can be specified as follows

$$\begin{aligned} \boldsymbol{N} &= \{\boldsymbol{N}_0, N_1 N_2 \ldots N_n \ldots N_m \ldots N_{n+m} \ldots N_{Nv}\} \\ \boldsymbol{N}' &= \{N_0, N_1 N_2 \ldots N_n - 1 \ldots N_m - 1 \ldots N_{n+m} + 1 \ldots N_{Nv}\}. \end{aligned} \tag{4.6}$$

That means the transition probability $w(\boldsymbol{N}' \mid \boldsymbol{N})$ is related to a cluster growth via the reaction $A_n + A_m \rightarrow A_{n+m}$.

We have to consider further that during a transition $\boldsymbol{N} \rightarrow \boldsymbol{N}'$ also the temperature $T_s(\boldsymbol{N})$ and the pressure $p_s(\boldsymbol{N})$ of the system change.

We make now the following assumption for the transition probability of cluster growth [12]:

$$w(\boldsymbol{N}' \mid \boldsymbol{N}) = w^+(N_n, N_m) = \alpha_{n,m}(T_s) \cdot N_n N_m / V_s. \tag{4.7}$$

This ansatz agrees with usual assumptions of the kinetic theory of particle interactions in the gaseous state [15]. It means that the probability of a reaction between two clusters of sizes n, m increases with the number of clusters and decreases with the volume of the system. In the case $n = m$ we have to choose instead of eq. (4.7) $w^+(N_n) \sim N_n(\mathrm{N_n} - 1)/V_s$.

The parameter $\alpha_{\mathrm{n,m}}(T)$ describes the time scale of the stochastic process. It is determined in close relation to the classical kinetic gas theory. We choose the following ansatz [15]:

$$\alpha_{n,m}(T) = \pi(r_n + r_m)^2 \, v_{n,m} \exp\left\{-\frac{E_{n,m}}{k_B T}\right\} \tag{4.8}$$

r_n and r_m are the radii of the spherical assumed clusters, the value $\pi(r_n + r_m)^2$ gives the total cross section of the interaction of both clusters. $v_{n,m}$ is the mean relative velocity of the clusters refered to each other [15]:

$$v_{n,m} = \left\{\frac{8 k_B T}{\pi \mu}\right\}^{1/2} \quad ; \quad \mu = \left\{\frac{m \cdot n}{m + n}\right\} \cdot \frac{M}{N_A} \tag{4.9}$$

where μ gives the reduced mass of the clusters; M is the molar mass and N_A the Avogadro constant.

The exponential considers, that the clusters only react if their relative kinetic energy is

larger than a certain amount E, which is known to be the activation energy $E_{n,m} = E_A$. Since the kinetic energy obeys a Boltzmann distribution, only an amount $\exp(-E_A/k_B T)$ of collisions takes place with an relative energy larger than E_A.

In order to determine the opposite transition probability $w(\boldsymbol{N}|\,\boldsymbol{N}')$ for the split of a cluster: $A_{n+m} \to A_m + A_n$, we have to calculate the exponential of eq. (4.5), taking into account that in a constant volume element v_s the cluster distribution changes and due to the latent heat also the temperature of the system. The result has been derived in a previous paper [12]. With a transformation

$$\boldsymbol{N} \to \boldsymbol{N}'', \boldsymbol{N}' \to \boldsymbol{N} \text{ with } \boldsymbol{N}'' = \{N_0, {}_1N_2 \ldots N_n + 1 \ldots N_m + 1 \ldots N_{m+n} + 1 \ldots N_{Nv}\}$$

we arrived at:

$$w(\boldsymbol{N}''\,|\,\boldsymbol{N}) = w^-(N_{m+n}) = (8\pi k_B T)^{1/2}\mu \left(\frac{N_A}{M}\right)^{3/2} (r_n + r_m)^2 \cdot N_{m+n} \frac{1}{\lambda_1{}^3(T)} \cdot \exp\left\{\frac{f_{m+n} - f_n - f_m}{k_B T} - \frac{E_A}{k_B T}\right\}. \tag{4.10}$$

The value $\Delta E = f_{m+n} - f_m - f_n$ gives the change of the cluster energies for a reaction $A_m + A_n \to A_{m+n}$. If the cluster of size $(m + n)$ is more stable than the single clusters m, n, it holds $\Delta E < 0$ (see Fig. 2). In this case a split of the large cluster into pieces is rather unprobably because the energy barrier is higher for such a reaction than in the case of coagulation.

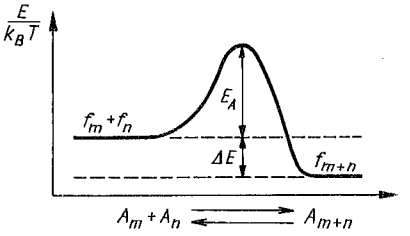

Fig. 2. Energy levels for the coagulation of two small clusters with respect to the activation energy E_A [12]

5. Discussion

5.1. Determination of the Potential Term f_n

Let us first discuss the term f_n, which describes the potential cluster energy. For the free particles of the carrier gas ($n = 0$) we define $f_0 = 0$. For the clusters of the condensable vapor we choose a first approximation similar to the theory of atomic nuclei which includes only volume and surface effects [12]:

$$f_n = -A(T)\,(n-1) + B(T)\,(n-1)^{2/3}. \tag{5.1}$$

The first term of eq. (5.1) corresponds to the binding energy in the cluster, the second term to the surface energy. In particular it follows for the free particles of the condensable vapour (monomers) $f_1 = 0$.

In comparison with thermodynamic results the following expression for A was derived [16]:

$$A(T) = -k_B T \ln \frac{p^s(T)\,\lambda_1{}^3(T)}{k_B T} \tag{5.2}$$

$p^s(T)$ means the equilibrium vapor pressure of the condensable vapor at the given temperature. Its temperature dependence is given by the known relation [17]:

$$p^s(T_A) = p^s(T_0) \exp\left\{\frac{q}{k_B}\left[\frac{1}{T_0} - \frac{1}{T_A}\right]\right\} \tag{5.3}$$

where q means the evaporation heat per particle.

The surface energy its proportional to the surface area and to the surface tension σ. Assuming a spherical cluster it yields for the constant B [16]:

$$B(T) = 4\pi\sigma \left(\frac{4\pi}{3} c_\alpha\right)^{-2/3} \tag{5.4}$$

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.

5.2. Scenario of the Evolution of the Cluster Distribution

The model presented above can be studied by means of computer simulations using a similar mechanism as in our previous papers [10, 12]. The results will be discussed in a subsequent paper. Here we are dealt only with a general scenario of the evolution of the cluster distribution during the adiabatic expansion. Let us discuss different situations concerning the initial distribution which leaves the chamber.

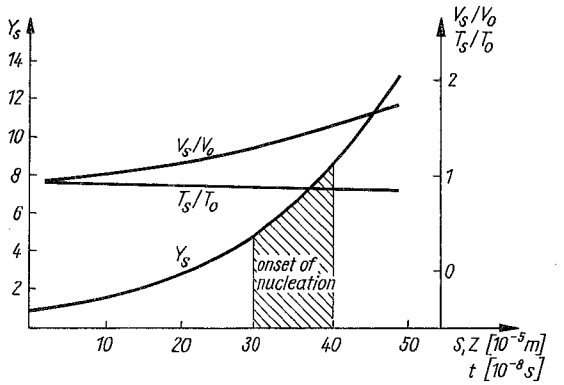

Fig. 3. Supersaturation y_s and ratios V_s/V_0, T_s/T_0 vs. disk number s, distance z, time t respectively

(i) Assuming for the time, that the initial distribution consists only of free particles of the condensable vapor and a magnitude of the carrier gas. Neglecting further the depletion of

free particles and the increase of the temperature during the cluster formation, the supersaturation in disk s is given by:

$$y_s = N_s k_B T_s / V_s p^s(T_s). \tag{5.5}$$

If the vapor in disk $s = 0$ is assumed to be saturated ($y_0 = 1$), Fig. 3 presents the initial supersaturation (5.5) and the ratios V_s/V_0, T_s/T_0 in dependence of the disk number s. It is shown, that despite small variations of V_s and T_s in comparison with the initial values V_0, T_0 in a range of $s = 30$ to 40 (that means 3×10^{-4} to 4×10^{-4} m behind the nozzle) the supersaturation reaches such a value, that a remarkable cluster formation should be expected.

(ii) Assuming now that inside the chamber an equilibrium cluster distribution has been established (this depends mainly on the time of delay in the chamber). This distribution is located around a certain stable cluster size n_{st}. When the supersaturation increases during the expansion, the former stable clusters are able to grow further, because the critical cluster size decreases and the stable cluster size increases too. We expect, that the result of this new growth process strongly depends on the two different time scales: If the supercooling is much more faster than the process of cluster growth, the cluster distribution is not able to reach its new equilibrium state during the short time, and we will find a non-equilibrium cluster distribution, which is frozen. The clusters cannot grow further, if the average distance between two elementary particles is growing faster by the expansion than it is decreasing by the nucleation.

References

[1] BECKER, E. W., K. BIER and W. HENKES: Z. Phys. **146** (1956) 333.
[2] WEGENER, P. P. (Ed.): Molecular Beams and Low Density Gas Dynamics. New York: Dekker 1974.
[3] JENA, P. (Ed.): Proc. Int. Symp. on the Physics and Chemistry of Small Clusters. New York: Wiley 1987.
[4] JORTNER, J., A. PULLMANN and B. PULLMANN (Eds.): Large Finite Systems. Dordrecht: Reidel 1987.
[5] RADEMANN, K., B. KAISER, U. EVEN and F. HENSEL: Phys. Rev. Lett. **59** (1987) 2319.
[6] BENEDEK, G., T. P. MARTIN and G. PACCHIONI (Eds.): Elemental and Molecular Clusters. Berlin: Springer 1988.
[7] RADEMANN, K.: Ber. Bunsenges. Phys. Chem. **93** (1989) 653.
[8] POMPE, W.: Thin Solid Films **144** (1986) 77; Wiss. Ber. ZFW Nr. **26** (1984) 87.
[9] SCHIMANSKY-GEIER, L., F. SCHWEITZER, W. EBELING and H. ULBRICHT: in: Selforganization by Nonlinear Irreversible Processes (Eds.: W. EBELING, H. ULBRICHT), Berlin: Springer 1986.
[10] SCHWEITZER, F., L. SCHIMANSKY-GEIER, W. EBELING and H. ULBRICHT: Physica **A150** (1988) 261.
[11] SCHWEITZER, F., L. SCHIMANSKY-GEIER, W. EBELING and H. ULBRICHT: Physica **A153** (1988) 573.
[12] SCHWEITZER, F., and L. SCHIMANSKY-GEIER: Rostocker Physik. Manuskr. **13** (1989) 58–81.
[13] GARDINER, C. W.: Handbook of Stochastic Methods. Berlin/Heidelberg/New York: Springer 1984.
[14] KLIMONTOVICH, YU. L.: Statistical Physics, Moscow 1982, New York 1985.
[15] KEHLEN, H., F. KUSCHEL and H. SACKMANN: Grundlagen der chemischen Kinetik. Berlin: Akademie-Verlag 1986.
[16] SCHWEITZER, F., and L. SCHIMANSKY-GEIER: J. Colloid Interface Sci. **119** (1987) 67.
[17] KORTÜM, G.: Einführung in die chemische Thermodynamik. Göttingen 1963.