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ON THE KINETICS OF FIRST-ORDER PHASE TRANSITIONS IN ADSORBED LAYERS

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ABSTRACT: Based on the earlier developed thermodynamic description of homogeneous and heterogeneous adsorbed monolayers (10) a kinetic description of first-order phase transitions in adsorbed layers (2d-condensation, 2d-decomposition of multicomponent layers) is proposed. It is shown that for the special type of transitions considered both the general scenario and the kinetics of the process are qualitiatively the same as for its three-dimensional analogue.

The results are applied to an explanation of the results of the computer calculations by Koch et. al. (9) of the process of condensation in adsorbed monolayers, consisting of particles interacting via a Lennard-Jones potential.

INTRODUCTION

In the last decades, based on the works of Gibbs, Rayleigh, Pockels, Devaux, Marcelin, Langmuir, Adam and others, the investigation of the properties of adsorbed layers became a rapidly developing area of research in physical chemistry with a large number of applications (1-4). In particular, it was noticed that adsorbed layers may exist in different states, resembling the three-dimensional solid, liquid and gas phases, and that sharp trasitions between the different states may occur (5-8).

The topic of our present investigation is the kinetic description of first-order phase transitions in physisorbed monolayers, eg., the 2d-liquid-vapour transition or the decomposition of a 2d-multicomponent layer. It is assumed that the 2d system is closed (conservation of the number of particles) and that the temperature T is kept constant.

Based on a thermodynamic investigation of the process of formation of clusters of the newly evolving phase a general scenario of the transition and a kinetic description of different stages are given. It is shown that for the type of process discussed both the scenario and the kinetics of the transition are qualitatively the same as that of the three-dimensional analogue.

2. Thermodynamic Description of the Formation of One Cluster in Monomolecular Films

In the following discussion we consider the process of formation and growth of clusters with a higher surface density of particles Γ_α(2d-liquid) compared with the molar density Γ_β of the less dense initial (2d-vapour) phase in a one-component physisorbed layer. The thermodynamic parameters are chosen in such a way that the initially homogeneous 2d-vapour is in a metastable state.

Two types of constraints are considered. As a first example, it is assumed that the state of the 2d-vapour is not affected by the process of formation and growth of the clusters. This assumption is correct, if the surface area of the system is varied in the course of the transition (Fig. 1).

If, in contrast, the surface area A is fixed, then the formation of a cluster is accompanied by depletion effects. This is the second case to be studied here. Since this second case is realized in the computer calculations of Koch et.al. (9), their work can be taken as one example our investigations can be compared with.

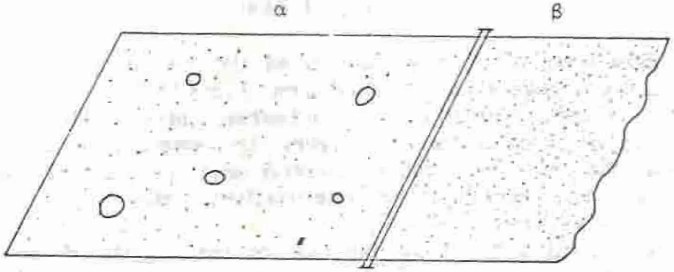

Fig.1: Model used for the investigation of phase transitions in adsorbed layers. The two considered boundary conditions are realized by a free motion or by a fixation of the position of the barrier, respectively.

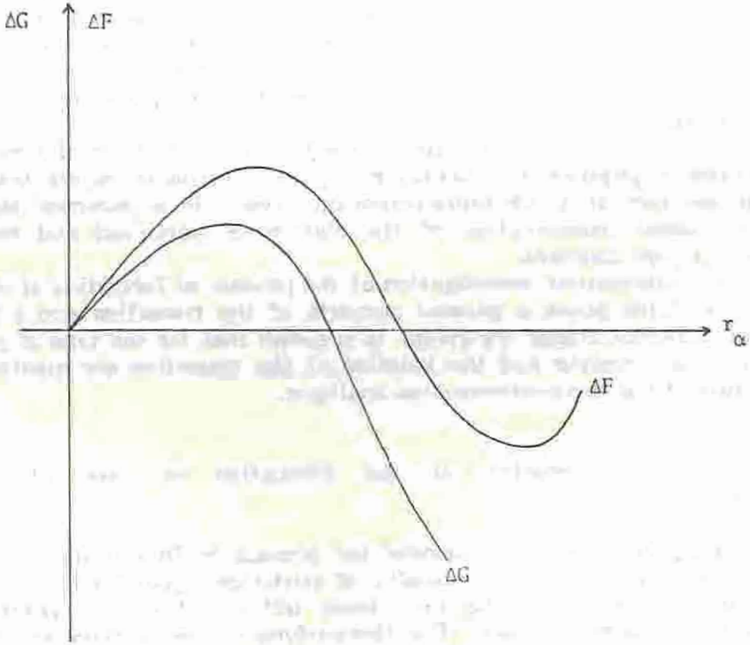

Fig. 2: Change of the thermodynamic potential as a function of the cluster radius for both considered cases. For ΔG only one extremum exists, depletion effects lead to the existence of an additional minimum of ΔF for a relatively large size of the cluster.

The different constraints are illustrated by Fig. 1. In both cases studied the number of monomers in the layer is assumed to be constant. In the first case the position of the barrier is varied in the course of the transition to retain equality of the surface tension at both sides, while in the second case its position is fixed.

The characteristic potentials describing both situations are the Gibbs free energy G and the Helmholtz free energy F, respectively. For the case only one cluster is formed in the system, these potentials can be expressed in the following way (10)

$$
\begin{aligned}
G &= (\sigma_\alpha - \sigma_\beta) A_\alpha + \mu_\alpha n_\alpha + \mu_\beta n_\beta + \kappa L \\
F &= \sigma_\alpha A_\alpha + \mu_\alpha n_\alpha + \sigma_\beta A_\beta + \mu_\beta n_\beta + \kappa L
\end{aligned}
\qquad (2.1)
$$

σ is the surface tension, A the surface area, μ the chemical potential, n the mole number, κ the line tension and L the length of the dividing line between the cluster (specified by the subscript α) and the surrounding vapour (specified by β).

Since σ and μ can be considered as functions of the surface densities of particles Γ and the temperature T, in the first case both quantities remain unchanged in the process of formation of the clusters. Thus in expression for G we may substitute $\sigma_\beta = \sigma, \mu_\beta = \mu$, where the quantities without a subscript refer to the homogeneous metastable initial state.

Moreover, based on the Gibbs adsorption equation

$$d\sigma_\alpha = - \Gamma_\alpha \, d\mu_\alpha \qquad (2.2)$$

assuming incompressibility of the 2d-liquid, we obtain

$$\sigma_\alpha - \sigma^+ = - \Gamma_\alpha \, [\mu_\alpha (\sigma_\alpha) - \mu_\alpha (\sigma^+)] \qquad (2.3)$$

For the calculation of G we take as the reference value for σ the external tension

$$\sigma^+ = \sigma \qquad (2.4)$$

and for the calculation of F we set

$$\sigma^+ = \sigma' \qquad (2.5)$$

where σ' is the value of the surface tension for a stable 2d liquid-vapor coexistence at a straight 1d interface.

With eqs. (2.2)-(2.5) eqs. (2.1) are transformed into the following expression

$$
\begin{aligned}
G &= n_\alpha \mu_\alpha (\sigma) + n_\beta \mu_\beta (\sigma) + \kappa L \\
F &= (\sigma' - \sigma_\beta) A_\alpha + (\mu' - \mu_\beta) n_\alpha + \kappa L + \sigma_\beta A + \mu_\beta n
\end{aligned}
\qquad (2.6)
$$

In the calculation of F in addition the condition $A = A_\alpha + A_\beta$ was used.

Instead of the potentials G and F it is more convenient to deal with the difference between their values in the heterogeneous state cluster in the medium and the homogeneous initial state for the description of cluster formation. Taking into account eqs.(2.7), describing F and G for homogeneous layers (10),

$$F_{hom} = \sigma A + \mu n \tag{2.7}$$

$$G_{hom} = \mu n$$

we get

$$\Delta G = n_\alpha [\mu_\alpha(\sigma) - \mu_\beta(\sigma)] + \kappa L$$

$$\Delta F = (\sigma' - \sigma_\beta) A_\alpha + (\mu' - \mu_\beta) n_\alpha + \kappa L + (\sigma_\beta - \sigma) A + (\mu_\beta - \mu) n \tag{2.8}$$

A phase transition may occur if the chemical potential of the particles in the cluster is less than in the vapour phase. If this condition is fulfilled, ΔG and ΔF show a dependence on the cluster radius r_α, a behaviour, as presented in Fig. 2.

The extrema of ΔG and ΔF are determined by two-dimensional Gibbs-Thomson equations

$$\frac{\partial \Delta G}{\partial r_\alpha} = 2\pi r_\alpha [\Gamma_\alpha [\mu_\alpha(\sigma) - \mu_\beta(\sigma)] + \frac{\kappa}{r_\alpha}] = 0$$

$$\frac{\partial \Delta F}{\partial r_\alpha} = 2\pi r_\alpha [\sigma' - \sigma_\beta + \Gamma_\alpha [\mu'(\sigma') - \mu_\beta(\sigma_\beta)] + \frac{\kappa}{r_\alpha}] = 0 \tag{2.9}$$

The second derivatives at the extrema are given by

$$\frac{\partial^2 \Delta G}{\partial r_\alpha^2} = -\frac{2\pi \kappa}{r_\alpha}$$

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = -\frac{2\pi \kappa}{r_\alpha}[1 - \frac{2\pi r_\alpha^3 (\Gamma_\alpha - \Gamma)^2}{\kappa A (1 - \frac{A_\alpha}{A})^3} \frac{\partial \mu_\beta}{\partial \Gamma_\beta}] \tag{2.10}$$

While for ΔG only one extremum (maximum) exists, depletion effects result, additionally, also in a minimum of ΔF, corresponding to a thermodynamically stable heterogeneous state.

3. Generalization to Ensembles of Clusters

In the stage of nucleation, a large number of clusters is usually formed. Consequently, for this general case we have to generalize the thermodynamic description of clusters in the otherwise homogeneous medium.

Denoting by N the total number of clusters in the system, the characteristic potentials of an ensemble of clusters with different sizes are given by

$$G = \sum_{j=1}^{N} [(\sigma_\alpha^{(j)} - \sigma_\beta) A_\alpha^{(j)} + \mu_\alpha^{(j)} n_\alpha^{(j)} + \kappa^{(j)} L^{(j)}] + \mu_\beta n_\beta$$

$$F = \sum_{j=1}^{N} [\sigma_\alpha^{(j)} A_\alpha^{(j)} + \mu_\alpha^{(j)} n_\alpha^{(j)} + \kappa^{(j)} L^{(j)}] + \mu_\beta n_\beta + \sigma_\beta A_\beta \tag{3.1}$$

the superscript (j) specifying the different clusters.

In the case of N identical 2d-drops these equations can be transformed into

$$\Delta G = N[\,n_\alpha\,[\mu_\alpha(\sigma) - \mu_\beta(\sigma)] + \kappa\, L] \tag{3.2}$$

$$\Delta F = N[\,(\sigma' - \sigma_\beta)\,A_\alpha + n_\alpha(\mu' - \mu_\beta) + \kappa\, L\,] + A(\sigma_\beta - \sigma) \;+ n\,(\mu_\beta - \mu)$$

In the derivations of eqs. (3.2) the same approximations as in the preceding chapter were used.

ΔG and ΔF, expressed by eqs. (3.2), depend on two variables, the common radius r_α and the number of clusters N. For a fixed value of N the extrema of the thermodynamic potentials are again given by equations of the type (2.9),

$$\left(\frac{\partial \Delta G}{\partial r_\alpha}\right)_N = 2\pi\, r_\alpha\, N[\Gamma_\alpha[\mu_\alpha(\sigma) - \mu_\beta(\sigma)] + \frac{\kappa}{r_\alpha}] = 0$$

$$\left(\frac{\partial \Delta F}{\partial r_\alpha}\right)_N = 2\pi\, r_\alpha\, N[\,\sigma' - \sigma_\beta + \Gamma_\alpha\,[\mu'(\sigma') - \mu_\beta(\sigma_\beta)] + \frac{\kappa}{r_\alpha}] = 0 \tag{3.3}$$

The second-order derivatives read, now

$$\left(\frac{\partial^2 \Delta G}{\partial r_\alpha^2}\right)_N = -\frac{2\pi\,\kappa\, N}{r_\alpha} \tag{3.4}$$

$$\left(\frac{\partial^2 \Delta F}{\partial r_\alpha^2}\right)_N = -\frac{2\pi\,\kappa\, N}{r_\alpha}(1+y)\;,\quad y = \frac{2\pi\, r_\alpha^3\, N(\Gamma_\alpha - \Gamma)^2}{A\,\kappa\,(1-\frac{NA_\alpha}{A})^3}\;\frac{\partial \mu_\beta}{\partial \Gamma_\beta}$$

Taking into account that, according to eq. (3.3), the critical cluster size is given by

$$r_c = \frac{\kappa}{\Gamma_\alpha[\mu_\beta(\sigma) - \mu_\alpha(\sigma)]} \tag{3.5}$$

the expression for ΔG can be written as

$$\Delta G = N\Delta G_c\;[2\frac{r_\alpha}{r_c} - (\frac{r_\alpha}{r_c})^2\,]\;,\quad \Delta G_c = \pi\,\kappa\, r_c \tag{3.6}$$

where ΔG_c is the extremum value of ΔG for the case only one cluster is present in the system.

Thus the position of the extrema of ΔG and the point of intersection of the function $\Delta G = \Delta G(r_\alpha)$ with the r_α-axis do not depend on the number of cluster (see Fig.3).

The situation is quite different if we calculate $\Delta F = \Delta F(r_\alpha)$ for different values of the number of clusters N. According to eq. (3.3) the position of the extrema for this second case depends on the number of clusters N. Considering N as a continuous variable, from the generalized Gibbs-Thomson equation (3.7)

$$\sigma' - \sigma_\beta + \Gamma_\alpha [\mu' - \mu_\beta] + \frac{\kappa}{r_\alpha} = 0 \tag{3.7}$$

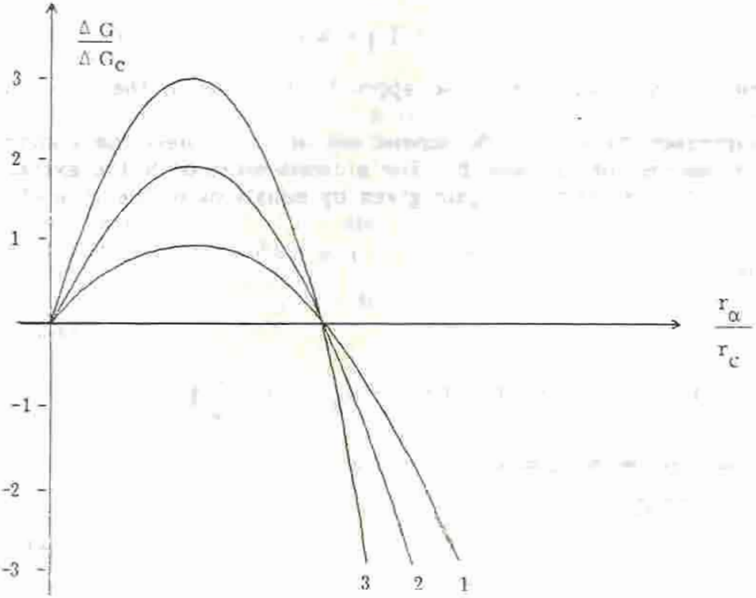

Fig.3: ΔG as a function of the radius for different values of the numbers of clusters (N = 1,2,3)

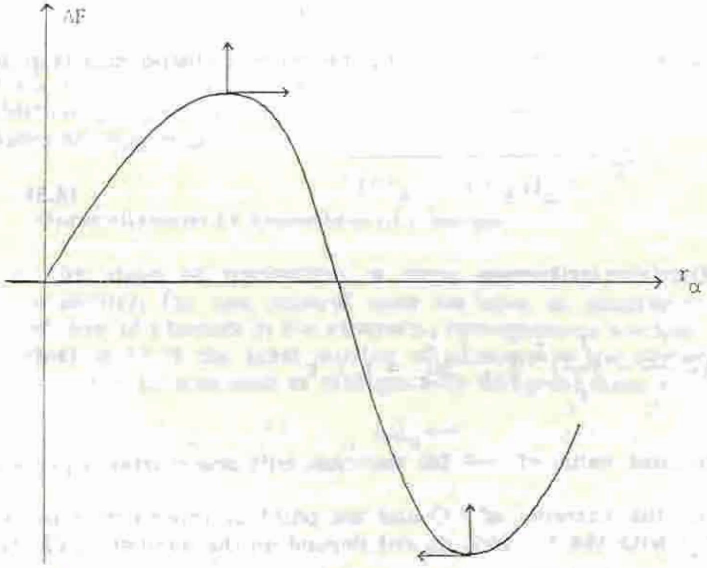

Fig. 4: ΔF as a function of the radius for a fixed number of clusters N in the system. The direction of the variation of the extrema with an increasing number of clusters is indicated by arrows.

the following expression for the variation of the position of the extrema with an increase of N is obtained;

$$\frac{dr_\alpha}{dN} = - \frac{r_\alpha}{2N} \frac{y}{1+y} \tag{3.8}$$

Moreover, since for the extrema $(\partial\Delta F/\partial r_\alpha = 0)$ we may write

$$\frac{d\Delta F}{dN} = \left(\frac{\partial\Delta F}{\partial N}\right)_{r_\alpha} + \left(\frac{\partial\Delta F}{\partial r_\alpha}\right)_N \frac{dr_\alpha}{dN} = \left(\frac{\partial\Delta F}{\partial N}\right)_{r_\alpha} \tag{3.9}$$

resulting in

$$\frac{d\Delta F}{dN} = \frac{1}{2} \kappa L_c \quad , \quad L_c = 2\pi r_c \tag{3.10}$$

r_c in eq.(3.10) is one of the possible two solutions for r_α of eq.(3.7).

From the extremum conditions eq.(3.4) we find further

$$1 + y > 0 \quad , \quad \frac{dr_\alpha}{dN} > 0 \tag{3.11}$$

for the maxima and

$$1 + y < 0 \quad , \quad \frac{dr_\alpha}{dN} < 0 \tag{3.12}$$

for the minima of ΔF.

The variation of the position of the extrema of ΔF with an increasing number of clusters is indicated in Fig.4 by arrows. There exists a critical number of clusters N^c for which both extrema coincide in a point of inflexion. N^c and the corresponding value of r_α for the point of inflexion are given by

$$\left(\frac{\partial\Delta F}{\partial r_\alpha}\right)_N = \left(\frac{\partial^2\Delta F}{\partial r_\alpha^2}\right)_N = 0 \tag{3.13}$$

In Fig. 5 ΔF is presented as a function of r_α for different values of the number of clusters N. The resulting figure suggests, that in analogy to three-dimensional case (see, e.g., (11)) phase transitions in 2d-layers starting from metastable initial states may proceed via three main stages, a first stage of nucleation and a possible simultaneous growth of the already formed supercritical clusters (dotted curve), a second stage of practically independent growth of the clusters their number being nearly constant (dashed-dotted curve) and a third stage of competitive growth, of Ostwald ripening, resulting in a decrease of the number of clusters and an increase of their mean radius (dashed curve).

It should be stressed that this scenario holds strictly only if the underlying thermodynamic description assumptions are fulfilled (e.g., physisorption on smooth surfaces, absence of additional heterogeneities in the layer) and if the growth of the clusters proceeds mainly by diffusion-like processes. It is believed, however, that such additional factors, which may influence the transition, not necessarily result in a totally different scenario, though modifications, of course, are possible (compare (15)).

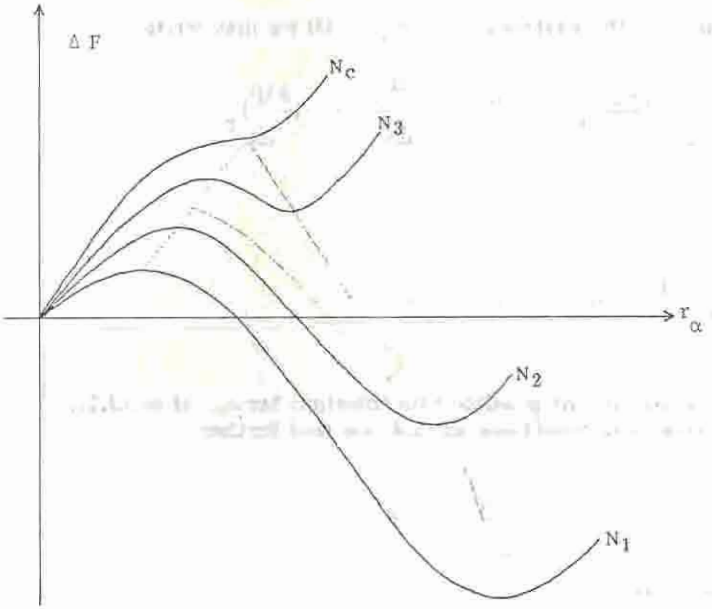

Fig. 5: ΔF as a function of the radius for different values of the number of clusters ($N_1 < N_2 > N_3 < N^c$).

The results of the thermodynamic investigations are used now, to give a kinetic description of the growth of the clusters. Hereby it is assumed that the growth proceeds mainly via an addition of monomers. The process of nucleation can again be described in terms of a quasi-steady-state nucleation rate (see, e.g., (11)) and is, therefore, not discussed in detail here.

4. Kinetics of Growth of Single Clusters

The kinetic description of the growth of the 2d-clusters, outlined here, is based on a general equation for the density of fluxes $\bar{j}$ of particles through the interface between two phases, derived earlier by one of the authors in cooperation with I. Gutzow (see, e.g., (11),12)). For the considered case this equation can be written as

$$\bar{j} = \frac{D\Gamma_\beta}{RT}\,\frac{1}{l}\,\frac{\partial\phi}{\partial n_\alpha}\,\bar{e}_r \qquad (4.1)$$

D is the diffusion coefficient of the monomers in the medium, R the universal gas constant, ϕ the characteristic thermodynamic potential of the heterogeneous system (cluster in the otherwise homogeneous medium), 1 a parameter with the physical meaning of the width of the inhomogeneous region between the different phases, $\bar{e}_r$ a unit vector directed perpendicular to the surface of the cluster.

The universal applicability of the equation (4.1) arises from the fact, that all thermodynamic information about the system of interest is contained in ϕ, while the type of growth is described by the parameter I. 1 is equal to a constant of molecular dimensions for (interface) kinetic limited growth; it is equal, at least to a good approximation, to the radius of the cluster for diffusion limited growth (12,14). The total flux of particles through the interface of the cluster and, consequently, the change of the number of moles in the cluster are given by

$$\frac{dn_\alpha}{dt} = -2\pi r_\alpha \frac{D\Gamma_\beta}{RT} \frac{1}{1} \frac{\partial\phi}{\partial n_\alpha} \tag{4.2}$$

Assuming incompressibility of the cluster phase we may write also

$$\frac{dA_\alpha}{dt} = -\frac{D\Gamma_\beta}{\Gamma_\alpha^2 RT} \frac{1}{1} \frac{\partial\phi}{\partial r_\alpha} \tag{4.3}$$

For the constraints described by Gibbs' free energy ϕ has to be replaced by ΔG. Moreover, $\Gamma_\beta = \Gamma$ and we get

$$\frac{dr_\alpha}{dt} = \frac{D\Gamma\kappa}{\Gamma_\alpha^2 RT} \frac{1}{1} \left\{ \frac{1}{r_c} - \frac{1}{r_\alpha} \right\} \tag{4.4}$$

r_c being determind by eq. (3.5).

If $r_\alpha >> r_c$, then the cluster grows as $r_\alpha^2 \sim t$ for diffusion limited growth and as $r_\alpha \sim t$ for kinetic limited growth. If $r_\alpha < r_c$, then the cluster shrinks and disappears.

The same structure of the growth equation is obtained also if ΔG is replaced by ΔF for the second type of constraints, but in this case the critical cluster size depends on the radius of the growing cluster via

$$r_c = \frac{\kappa}{\sigma_\beta - \sigma' + \Gamma_\alpha [\mu_\beta - \mu']} \tag{4.5}$$

It is evident that the kinetic equations describing the growth of the clusters are consistent with the results of the thermodynamic analysis, discussed in section 2.

5. Kinetics of Growth of Ensembles of Clusters

For an arbitary number of clusters present in the system, the growth equation for the j-th cluster can be written as

$$\frac{dA_\alpha^{(j)}}{dt} = -\frac{D\Gamma_\beta}{\Gamma_\alpha^2 RT} \frac{1}{1^{(j)}} \frac{\partial\phi}{\partial r_\alpha^{(j)}} \tag{5.1}$$

ϕ in eq. (5.1) is given by eqs. (3.1) for both considered cases.

If the state of the medium is not changed by the growth of the clusters ($\phi = \Delta G$), the clusters grow independently of each other and the growth equations for each of them are again reduced to eqs.(3.5) and (4.4), again.

For finite systems with a constant surface ($\phi = \Delta F$), however, the growth of each of the clusters is affected by the size and the total number of all clusters present in the system. The growth equation is given by eq. (4.4) but r_c (eq. (4.5)) depends through Γ_β on the total number of particles in the α-phase.

While in the second stage of the phase transition (dashed-dotted curve in Fig. 5) this dependence plays no significant role - most clusters grow at the expense of the monomers in the vapour phase with $r_\alpha^2 \sim t$ and $r_\alpha \sim t$, respectively - it determines the evolution in the third stage, the stage of competitive growth or Ostwald ripening (dashed curve in Fig.5).

For the derivation of the kinetic equations, describing Ostwald ripening in adsorbed layers, we start with equation (5.1) and assume in addition, that the total mass of the new phase is distributed between N nearly identical clusters. Taking the sum over all clusters, we obtain

$$N \frac{dA_\alpha}{dt} = - \frac{D\Gamma_\beta}{\Gamma_\alpha^2 RT} \frac{1}{l} \frac{\partial \phi}{\partial r_\alpha} \tag{5.2}$$

where ϕ is given now by the second of the eqs. (3.2).

Moreover, since the thermodynamic driving force of the competitive growth is the decrease of ΔF, connected with the decrease of the number of clusters, we replace

$$\frac{\partial \phi}{\partial r_\alpha} \rightarrow \frac{\partial \phi}{\partial N} \frac{dN}{dr_\alpha} \tag{5.3}$$

A substitution of eqs. (3.9), (3.10) and (5.3) into eq. (5.2) yields

$$\frac{dr_\alpha}{dt} = \frac{\omega D \Gamma_\beta \kappa}{\Gamma_\alpha^2 RT} \frac{1}{l r_\alpha} (1 + y^{-1}) \tag{5.4}$$

The numerical factor ω is introduced here to account for the approximations due to the consideration of a system of nearly identical clusters in the calculation of the thermodynamic driving force of Ostwald ripening. It will be determined later.

Eq. (5.4) is to be considered as a description of the time-dependence of the mean size of the ensemble of clusters in the stage of Ostwald ripening. It has to be supplemented by a second equation for the description of the time-evolution of the number of clusters.

This second equation can be obtained from eq. (3.8) or by a derivation of eq. (3.7) with respect to time. It reads

$$\frac{d}{dt} \left[\ln \left(\frac{NA_\alpha}{A} \right)\right] = - \frac{1}{y} \frac{d}{dt} \left[\ln(r_\alpha^2)\right] \tag{5.5}$$

The system of equation (5.4) and (5.5) can be solved numerically in a relatively simple way. In the asymptotic region y^{-1} tends to zero and we obtain as asymptotic solutions

$$r_\alpha^3 = 3 \frac{\omega D \Gamma' \kappa}{\Gamma_\alpha^2 RT} t \quad , \quad l = r_\alpha \tag{5.6}$$

$$r_\alpha^2 = 2 \frac{\omega D \Gamma' \kappa}{\Gamma_\alpha^2 RT l_o} t \quad , \quad l = l_o = \text{const.} \tag{5.7}$$

In the asymptotic region, the mass or the surface area of the liquid phase is nearly constant (the right-hand side of eq.(5.5) tends to zero). The value of this constant can be determind from the Gibbs-Thomson equation, which in the asymptotic region is given approximately by

$$\mu_\beta - \mu' = 0 \tag{5.8}$$

A Taylor expansion of μ_β results in

$$\mu_\beta = \mu - \Gamma \frac{N n_\alpha}{n} \frac{\partial\mu}{\partial\Gamma} \tag{5.9}$$

and we obtain

$$N \cong \frac{A(\mu - \mu')}{\Gamma_\alpha \frac{\partial\mu}{\partial\Gamma}} \frac{1}{A_\alpha} \tag{5.10}$$

Thus N depends on time as $N \sim t^{-2/3}$ for diffusion limited growth and as $N \sim t^{-1}$ for interface kinetic limited growth, where the constant of proportionality is easily obtained from eqs. (5.6), (5.7) and (5.10).

Applying the method of Lifshitz and Slyozov (16) to eq.(4.4) with $\Gamma_\beta = \Gamma'$ we get for diffusion limited growth the following asymptotic solution

$$r_\alpha^3 = \frac{4}{9} \frac{D \kappa \Gamma'}{\Gamma_\alpha^2 RT} t \tag{5.11}$$

Since for the asymptotic region the results of Lifshitz and Slyozov are accurate, we set

$$\omega = \frac{4}{27} \tag{5.12}$$

to get an agreement with our approach for this limiting case.

DISCUSSION

Our investigations confirm the result of Koch et. al. (9), that for kinetic limited growth under isothermal conditions the mean size of the clusters in the stage of Ostwald ripening grows as $r^2 \sim t$ in the asymptotic region. Moreover, our investigations also give an explanation for its initially slow increase, since in the vicinity of the highest point of the valley of ΔF (dashed curve in Fig. 5) y^{-1} is nearly equal to minus one and the time derivative of r_α is small (see eq.(5.4).

REFERENCES

1. A.W. Adamson, Physical Chemistry of Surfaces, 3rd edition, Wiley 1976.
2. R. Aveyard and D.A Haydon, An Introduction to the Principles of Surface Chemistry, Cambridge University Press, 1973.
3. M.J. Jaycock and G.D. Parfitt, Chemistry of Interfaces, Chichester, 1981.
4. K.D. Leaver, K.D. and B.N. Chapman, Thin Films, London, Winchester, 1971.
5. J.G Dash, Physics Today, **38** (12), 26 (1985).
6. R.W. Vook, Optical Engineering, **23**, 343 (1984).
7. Vilches, O. E.: Ann. Rev. Phys. Chem., **31**, 463 (1980).
8. M.E. Fisher, J. Chem Soc., Faraday Trans.II, **82**, 1569 (1986).
9. S.W. Koch, R.C. Desai and F.F Abraham, Phys. Rev., **A27**, 2152 (1983).
10. J Schmelzer and T. Gebre-medhin, On the Thermodynamic Description of Thin films, in press.
11. J. Schmelzer and H. Ulbricht, Thermodynamics of Finite Systems and the Kinetics of first-order Phase Transitions, J. Colloid and Interface Science, in press.
12. J. Schmelzer, Z. Phys.Chem. (Leipzig), **266**, 1057 (1985).
13. J. Schmelzer and I. Gutzow, Zeitschrift der Wilhelm-Pieck-Universitat Rostock NR, **35**, 5 (1986).
14. J. Marqusee, J.Chem. Phys.,**81**, 976 (1984).
15. E.D. Siggia, Phys. Rev., **A20**, 595 (1979).
16. I.M. Lifshitz and V.V.Slyozov, J.Phys. Chem.Sol., **19**, 35 (1961).