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STOCHASTIC APPROACH TO NUCLEATION AND COAGULATION IN ADIABATICALLY CLOSED GASES

The outlined theory leads to proper transition probabilities of coagulation and split of clusters under adiabatic conditions. It includes cluster-cluster interactions as well as particle-cluster interactions and considers further the change of the temperature and the volume/pressure of the system due to the elementary reactions. Moreover, kinetic equations for the mean cluster distribution are derived and discussed.

1. The Supersaturated State

We consider initially a system of N particles at a temperature T_A and a volume V_A. The parameters T_A and V_A are fixed in such a way that the N particles exist in a gaseous state.
We assume further two different kinds of particles

$$N = N_v + N_o = \text{const.} \qquad (1.1)$$

N_v means the number of particles of a condensable vapour, which are able to create clusters; N_o is the number of particles of a carrier gas. This gas is uncondensable for the given constrains, but it takes over the latent heat which is released during the condensation process and thus acts as an heat bath.

Since the system is closed, the particle numbers N_v and N_o are both constants. Let us now assume that in the initial state, indicated by the index A, only free particles exist in the system. Assuming an ideal gas mixture it holds for the initial pressure of the system:

$$p_A = p_{Av} + p_{Ao} = \frac{(N_o+N_v)k_B T_A}{V_A} \qquad (1.2)$$

p_{Av} and p_{Ao} are the partial pressures of both components.

A phase transition occurs only for a certain supersaturation in the system, that means the system must exist initially in a state far from equilibrium. Let us define the initial supersaturation as follows:

$$y_A = \frac{p_{Av}}{p^*(T_A)} = \frac{N_v k_B T_A}{p^*(T_A)V_A} \quad ; \quad p_{Av} > p^*(T_A) \qquad (1.3)$$

$p^*(T_A)$ means the equilibrium pressure of the system for the given temperature T_A. Its temperature dependence is given by the known relation /1/

$$p^*(T_A) = p^*(T_o)\ \exp\left\{\frac{q}{k_B}\left(\frac{1}{T_o} - \frac{1}{T_A}\right)\right\} \qquad (1.4)$$

where q means the evaporation heat per particle.
The phase transition which occurs in the supersaturated system can be considered now for two different thermodynamic constrains (see Fig.1):
(i) The system volume is fixed at the value $V_o=V_A$. Since the number of free particles of the condensable vapour is decreased during the condensation process, the pressure in the system is changed by the vapour depletion and by the heat released during the cluster formation /2,3,5,6/.

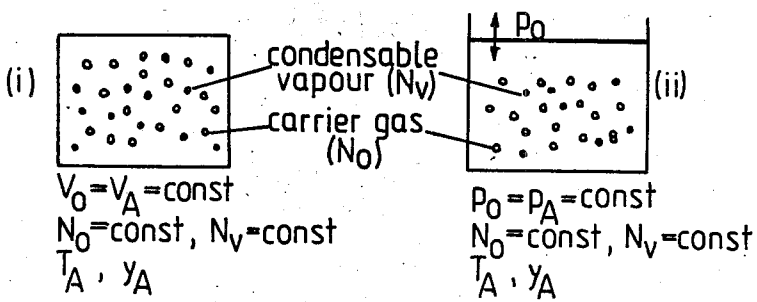

Fig. 1.:
Sketch of the initially supersaturated system, for the considered thermodynamic constraints. In both cases we have no heat contact with the surroundings (adiabatic conditions)

(ii) The system is closed by a movable piston under a constant pressure p_o. In this case the system volume changes because of the depletion of free particles and the change of the internal temperature, while the pressure of the system is always equal to the external pressure.
In order to compare the behaviour of both systems we assume the same initial supersaturation in both cases. This is fulfilled if the external pressure p_o is chosen equal to p_∞ (eq. (1.2)).

2. Thermodynamic Investigations of the System

The important distinction between both systems results from the fact that the latter is able to exchange volume work with the surroundings. Remembering the first law of thermodynamics

$$dU = \delta Q - p\,dV \tag{2.1}$$

it yields for an adiabatically isolated system ($\delta Q=0$) in the considered cases:

$$\text{(i) } U(T,V,N) = \text{const.}; \quad \text{(ii) } H(T,p,N) = U + pV = \text{const.} \tag{2.2}$$

where U is the internal energy and H the enthalpy of the system.
We must now consider that the particles of the condensable vapour are distributed in clusters of different sizes, when a phase transition occurs. Introducing a discrete cluster distribution /4/:

$$\underline{N} = \{N_o, N_1, N_2, \ldots N_{n-1}, N_n \ldots\} \tag{2.3}$$

where N_o 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.
Because of the limitation of the particle number it holds:

$$N_o = \text{const.}, \quad N_v = \sum_{n=1}^{N} n\,N_n = \text{const.} \tag{2.4}$$

For the maximum number of clusters of a given size n it yields:

$$0 \le N_n \le N_v/n \tag{2.5}$$

Assuming the clusters and free particles of the condensable vapour and the carrier gas as an ideal mixture we may express the actual pressure in system (i) or the actual volume of system (ii), respectively, as follows:

$$\text{(i) } p(\underline{N}) = \sum_{n=o}^{N} N_n \frac{k_B T(\underline{N})}{V_o} \qquad \text{(ii) } V(\underline{N}) = \sum_{n=o}^{N} N_n \frac{k_B T(\underline{N})}{p_o} \tag{2.6}$$

Caused by the heat isolation the actual temperature in both systems depends on the established cluster distribution because of the latent heat released. We assume that $T(\underline{N})$ is a global parameter, which must be obtained from the conservation of energy or enthalpy (eq. (2.2)).
Previous investigations of system (i) /2,3/ lead to the following equation for the internal energy of an ideal mixture of clusters and free particles:

$$U(T,V,\underline{N}) = \sum_{n=o}^{N} N_n \left\{ \frac{3}{2} k_B T + f_n - T \frac{\partial f_n}{\partial T} \right\} \tag{2.7}$$

Here f_n is a potential term characterizing the energy of a cluster of size n. It is specified later, for the moment we consider only its temperature dependence.
The enthalpy H is obtained from the relation $H(T,p_o,\underline{N}) = U(T,V,\underline{N}) + p_o \cdot V(\underline{N})$, where V is given by eq. (2.6). Since in both cases the energy or the enthalpy are constants we find the following expressions for the temperature in dependence on the actual cluster distribution

$$\text{(i) } T(U,V_o,\underline{N}) = \frac{U - \sum_{n=o}^{N} N_n f_n}{\sum_{n=o}^{N} N_n \left\{ \frac{3}{2} k_B - \frac{\partial f_n}{\partial T} \right\}}$$

$$\text{(ii) } T(H,p_o,\underline{N}) = \frac{H - \sum_{n=o}^{N} N_n f_n}{\sum_{n=o}^{N} N_n \left\{ \frac{5}{2} k_B - \frac{\partial f_n}{\partial T} \right\}} \tag{2.8}$$

The proper thermodynamic potential of the isolated system is the entropy S. It has been derived in previous works /2,3/:

$$S(\underline{N}) = \Sigma N_n \left\{ - \frac{\partial f_n}{\partial T} - k_B \ln \frac{N_n}{V} \lambda_n^3 + \frac{5}{2} k_B \right\} \qquad (2.9)$$

Here λ_n is the de Broglie wavelength:

$$\lambda_n(T) = \lambda_1(T) n^{-1/2} = h(2\pi m_1 k_B T)^{-1/2} n^{-1/2} \qquad (2.10)$$

According to whether we consider the system (i) or (ii), the entropy is a function $S=S(U,V,\underline{N})$ (i) or a function $S=S(H,p,\underline{N})$ (ii). This distinction depends only on the temperature $T(U,V,\underline{N})$ or $T(H,p,\underline{N})$, (eq. (2.8)) which must be inserted into the equation of the entropy to obtain the right thermodynamic potential.

3. Kinetics of the Phase Transition

3.1. Kinetic Assumptions and Master Equation

The phase transition occurs by the formation of clusters and their growth and shrinkage. The cluster evolution is presented by the time development of the distribution $\underline{N}=(N_0,N_1 \ldots N_{N\infty})$. In order to discuss this evolution we suppose the following assumptions:

(i) The cluster growth and shrinkage may be expressed by a stochastic reaction, which is denoted in terms of chemical kinetics:

$$A_n + A_m \underset{w^-}{\overset{w^+}{\rightleftharpoons}} A_{n+m} \quad , \; n,m \geq 0 \qquad (3.1)$$

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 (3.1) includes a variety of possible processes:

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

- For m≥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:

$$A_K + A_m + A_n \rightleftharpoons A_K + A_{m+n} \rightleftharpoons A_{K+m+n} \qquad (3.2)$$

(ii) From a statistic point of view every possible distribution $\underline{N}$ is found with a certain probability for a given time, defined by

$$P(\underline{N},t) = P(N_0, N_1 N_2 \ldots N_n \ldots N_{N\infty}, t) \qquad (3.3)$$

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

$$\frac{\partial P(\underline{N},t)}{\partial t} = \sum_{\underline{N}'} \{ w(\underline{N}|\underline{N}') P(\underline{N}',t) - w(\underline{N}'|\underline{N}) P(\underline{N},t) \} \qquad (3.4)$$

The quantities $w(\underline{N}'|\underline{N})$ are the transition probabilities per unit time for the transition from $\underline{N}$ to $\underline{N}'$. $\underline{N}'$ specifies those distributions which are attainable from the assumed distribution $\underline{N}$ via the reactions (3.3).

We make the assumption that the kinetics of phase transition can be described by the master equation (3.4) 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 $\partial P(\underline{N},t)/\partial t = 0$. From this condition we find $\Sigma J(\underline{N}|\underline{N}') = 0$ with $J(\underline{N}|\underline{N}') = w(\underline{N}|\underline{N}') P(\underline{N}',t) - w(\underline{N}'|\underline{N}) P(\underline{N},t)$ being the probability flux between the states $\underline{N}'$ and $\underline{N}$.

Since the system is not pumped the equilibrium condition is given by the more restricted condition of detailed balance. It means $J(\underline{N}|\underline{N}') = 0$ resulting in /7/

$$w(\underline{N}|\underline{N}') P^e(\underline{N}') = w(\underline{N}'|\underline{N}) P^e(\underline{N}) \qquad (3.5)$$

Here $P^e(\underline{N})$ is the equilibrium probability to find a certain cluster distribution. It can be derived from microscopic

considerations /2/.

3.2. Equilibrium Probability Distribution

In thermodynamic equilibrium the probability $P^o(\underline{N})$ to find a certain distribution of clusters in the bath of the particles of the carrier gas is defined by the following relation /2,4,22/

$$P^o(\underline{N}) = \int_{C(\underline{N})} e^o(q_1 \ldots p_N)\, dq_1 \ldots dp_N \qquad (3.6)$$

Here $e^o(q_1 \ldots p_N)$ means the equilibrium probability distribution for the N particles in the spatial and momentum coordinates of all particles. For a fixed total energy U (system (i)) the microscopic partical configuration is given by the microcanonical ensemble, that means:

$$e^o(q_1 \ldots p_N) = \begin{cases} \exp\left(-\frac{S(U,V,N)}{k_B}\right) = \text{const} & \text{for } U-\delta U \le \mathcal{H} \le U+\delta U \\ 0 & \text{else} \end{cases} \qquad (3.7)$$

$\mathcal{H}$ is the Hamiltonian of the N particles system and δU the thickness of the energy shell. S(U,V,N) in eq. (3.7) is the entropy of the N particles system which is known to be /23/:

$$S(U,V,N) = +k_B \ln \int d\Omega, \quad d\Omega = dq_1 \ldots dq_N dp_1 \ldots dp_N \qquad (3.8)$$

The equilibrium probability distribution $P^o(\underline{N})$ (eq. (3.6)) is defined by an integration over a subspace $C(\underline{N})$ of the assumed cluster distribution. Inserting eq. (3.7) we find from eq. (3.6):

$$P^o(\underline{N}) = \exp\left(-\frac{S(U,V,N)}{k_B}\right) \int_{C(\underline{N})} dq_1 \ldots dp_N \qquad (3.9)$$

In agreement with eq. (3.8) we introduce now the entropy of the particle configuration $\underline{N}$ by

$$S(U,V,\underline{N}) = k_B \ln \int_{C(\underline{N})} d\Omega \qquad (3.10)$$

and find the equilibrium probability distribution $P^o(\underline{N})$ finally in the form:

$$P^o(N_o, N_1 \ldots N_N) = \exp\left\{\frac{S(U,V,N_o,N_1 \ldots N_{N\upsilon}) - S(U,V,N)}{k_B}\right\} \qquad (3.11)$$

where S(U,V,N)=const. acts as a normalization /8/.
Considering system (ii) we find in the same way eq. (3.11) with the only distinction, that now $S(\underline{N})=S(H,P,\underline{N})$ with the normalization S(H,p,N)=const.
The investigation of system (i) with the thermodynamic constrains U,V,N_υ,N_o=const. allows us to derive two limit cases for the equilibrium probability distribution $P^o(\underline{N})$.

Because of the relation U=F+TS, F being the free energy of the system, it yields for the isolated system with the given constrains:

$$dU = dF + d(TS) = 0 \qquad (3.12)$$

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

$$dS = dS_\upsilon + dS_o \qquad (3.13)$$

We can now discuss the limit cases:

(a) $N_o \gg N_\upsilon$: In this case the temperature (eq. (2.8) (i)) can be approximated by

$$T \approx T_o = 2U/3k_B N_o = \text{const.} \qquad (3.14)$$

That means the latent heat which is released during the condensation process will be transmitted to the carrier gas. It plays the role of a heat bath. Therefore we have isothermal conditions.
It results from eq. (3.12) 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:

$$P^o(\underline{N}) \sim \exp\left\{-\frac{F(T,V,\underline{N})}{k_B T}\right\}; \qquad T = \text{const.} \qquad (3.15)$$

(b) $N_\circ \longrightarrow 0$: If no carrier gas is present, the latent heat of the condensation process leads to an increase of the temperature of the system. It results from eq. (2.9) $S_\circ \longrightarrow 0$ in the limit $N_\circ \longrightarrow 0$. Therefore, we obtain from eq. (3.13) $dS = dS_v$ leading to

$$P^o(\underline{N}) \sim \exp\left\{\frac{S_v(U,V,\underline{N})}{k_B}\right\} \qquad N_\circ \longrightarrow 0 \qquad (3.16)$$

Thus the nucleation process in the considered binary vapour for V=const. reduces in the limit cases given above either to an isothermal nucleation process in an one-component vapour (a) or to an isoenergetic nucleation process in an one-component vapour (b). Both cases have been investigated separately in refs. /2,3/.

The real process of the phase transition via nucleation and cluster growth in a system with constant volume 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.

3.3. Transition Probabilities

Inserting the equilibrium probability distribution $P^o(\underline{N}) \sim \exp(S(\underline{N})/k_B)$ where $S(\underline{N})$ is given by eq. (2.9), into the condition of detailed balance, eq. (3.5), we arrive at:

$$w(\underline{N}|\underline{N}') = w(\underline{N}'|\underline{N}) \exp\left\{\frac{S(\underline{N})-S(\underline{N}')}{k_B}\right\} \qquad (3.17)$$

We find that the transition probabilities $w(\underline{N}|\underline{N}')$ and $w(\underline{N}'|\underline{N})$ are in a strong relation due to the knowledge of the entropy $S(\underline{N})$. 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. (3.17).

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 excluded from our point of view.

For the assumed reactions (3.1) the distributions $\underline{N}$ and $\underline{N}'$ can be specified as follows:

$$\begin{aligned} \underline{N} &= \{N_\circ, N_1 N_2 \ldots N_n \ldots N_m \ldots N_{n+m} \ldots N_{N_v}\} \\ \underline{N}' &= \{N_\circ, N_1 N_2 \ldots N_n - 1 \ldots N_m - 1 \ldots N_{n+m} + 1 \ldots N_{N_v}\} \end{aligned} \qquad (3.18)$$

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

We have to consider further that during a transition $\underline{N} \rightarrow \underline{N}'$ also the temperature $T(\underline{N})$ and the pressure $p(\underline{N})$ or the volume $V(\underline{N})$ of the system change.

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

$$w(\underline{N}'|\underline{N}) = w^+(N_n, N_m) = \alpha_{n,m}(T) \cdot N_n N_m / V \qquad (3.19)$$

This ansatz agrees with usual assumptions of the kinetic theory of particle interactions in the gaseous state /9/. 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. (3.19) $w^+(N_n) \sim N_n(N_n-1)/V$.

The parameter $\alpha_{n,m}(T)$ 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 /9/:

$$\alpha_{n,m}(T) = \pi(r_n + r_m)^2 \, \bar{v}_{n,m} \exp\left\{-\frac{E_{n,m}}{k_B T}\right\} \qquad (3.20)$$

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. Assuming a Maxwell distributed velocity of every species of clusters, the mean relative velocity is expressed by /9/:

$$\bar{v}_{n,m} = \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2} \quad ; \quad \mu = \left(\frac{m \cdot n}{m+n}\right) \cdot \frac{M}{N_A} \qquad (3.21)$$

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 $\exp(-E_A/k_BT)$ of collisions takes place with an relative energy larger than E_A.
We note that the transition probabilities of cluster growth are correlated, since the total number of particles is conserved. Therefore, the clusters do not evolve independently /2,4/. This means consequently for the master equation (3.4) that the probability $P(\underline{N},t)$ does not factorize and the stochastic description will not reduce to a number of independent linear random walk processes as discussed in /10-12/.
In order to determine the opposite transition probability $w(\underline{N}|\underline{N}')$ for the split of a cluster: $A_{n+m} \dashrightarrow A_m + A_n$, we have first to calculate the exponential of eq. (3.17), taking into account that the cluster distribution changes as well as the temperature and, in general, the volume of the system. We want to discuss in the following this latter and more complicated case, where $S=S(H,p,\underline{N})$.
Denoting by V',T',N_n',f_n' the values after the change, a careful evaluation of the exponential leads to:

$$\exp\frac{S(\underline{N})-S(\underline{N}')}{k_B} = \frac{N_{m+n}+1}{N_nN_m}\,V'\left(\frac{n\cdot m}{m+n}\right)^{3/2}\frac{1}{\lambda_1^3(T')} * \qquad (3.22)$$

$$* \exp\left\{\frac{3}{2} - \frac{1}{k_B}\sum N_n\frac{\partial f_n}{\partial T} + \frac{1}{k_B}\sum N_n'\frac{\partial f_n'}{\partial T} + \sum N_n\left(\frac{3}{2}\ln\frac{T}{T'} + \ln\frac{V}{V'}\right)\right\}$$

For a further discussion we must consider, that the change of the volume is related with the change of the temperature (see eq. (2.6)). Assuming for the moment, that the cluster distribution does not change, that means $\sum N_n = \sum N'_n = \text{const.}$, we find this relation from the first law of thermodynamics, $dU + pdV = 0$, resulting in:

$$\sum N_n\left\{\frac{3}{2}\ln\frac{T}{T'} + \ln\frac{V}{V'}\right\} = \sum N_n\frac{1}{k_B}\left\{\frac{\partial f_n}{\partial T} - \frac{\partial f_n'}{\partial T}\right\} \qquad (3.23)$$

This equation considers the change of the potential energy of the clusters, $f_n(T) \rightarrow f_n(T')$, during the change of the temperature or the volume, respectively. In the most simplest case (only free particles in the system) eq. (3.23) agrees with the known relation $T^{3/2}\cdot V=\text{const.}$
If we take into account additionally the change of the cluster distribution, eq. (3.23) gets a more complicated form:

$$\sum N_n\left\{\frac{3}{2}\ln\frac{T}{T'} + \ln\frac{V}{V'}\right\} = \sum N_n\left\{\ln\sum N_n + \frac{1}{k_B}\frac{\partial f_n}{\partial T}\cdot\frac{f_n}{k_BT'}\right\}$$
$$- \sum N_n'\left\{\ln\sum N_n' + \frac{1}{k_B}\frac{\partial f_n}{\partial T} - \frac{f_n'}{k_BT'}\right\} - \frac{5}{2} \qquad (3.14)$$

Inserting this equation into eq. (3.12) we obtain after a careful calculation the transition probability <u>exactly</u> as:

$$w(\underline{N}|\underline{N}') = w^-(N_{m+n}+1) = \alpha(T)(N_{m+n}+1)\left(\frac{m\cdot n}{m+n}\right)^{3/2}\frac{1}{\lambda_1^3(T')} *$$
$$* \exp\left(\frac{\sum N_n'f_n' - \sum N_nf_n}{k_BT'}\right) \qquad (3.25)$$

The exponential can be simplified as follows:

$$\frac{\Sigma N_n'f_n' - \Sigma N_nf_n}{k_BT'} = \frac{f_{m+n}'-f_m'-f_n'}{k_BT'} + \sum N_n\frac{1}{k_B}\frac{\partial f_n'}{\partial T}\left(1-\frac{T}{T'}\right) \qquad (3.26)$$

If we demand that $w(\underline{N}|\underline{N}')$ must depend only on values ('), a transformation $\alpha_{n,m}(T) \rightarrow \alpha_{n,m}(T')$ is needed. In order to derive an analytic result for w^- we further neglect in a first approximation all terms with a factor $(1-T/T')\approx 0$ compared with the others. After a final transformation $\underline{N} \rightarrow \underline{N}''$, $\underline{N}' \rightarrow \underline{N}$ with $\underline{N}'' = (N_0,N_1N_2\ldots N_n+1\ldots N_m+1\ldots N_{m+n}+1\ldots N_{N\infty})$ we arrive at:

$$w(\underline{N}''|\underline{N}) = w^-(N_{m+n}) = (8\pi k_BT)^{1/2}\,\mu\left(\frac{N_A}{M}\right)^{3/2}(r_n+r_m)^2 * N_{m+n}\frac{1}{\lambda_1^3(T)}$$
$$* \exp\frac{f_{m+n}-f_n-f_m}{k_BT} - \frac{E_A}{k_BT} \qquad (3.27)$$

The value $\Delta E = f_{m+n}-f_m-f_n$ gives the change of the cluster energies for a reaction $A_m+A_n \rightarrow A_{m+n}$. 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.

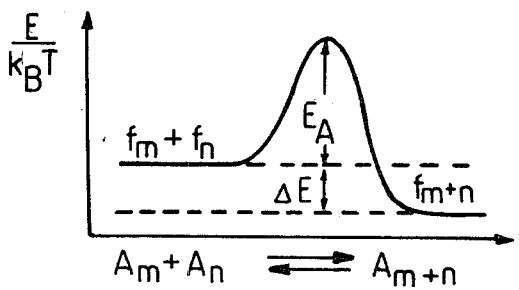

Fig. 2:
Energy levels for the coagulation of two clusters with respect to the activation energy E_A

4. Discussion of Special Results

4.1. Determination of the Potential Term f_n

The term f_n, which describes the potential cluster energy, shall be specified in the following:

- For the free particles of the carrier gas (n=0) we define $f_0=0$.
- For the clusters of the condensable vapour we choose a first approximation similar to the theory of atomic nuclei which includes only volume and surface effects:

$$f_n = -A(T)(n-1) + B(T)(n-1)^{2/3} \qquad (4.1)$$

The first term of eq. (4.1) corresponds to the binding energy in the clustar, the second term to the surface energy.
In comparison with thermodynamic results the following expression for A was derived /13/:

$$A(T) = -k_B T \ln \frac{p^\infty(T)\lambda_1^3(T)}{k_B T} \qquad (4.2)$$

$p^\infty(T)$ means the equilibrium vapour pressure of the condensable vapour at the given temperature (eq. (1.4)).

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 /13/:

$$B(T) = 4\pi\sigma\left(\frac{4\pi}{3}c_\infty\right)^{-2/3} \qquad (4.3)$$

c_∞ 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 (4.1) for f_n is valid not only for large clusters, where a real surface can be divided from the inner part of the clusters, it yields also a good approximation for small clusters in agreement with computer simulations and experimental results /14-16/. In particular it follows for the free particles of the condensable vapour (monomers) $f_1=0$.

Inserting eq. (4.1) into eq. (3.27) the transition probability w^- is found in the form:

$$w^-(N_{m+n}) = \beta_{n,m}(T)N_{m+n}P^\infty(T)*$$
$$* \exp\left\{\frac{B}{k_B T}\left[(m+n-1)^{2/3}-(m-1)^{2/3}-(n-1)^{2/3}\right]-\frac{E_A}{k_B T}\right\} \qquad (4.4)$$

with the constant $\beta_{n,m}(T) = (8\pi/k_B T)^{1/2}\,\mu\left(\frac{N_A}{M}\right)^{2/3}(R_n+R_m)^2$

The exponential now express only the change of the surface energy due to the split of the cluster.
If we consider the special case that only free particles detach from the cluster eq. (4.4) gets the known form /2,4/:

$$w^-(N_{m+1}) = \beta_{m,1}(T)N_{m+1}P^\infty(T)\exp\left\{\frac{2}{3}\frac{B}{k_B T}\frac{1}{(m+1)^{1/3}}-\frac{E_A}{k_B T}\right\} \qquad (4.5)$$

The exponential now reflects the curvature dependence of the saturation pressure above the cluster surface:

$$P^\infty(r_m) = P^\infty(T)\exp\left\{\frac{2}{3}\frac{B}{k_B T}m^{-1/3}\right\} = p^\infty(T)\exp\left(\frac{d_0}{r_m}\right) \qquad (4.6)$$

d_0 is the capillary length.
The temperature dependence of $p^\infty(T)$ is given by eq. (1.4). For

a further discussion of the cluster-particle interactions in the given system see /2,3/.

We want to specify finally the actual temperature in the system in dependence on the cluster distribution (eq. (2.8)). For f_n in the considered case (eq. (4.1)), neglecting only the temperature dependence of the surface tension σ and the density c_∞, eq. (2.8) results in:

$$\text{(i)}\quad T(U,V_o,\underline{N}) = \frac{U + \sum_{n=1}^{N} N_n\{q(n-1)-B(n-1)^{2/3}\}}{\frac{5}{2}\,k_B(N_o+N_v) - k_B(N_o+\sum_{n=1}^{N} N_n)} \tag{4.7}$$

$$\text{(ii)}\quad T(H,p_o,\underline{N}) = \frac{H + \sum_{n=1}^{N} N_n\{q(n-1)-B(n-1)^{2/3}\}}{\frac{5}{2}\,k_B(N_o+N_v)}$$

We note firstly that the change of the temperature depends strongly on the ratio of the carrier gas (N_o) /2/, secondly, that the temperature of the isochoric isolated system (i) changes more remarkable because no volume work is performed.

4.2. Transition Probabilities of a Single Cluster

In order to explain the given results we discuss the transition probabilities for the evolution of a single cluster, which interacts only with monomers. Neglecting the activation energy E_A and multiply the transition probabilities (eqs. (3.19), (4.5)) with a factor $(k_BT)^{1/2}$ we arrive at the simple transition probabilities

$$w_n^+ = c_1 k_B T\, n^{2/3}\,\frac{N_1}{V}\quad,\quad N_1 = N_v - n \tag{4.8}$$

$$w_n^- = c_2 k_B T\, n^{2/3}\, p^\infty(T_o)\, \exp\left\{\frac{q}{k_B}\left(\frac{1}{T_o}-\frac{1}{T}\right) + \frac{2}{3}\,\frac{B}{k_BT}\,n^{-1/3}\right\} \tag{4.9}$$

where c_1 and c_2 are temperature independent constants.

Considering system (i) with the constraints U,V_o,N=const., the temperature (eq. (4.7)) is now given by:

$$T(U,V_o,n) = \frac{U+q(n-1)-B(n-1)^{2/3}}{3/2\;k_BN_v(1+N_o/N_v)+nk_B} \tag{4.10}$$

The temperature of the initial system, where no cluster exists, can be introduced as follows:

$$T_A = \frac{2U}{3k_BN_v(1+N_o/N_v)} \tag{4.11}$$

The initial partial supersaturation y_A is given by eq. (1.3). It is known from previous works /2/ that the supersaturation decreases and the temperature increases during the formation of the cluster because of the latent heat released. The strength of the change depends considerably on the ration N_o/N_v=R. A larger value of R leads to nearly isothermal conditions, for $R \longrightarrow 0$ we find isoenergetic conditions as has been discussed in Sect. 3.2.

Fig. 3 presents the transition probabilities for the attachment and evaporation of free particles to/from the single cluster in dependence on the cluster size for two different values of R. In order to discuss comparable situations we assume that the initial temperature T_A and the initial supersaturation y_A are both the same for the considered cases.

Compared with Fig. 3a the transition probability w^+ increases in Fig. 3b 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_A 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 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 systems and from the increase of the equilibrium vapour pressure. It 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. The Figs. 3a,b demonstrate, that the critical cluster size increases and the stable cluster size decreases for a decreasing ratio $A=N_o/N_v$. 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.

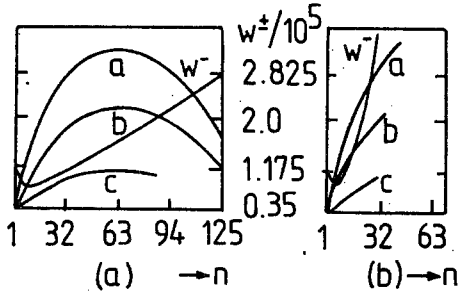

Fig. 3.:

Transition probabilities w_n^+ (eq. (4.8)) and w_n^- (eq. (4.9)) in dependence on the cluster size n. Fig. 3a: $R=N_o/N_v=200$, Fig. 3b: $R=N_o/N_v=20$. Parameter: initial supersaturation y_A (eq. (1.3)). w_n^+ is presented for (a) $y_A=12$, (b) $y_A=8$, (c) $y_A=4$. w_n^- does not depend on y_A. System volume $V=1.7 \cdot 10^{-23} m^3$, $N_v=150$, $T_A=280K$.

The specific properties of the vapour are obtained from ethanol.

4.3. Contribution of Coagulation and Split of Clusters

The question is very important whether the contribution of coagulation and split of clusters can be neglected or not, compared with the reactions between clusters and free particles. In order to investigate this problem we averaged 4 runs of computer simulations of a phase transition in system (ii) with the constraints $H, p_o, N=const$. The transition probabilities of nucleation and evaporation, coagulation and split of clusters are given by eqs. (3.19) and (4.4). We have assumed $E_A=0$. The actual temperature in the system is given by eq. (4.7) (ii), the actual volume results from eq. (2.6) (ii).

The contribution of reactions of the type $A_n+A_m \Longleftrightarrow A_{m+n}$; $n,m \geq 2$, is presented in Fig. 4. We suppose that this result depends on the special initial conditions assumed; therefore, Fig. 4 gives only a first estimation of the problem.

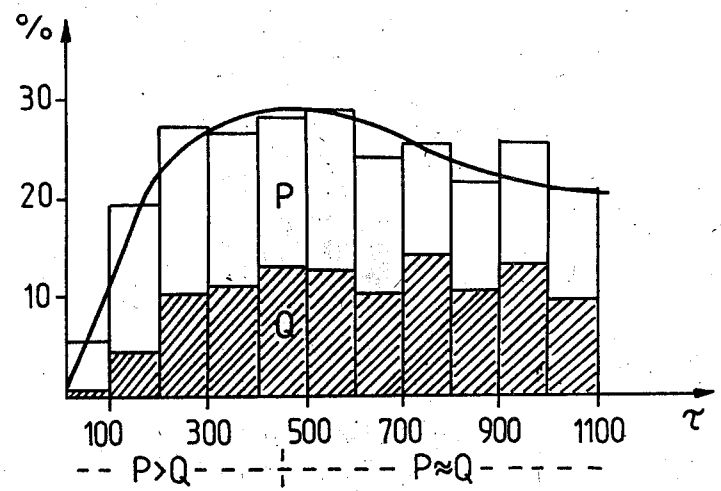

Fig. 4.:

Amount of coagulation processes (P) and split of clusters (Q) in % vs. total number of reactions τ (averaged over 4 runs) system parameter: initial supersaturation $y_A=12.5$, $T_A=290K$, $N_v=250$, $R=N_o/N_v=50$, $V_A=0.85 \cdot 10^{-21} m^3$.

The specific properties of the vapour are obtained from ethanol.

To explain Fig. 4, P gives the percentage of the reactions $A_m+A_n \rightarrow A_{m+n}$ and Q the percentage of the reactions $A_{m+n} \rightarrow A_m+A_n$. The opposite 100%-P-Q gives the percentage of all reactions with free particles: $A_n+A_1 \Longleftrightarrow A_{n+1}$.

τ means the total number of reactions, it determines the time scale. In the considered case 1100 reactions involve a real time of about 100 ns.

It is to be seen that the contribution of coagulation of clusters increases during the first time because of the predominant formation of small clusters. In a second time stage it yields approximately an equilibrium between coagulation and split of clusters: $P \sim Q$, while the total amount P+Q decreases. This fact results from the decrease of the total number of clusters during the last stage of the phase transition. It is of interest, that for the system considered here nearly 25% of all reactions include participates with $n,m \geq 2$.

4.4. Applications of the Model to Free Adiabatic Expansion

A situation of practical importance in the field of phase transition is the formation of clusters during a free adiabatic expansion of a gas. This situation is given in the early evolution of the cosmos, or during the first stages of laser plasma vapour deposition of thin films /20/.

The theory outlined here leads to proper transition probabilities which are applicable to such problems, since they includes also the change of the thermodynamic properties of the system.

We now discuss a special case of the system (i1) (cf. Fig. 1), where the external pressure p_∞ tends to zero. That means a free adiabatic expansion of the volume V leading to an increase of the supersaturation and, therefore, to a stage of cluster formation and coagulation. The increase of the volume dV shall be considered only in one space direction s. Then it yields:

$$dV \sim ds = v\,dt \tag{4.11}$$

where v is the mean velocity of the expanding particles. Since the monomers have the largest velocity, their actual position

shall define the actual volume. The mean velocity of the monomers in the space direction is related to the actual temperature via the equation:

$$\frac{m_1}{2} v_1^2 = \frac{1}{2} k_B T \tag{4.12}$$

Eq. (4.11) now results in

$$dV \sim \left(\frac{k_B}{m_1}\right)^{1/2} \sqrt{T(\underline{N},V)}\; dt \tag{4.13}$$

It is known from eq. (4.7) that the temperature of the system depends on the actual volume and on the established cluster distribution $\underline{N}$, because of the latent heat released. In order to describe the free adiabatic expansion with respect to the stochastic cluster formation and coagulation we propose therefore the following advance:

1. For given values V and T a stochastic computer simulation of the cluster evolution is carried out by means of the transition probabilities (3.19), (3.27) (see, e.g., /4,18,21/) - a new distribution $\underline{N}'$ establishes with new values V', T'.
2. For the constant cluster distribution $\underline{N}'$ the volume V' expands during the life time of the distribution via eq. (4.13). The T-V relation is now given by eq. (3.23).
3. With the new values V", T" point 1. is carried out.

It is assumed here, that the temperature is a global parameter - that means also a change of the temperature in the clusters. In the case of a constant internal temperature of the clusters (heat drops e.g.) eq. (3.23) of point 2. reduces simply to $T^{3/2}V=\text{const}$. Results of the given scenario to describe the cluster formation during a free adiabatic expansion are presented in subsequent papers.

5. Kinetic Equations for the Mean Cluster Distribution

The mean number of clusters of size n is received from the first moment of the probability $P(\underline{N},t)$:

$$\langle N_n(t)\rangle = \sum_{\{N_i\}} N_n\, P(N_0,N_1\ldots N_n\ldots,t) \qquad (5.1)$$

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

By means of the master equation (3.4) the time dependence of the mean values $\langle N_n(t)\rangle$ can be expressed in the following form /17/:

$$\frac{d}{dt}\langle N_n(t)\rangle = \sum_j \Delta_j N_n \langle w_j(\underline{N}'|\underline{N})\rangle \qquad (5.2)$$

$\Delta_j N_n$ gives the value of the change of N_n for every possible stochastic reaction j where the N_n participate. $\langle w_j(\underline{N}'|N)\rangle$ denotes the averaged value of the related transition probability for the reaction j. Using the transition probabilities (3.19), (4.4) we obtain from eq. (5.2) the following system of equations:

$$\frac{d}{dt}\langle N_n\rangle = \frac{1}{2}\sum_{i+j=n}\langle w^+(N_iN_j)\rangle - \langle w^-(N_{i+j})\rangle - \sum_{j=1}^{j+n<N}(1+\vartheta_{j,n})\{\langle w^+(N_nN_j)\rangle - \langle w^-(N_{n+j})\rangle\} \qquad (5.3)$$

$$n=2,\ldots,N_{N-1}$$

with $\vartheta_{j,n}=1$ for $j=n$.

Going over to the densities $c_n=N_n/V$ and defining

$$k^+_{m,n} = \alpha_{m,n}(T)$$

$$k^-_{m,n} = \beta_{m,n}(T)p^{\ominus}(T)\exp\left\{\frac{B}{k_BT}[(m+n-1)^{2/3} - (m-1)^{2/3}-(n-1)^{2/3}] - \frac{E_a}{k_BT}\right\}$$

we may write the kinetic equations of the mean values in the form:

$$\langle c_n\rangle = \frac{1}{2}\sum_{i+j=n}\{k^+_{i,j}\langle c_i\rangle\langle c_j\rangle - k^-_{i,j}\langle c_n\rangle\} - \langle c_n\rangle\sum_{j=1}^{j+n\leq N}\{(1+\vartheta_{j,n})\,[k^+_{jn}\langle c_j\rangle - k^-_{jn}]\} \qquad (5.4)$$

From this equations two special cases can be derived:

(i) Assuming only interactions between clusters and free particles: $A_n+A_m<==>A_{n+i}$, eq. (5.4) can be transformed into a Fokker-Planck equation:

$$\langle c_n\rangle = -\frac{\partial}{\partial n}[k^+_{n,i}\langle c_i\rangle - k^-_{n-i,i}]\langle c_n\rangle + \frac{1}{2}\frac{\partial^2}{\partial n^2}[k^+_{n,i}\langle c_i\rangle - k^-_{n-i,i}]\langle c_n\rangle \qquad (5.5)$$

For a further discussion of eq. (4.5) see e.g. /4,18/.

(ii) Assuming that the split of clusters can be neglected - that means only cluster growth, $A_n+A_m->A_{n+m}$ $(m=1,\ldots N_n)$ eq. (5.4) reduces to the known Smoluchowski equation of coagulation theory /19,24/:

$$\langle c_n\rangle = \frac{1}{2}\sum_{i+j=n}k^+_{i,j}\langle c_i\rangle\langle c_j\rangle - \langle c_n\rangle\sum_{j}^{j+n<N}(1+\vartheta_{j,n})k^+_{jn}\langle c_j\rangle \qquad (5.6)$$

The two special cases demonstrate that the mean values equation for the cluster distribution derived here includes a variety of kinetic reactions. The main point of our theory is the determination of the reaction constants for the considered systems from a stochastic theory of coagulation. It involves also the change of the thermodynamic parameters of the system which gover the dynamics of the phase transition.

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