Ostwald Ripening of Bubbles in Liquid-Gas Solutions

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Abstract

The possibility of a stable coexistence of bubbles in supersaturated liquid-gas solutions is investigated. It is shown that in contrast to the conclusions derived by Ward et al. [1, 2], multi-bubble systems in the otherwise homgeneous medium are thermodynamically unstable.

Based on thermodynamic investigations, a theory of Ostwald ripening of gas bubbles in liquid-gas solutions is presented which includes the description of the initial stage of this process. Differential equations describing the time development of the mean radius and the number of bubbles are derived. For the a-symptotic region analytic solutions in agreement with the results of Lifshitz and Slyozov [3] are obtained.

The results can also be applied to a description of the growth of single droplets and ensembles of droplets in multicomponent vapours, demonstrating the analogy between the time development of ensembles of droplets and bubbles.

1. Introduction

In preceding papers [4–6] results of thermodynamic investigations concerning first order phase transitions were given and a new method of kinetic description of special stages of this process was proposed. It was assumed for the kinetic description of the growth of the clusters that the new phase can be considered as incompressible. Here the investigations are extended to multibubble systems, where the assumption of incompressibility cannot be applied. Our results are compared with the conclusions obtained by Ward et al. [1, 2], in an investigation of bubbles in liquid-gas solutions.

It was stated by these authors that in a closed volume of a liquid-gas-solution there can exist configurations of a single bubble and a number of bubbles in stable thermodynamic equilibrium within the otherwise homgeneous solution. We would like to show here, that, while the first is true, the second statement is

not valid. Under the conditions assumed by Ward et al. [1], a stable coexistence of bubbles in the liquid-gas solution is excluded and can, therefore, not be used for the explanation of a smaller nucleation threshold as compared with the predictions of homogeneous nucleation theory.

Moreover, it is shown that the thermodynamic investigation of a multi-bubble system leads to a deeper insight to the late stages of phase transitions usually denoted as Ostwald ripening [3], and a kinetic description of Ostwald ripening of an ensemble of bubbles is given.

2. General thermodynamic results

2.1 The model

We consider a closed system (liquid-gas solution) under a constant external pressure p and a constant temperature T. The thermodynamic parameters are chosen in such a way that the homogeneous initial state is metastable and therefore, a first order phase transition by nucleation and growth of clusters can occur.

The appropriate thermodynamic potential for the given thermodynamic constraints is the Gibbs free energy G [7, 8, 12]. The extremal properties of G, derived in classical thermodynamics, are based exclusively on the constancy of the external pressure p together with $T = \text{const.}$; $n_i = \text{const.}$; $i = 1, 2, \ldots, k$ (k-number of components, n_i-number of moles of the i-th component). The existence of regions inside the heterogeneous system considered with, in general, different values of the pressure does not affect, therefore, these conclusions of classical thermodynamics. (Compare, in contrast the arguments of Ward et al. [1, 2]).

The change of the Gibbs free energy ΔG due to the development of s clusters of a new phase can to a good approximation expressed by [8, 12]:

$$\Delta G = \sum_{j=1}^{s} \left\{ \left(P - P_\alpha^{(j)} \right) V_\alpha^{(j)} + \sum_{i=1}^{k} (\mu_{i_\alpha}^{(j)} - \mu_{i_\beta}) n_{i_\alpha}^{(j)} + \right.$$
$$\left. + \sigma_\alpha^{(j)} O_\alpha^{(j)} \right\} + \sum_{i=1}^{k} (\mu_{i_\beta} - \mu_i) n_i . \tag{2.1}$$

Here $V_\alpha^{(j)}$ is the volume, $\mu_\alpha^{(j)}$ the chemical potential, $\sigma_\alpha^{(j)}$ the surface tension and $O_\alpha^{(j)}$ the surface area of the j-th cluster. The subscripts (α) and (β) specify the thermodynamic parameters of the clusters (α) (bubbles) and the surrounding medium (β). Parameters without these subscripts refer to the homogeneous metastable initial state.

The extreme values of ΔG, which are of particular importance for the process of nucleation and growth of the clusters, are given by:

$$dG = \sum_{j=1}^{s} \left\{ \left(P - P_\alpha^{(j)} + O_\alpha^{(j)} \frac{dO_\alpha^{(j)}}{dV_\alpha^{(j)}} \right) dV_\alpha^{(j)} + \sum_{i=1}^{k} (\mu_\alpha^{(j)} - \mu_{i_\beta}) dn_{i_\alpha}^{(j)} \right\} = 0 \tag{2.2}$$

The number of degrees of freedom for the whole system is, therefore, $f = (k + 1)s$.

Equation (2.2) leads to the following necessary equilibrium conditions:

$$P_\alpha^{(j)} - P = \frac{2\sigma_\alpha^{(j)}}{r_\alpha^{(j)}} \; ; j = 1, 2, \ldots, s$$

$$\mu_\alpha^{(j)} = \mu_{i_\beta} \quad ; i = 1, 2, \ldots, k \tag{2.3}$$

where $r_\alpha^{(j)}$ denotes the radius of the j-th cluster.

In general, it can be shown that the states of the heterogeneous system, defined by (2.3), correspond either to local minima of the thermodynamic potential (thermodynamically stable states) or to unstable states of a saddle-point type (critical states). If additional assumptions concerning the thermodynamic properties of the system are added, for example incompressibility of the cluster, the number of degrees of freedom is decreased and saddle-points can degenerate into maxima [6].

2.2 Discussion of a special case

To simplify the derivations we restrict ourselves to binary systems and assume in addition, that the bubbles consist mainly of the second component (solute). These simplifications do not affect the main conclusions.

Taking into account the assumed simplifications ($k = 2$, $n_{1\alpha} = 0$) we obtain instead of (2.3):

$$P_\alpha^{(j)} - P_\alpha = \frac{2\sigma_\alpha^{(j)}}{r_\alpha^{(j)}} \; ; \qquad j = 1, 2, \ldots, s \; , \tag{2.4}$$

$$\mu_{2_\alpha}^{(j)} = \mu_{2_\beta} \; . \tag{2.5}$$

Since by assumption the bubbles consist only of one component the subscript "2" will be omitted in specifying their thermodynamic parameters.

Equations (2.4) and (2.5) can be fulfilled only if all clusters are characterized by the same values of the parameters r_α and n_α. In agreement with Ward et al. it was further shown [6] that also in the case considered in this paper for a given number of clusters s either two (r_{α_c}, n_{α_c}; r_{α_s}, n_{α_s}) or no solution exist. The two solutions can coincide under special conditions, discussed later.

The values of the solutions (r_{α_c}, n_{α_c}; r_{α_s}, n_{α_s}) depend on the number of clusters s. An increase of s leads to an increase of r_{α_c} and a decrease of r_{α_s} (cp. Fig. 1) [6]. Assuming all clusters to be identical (2.1) simplifies to:

$$\Delta G = (P - P_\alpha)sV_\alpha + (\mu_\alpha - \mu_{2_\beta})sn_\alpha + \sigma_\alpha sO_\alpha$$

$$+ \sum_{i=1}^{2} (\mu_{i_\beta} - \mu_i)n_i \; . \tag{2.6}$$

ΔG depends only on the two variables r_α and n_α, now. In Fig. 1 a cut through the surface $\Delta G = \Delta G(n_\alpha, r_\alpha)$ is shown, connecting the origin of the three dimensional space ($n_\alpha = 0$; $r_\alpha = 0$; $\Delta G = 0$) and the extreme values of ΔG.

Since the number of bubbles is large, s can be considered, approximately, as a continuous variable. A derivation of ΔG with respect to s leads to Eq. (2.7) describing the variation of the extremes of ΔG with an increase of s:

$$\frac{d}{ds}\Delta G = \frac{1}{3}\sigma_\alpha O_\alpha \,. \tag{2.7}$$

ΔG, therefore, increases with an increasing number of clusters. The variation of the extremes of ΔG, due to an increase of the number of bubbles, is indicated in Fig. 1 by arrows.
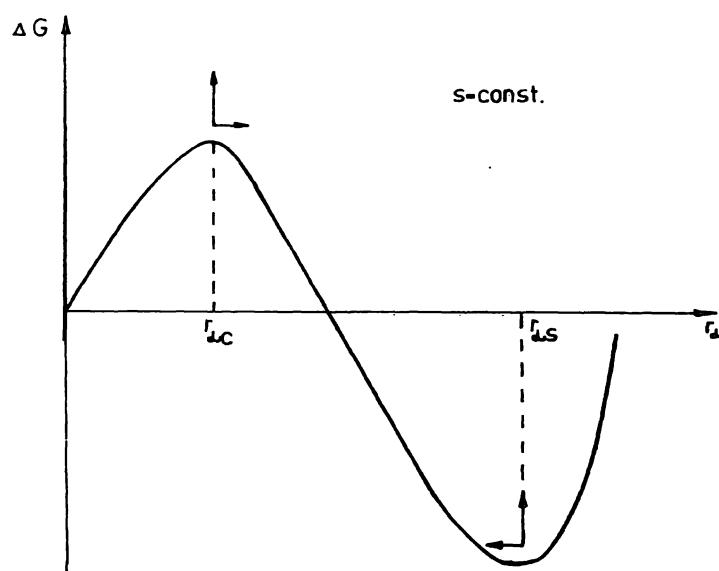

Fig. 1: Qualitative behaviour of the Gibbs free energy as a function of the common radius r_α for a fixed number of clusters. The arrows indicate the variation of the extrema with an increase of s.

2.3 Stability analysis

In Fig. 2 analogous curves as in Fig. 1 are presented for different values of the number of bubbles. Again, in agreement with Ward et al. [1, 2], it follows immediately, that one cluster can exist in stable equilibrium within the surrounding medium, since the state characterized by r_{α_s}, n_{α_s} and $s = 1$ corresponds to an absolute minimum of the thermodynamic potential.

In contrast to Ward et al., we conclude, however, that all heterogeneous state, consisting of more than one cluster in the otherwise homogeneous medium are thermodynamically unstable. This instability is due to the decrease of the thermodynamic potential with a decrease of the number of clusters as given by Eq. (2.7).

The same conclusions concerning the stability of the heterogeneous system also can be derived by an exact stability analysis [6, 8]. This analysis leads to the further conclusion, that there exists a maximum number of bubbles s^c, for which solutions of the equations (2.4) or (2.5) are possible.

Once a system of clusters is formed in the neighbourhood of this state $(r_\alpha^c, n_\alpha^c, s^c)$ the further evolution of the ensemble of clusters is expected to proceed along the "valley" of the Gibbs free energy indicated in Fig. 2 by a dashed curve (cp. also [9]). This development is characterized by a decrease of the number of clusters and an increase of their mean radius. These are the typical characteristics of the Ostwald ripening.

In the next paragraph, equations are developed, describing the growth of single bubbles. Based on the results of the thermodynamic investigation and these growth equations, it is further shown, that the development of an ensemble of bubbles along the path, indicated in Fig. 2 by the dashed curve, corresponds indeed to the process of Ostwald ripening.
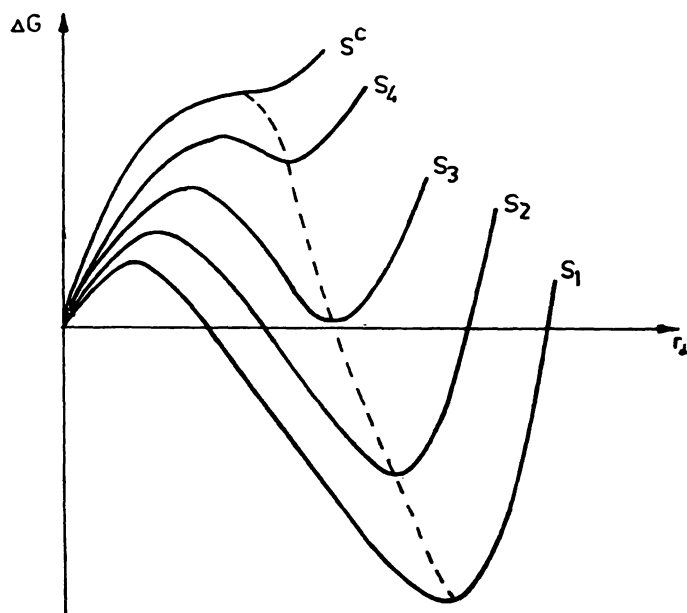

Fig. 2: The Gibbs free energy as a function of the common radius r_α for different numbers $s(s_1 < s_2 < \dots < s^c)$ of the clusters.

3. Kinetic description of diffusion limited growth of single bubbles

In preceding papers [4, 5] a general equation was derived describing the growth of a new phase in a first order phase transition. This equation is valid if the growth of the new phase proceeds by an addition of single particles (atoms, molecules).

In the special case, when the new phase consists of one spherical cluster, this growth equation can be transformed into the following expression:

$$\frac{dn_\alpha}{dt} = -4\pi r_\alpha^2 \frac{D\varrho_{2\beta}}{RT} \frac{1}{l} \frac{d\Phi}{dn_\alpha}, \tag{3.1}$$

D being the diffusion coefficient of the particles of the solute (second component) in the medium, R the universal gas constant, Φ a characteristic thermodynamic function, in our case G. The parameter l is a measure of the effective width of the inhomogeneous region, it is, in general, a constant of molecular dimensions for kinetic limited growth and it is equal to the radius of the cluster for diffusion limited growth [4, 5].

In the following diffusion limited growth is assumed (i.e. $l = r_\alpha$). All derivations can be easily repeated for the case of kinetic limited growth [4].

Equation (3.1) underlies the assumption that the variable n_α completely determines the state of the bubble. On the other hand, Eq. (2.2) shows that two independent variables are necessary for a complete description of a system containing one cluster. Therefore, another equation has to be added to Eq. (3.1). Since the mechanical equilibrium (2.4) is established much more rapidly than the diffusion equilibrium (2.5), one can assume a bubble at any instant to be in a quasi-equilibrium state with respect to Eq. (2.4). (See also [10].) In this case ϱ_α is determined by the equation of state of the gas:

$$\varrho_\alpha = \varrho_\alpha(p_\alpha, T), \tag{3.2}$$

where p_α is given by Eq. (2.4).

Taking into account these considerations (3.1) can be transformed to

$$\frac{dV_\alpha}{dt} = -\frac{D\varrho_{2\beta}}{\left(\frac{dn_\alpha}{dV_\alpha}\right)^2 RT} \frac{1}{r_\alpha} \frac{d\Delta G}{dr_\alpha}. \tag{3.3}$$

A derivation of Eq. (2.6) with respect to r_α yields:

$$\frac{d\Delta G}{dr_\alpha} = -4\pi r_\alpha^2 \left\{ \left(P_\alpha - P - \frac{2\sigma_\alpha}{r_\alpha} \right) - (\mu_\alpha - \mu_{2\beta}) \frac{dn_\alpha}{dV_\alpha} \right\} \tag{3.4}$$

Inserting this into (3.3) results in:

$$\frac{dr_\alpha}{dt} = \frac{D\varrho_{2\beta}}{\left(\frac{dn_\alpha}{dV_\alpha}\right)^2 RT} \frac{1}{r_\alpha} \left\{ \left(P_\alpha - P - \frac{2\sigma_\alpha}{r_\alpha} \right) - - (\mu_\alpha - \mu_{2\beta}) \frac{dn_\alpha}{dV_\alpha} \right\}. \tag{3.5}$$

Taking into account the quasi-equilibrium with respect to Eq. (2.4) the critical radius of a bubble can be determined by:

$$\mu_\alpha(P_\alpha) = \mu_{2\beta}(P, x_\beta). \tag{3.6}$$

A Taylor expansion of μ_α in the vicinity of $P_\alpha = P$, truncated after the second term leads together with Eq. (2.4) to:

$$r_{\alpha k} = \frac{2\sigma_\alpha}{\left(\dfrac{dn_\alpha}{dV_\alpha}\right)(\mu_{2\beta} - \mu_\alpha(P))}.$$

(3.7)

The growth of the bubble is accompanied by a decrease of the mole fraction x_β of the second component in the medium and, therefore, by a decrease of $\mu_{2\beta}$ and an increase of $r_{\alpha k}$. Using (3.7), Eq. (3.5) can be written as

$$\frac{dr_\alpha}{dt} = \frac{2D\varrho_{2\beta}\sigma_\alpha}{\left(\dfrac{dn_\alpha}{dV_\alpha}\right)^2 RT}\frac{1}{r_\alpha}\left\{\frac{1}{r_{\alpha k}} - \frac{1}{r_\alpha}\right\}.$$

(3.8)

Taking into account the equation of state of the gas (3.2), the derivative dn_α/dV_α can be expressed by:

$$\frac{dn_\alpha}{dV_\alpha} = \varrho_\alpha - \frac{\partial\varrho_\alpha}{\partial P_\alpha}\frac{2\sigma_\alpha}{3r_\alpha},$$

(3.9)

and for an ideal gas by:

$$\frac{dn_\alpha}{dV_\alpha} = \varrho_\alpha - \frac{1}{RT}\frac{2\sigma_\alpha}{3r_\alpha}.$$

(3.10)

For sufficiently large bubbles the density ϱ_α is nearly constant ($\varrho_\alpha = \varrho_\alpha(P, T)$) and the second term in (3.9) and (3.10) becomes small compared to the first one.

Based on Eq. (3.8) and assuming, further, the additional approximations

$$\varrho_{2\beta} = \varrho_{20}$$

$$\varrho_\alpha = \text{const.}$$

(3.11)

where ϱ_{20} is the density of the second component in the solution in equilibrium with the second component at a planar interface, Lifshitz and Slyozov [3] developed a theory of Ostwald ripening and obtained asymptotic solutions for the mean cluster radius and the number of clusters as a function of time.

The additional assumptions are good approximations in the asymptotic region but not for the beginning period of Ostwald ripening in the neighbourhood of $(r_\alpha^c, n_\alpha^c, s^c)$. In the next paragraph we propose another description which starts directly with Eq. (3.8) omitting the assumptions (3.11).

4. Ostwald ripening of bubbles in a liquid-gas solution

4.1 Extension of the growth equation to a multi-bubble system

We suppose that as a result of nucleation processes a number of bubbles is formed in the neighbourhood of the state $(r_\alpha^c, n_\alpha^c, s^c)$. The assumed initial state corresponds to the point of inflexion of the function $\Delta G = \Delta G(r_\alpha)$ and can be determined by the condition

$$\left(\frac{d}{dr_\alpha} \Delta G\right)_s = \left(\frac{d^2}{dr_\alpha^2} \Delta G\right) = 0 \,, \tag{4.1}$$

expressing first n_α via r_α by Eq. (3.2).

Each of the bubbles can be described by Eq. (3.3). Therefore we have

$$\frac{dV_\alpha^{(j)}}{dt} = -\frac{D\varrho_{2\beta}}{\left(\frac{dn_\alpha^{(j)}}{dV_\alpha^{(j)}}\right)^2 RT} \frac{1}{r_\alpha^{(j)}} \frac{d\Delta G^{(j)}}{dr_\alpha^{(j)}}; \qquad j = 1, 2, \ldots, s \tag{4.2}$$

where $\Delta G^{(j)}$ in accordance with (2.1) is given by:

$$\Delta G^{(j)} = \sum_{j=1}^{s} \{(P - P_\alpha^{(j)}) V_\alpha^{(j)} + (\mu_\alpha^{(j)} - \mu_{2\beta}) n_\alpha^{(j)} + \sigma_\alpha^{(j)} O_\alpha^{(j)}\}$$

$$+ \sum_{i=1}^{2} (\mu_{i\beta} - \mu_i) n_i \,. \tag{4.3}$$

$d\Delta G^{(j)}/dr_\alpha^{(j)}$ is the change of the Gibbs free energy due to the variation of the radius of the j-th bubble.

Since a general analytic solution of the problem, i.e. a determination of the distribution function of the radii and the number of clusters as a function of time [3] for given initial conditions is, in general, not possible (or not found yet) an approximate solution is derived here assuming in addition, that all clusters have nearly the same radius r_α.

Summing Eq. (4.2) over all s bubbles the following equation for the time development of the mean bubble volume is obtained:

$$S\frac{dV_\alpha}{dt} = -Q \frac{D\varrho_{2\beta}}{\left(\frac{dn_\alpha}{dV_\alpha}\right)^2 RT} \frac{1}{r_\alpha} \frac{d\Delta G}{dr_\alpha} \tag{4.4}$$

where ΔG is now given by Eq. (2.6).

Q is a numerical factor, which has been introduced to compensate the error which results from the assumption of the special distribution function. It will determined later.

4.2 The driving force of the development of the system

The thermodynamic driving force of the development of the ensemble of bubbles along the "valley" of the Gibbs free energy G is the change of ΔG resulting from the decrease of the number of bubbles s. It can be expressed, therefore, by

$$\frac{d\Delta G}{dr_\alpha} = \frac{d\Delta G}{ds} \frac{ds}{dr_\alpha}. \tag{4.5}$$

The equation $r_\alpha = r_\alpha(s)$ relating the number of bubbles s and their mean radius r_α along the expected path of evolution, is given by the generalized Gibbs-Thomson-equation (4.6):

$$\left(\frac{d\Delta G}{dr_\alpha}\right)_s = -4\pi r_\alpha^2 s \left\{ \left(P_\alpha - P - \frac{2\sigma_\alpha}{r_\alpha} \right) - (\mu_\alpha - \mu_{2\beta}) \frac{dn_\alpha}{dV_\alpha} \right\} = 0. \tag{4.6}$$

Taking into account the quasi-equilibrium (2.4), the Gibbs-Thomson equation leads to Eq. (3.6). A derivation of (4.6) with respect to r_α results in

$$\left(\frac{d^2\Delta G}{dr_\alpha^2}\right)_s = -8\pi\sigma_2 s \left\{ 1 + \frac{(dn_\alpha/dV_\alpha)r_\alpha^2}{2\sigma_\alpha} \cdot \left(\frac{\partial \mu_{2\beta}}{\partial r_\alpha}\right)_s \right\}. \tag{4.7}$$

Using (4.6) we get for $r_\alpha = r_\alpha(s)$:

$$\left(\frac{dr_\alpha}{ds}\right) = \frac{\left(\frac{dn_\alpha}{dV_\alpha}\right) \cdot \left(\frac{\partial \mu_{2\beta}}{\partial s}\right)}{\dfrac{1}{4\pi r_\alpha^2 s} \left(\dfrac{d^2\Delta G}{dr_\alpha^2}\right)}. \tag{4.8}$$

If we take into account that $\mu_{2\beta}$ depends explicitly on x_β and thus via

$$x_\beta = \frac{n_2 - sn_\alpha}{n_1 + n_2 - sn_\alpha} \tag{4.9}$$

on r_α and s, equations (4.7) and (4.8) can be written as

$$\left(\frac{d^2\Delta G}{dr_\alpha^2}\right)_s = -8\pi\sigma_\alpha s \left\{ 1 + Z - \frac{2\sigma_\alpha}{3r_\alpha \varrho_\alpha} \frac{\partial \varrho_\alpha}{\partial P_\alpha} \right\} \tag{4.10}$$

$$\frac{dr_\alpha}{ds} = -\frac{r_\alpha}{3s} \left(\frac{Z}{1 + Z - \dfrac{2\sigma_\alpha}{3\varrho_\alpha r_\alpha} \dfrac{\partial \varrho_\alpha}{\partial P_\alpha}} \right) \frac{\varrho_\alpha}{dn_\alpha/dV_\alpha} \tag{4.11}$$

with

$$Z \equiv -\frac{3r_\alpha s}{2\sigma_\alpha \varrho_\alpha} \left(\frac{dn_\alpha}{dV_\alpha}\right)^2 \left(\frac{\partial \mu_{2\beta}}{\partial x_\beta}\right) \frac{n_1 n_\alpha}{(n_1 + n_2 - sn_\alpha)^2} \tag{4.12}$$

Z is always negative, further it follows from the extremum conditions that along the "valley" of the Gibbs free energy the quantity $1 + Z - \dfrac{2\sigma_\alpha}{3 r_\alpha^j \varrho_\alpha} \dfrac{\partial \varrho_\alpha}{\partial P_\alpha}$ is less and, in the critical state (4.1) equal to minus one. A comparison of Eq. (4.8) with the results of the thermodynamic analysis yields

$$\left(\frac{dn_\alpha}{dV_\alpha}\right) > 0 \, .$$

Combining Eqs. (2.7), (4.4), (4.5) and (4.11), we get the growth equation

$$\frac{dr_\alpha}{dt} = Q \frac{D\varrho_{2\beta}\sigma_\alpha}{\varrho_\alpha \left(\dfrac{dn_\alpha}{dV_\alpha}\right) RT} \frac{1}{r_\alpha^2} \frac{\left(1 + Z - \dfrac{2\sigma_\alpha}{3\varrho_\alpha r_\alpha} \dfrac{\partial \varrho_\alpha}{\partial P_\alpha}\right)}{Z} \qquad (4.13)$$

for the mean radius of the bubbles.

4.3 Asymptotic solutions

After an initial period of slow growth ($Z^{-1} \cong -1$) the quantity Z^{-1} rapidly tends to zero, $\varrho_{2\beta}$ tends to ϱ_{20} and we obtain the asymptotic solution

$$\frac{dr_\alpha}{dt} = Q \frac{D\varrho_{20}\sigma_\alpha}{\varrho_\alpha \left(\dfrac{dn_\alpha}{dV_\alpha}\right) RT} \frac{1}{r_\alpha^2} \, . \qquad (4.14)$$

When the function $r_\alpha = r_\alpha(t)$ is known, $s = s(t)$ can be obtained by (4.11). For numerical calculations it is, however, more convenient to use a differential e-quation relating the mean radius and the number of droplets as the second independent equation. This equation can be obtained by a derivation of (3.6) with respect to time. It reads

$$\frac{d}{dt} [\ln(sn_\alpha)] = -\frac{1}{Z} \frac{d}{dt} [\ln(r_\alpha^3)] \cdot \frac{1}{\varrho_\alpha} \left(\frac{dn_\alpha}{dV_\alpha}\right) \, . \qquad (4.15)$$

In the asymptotic region ($Z^{-1} \to 0$) the overall mass (sn_α) of the new phase is nearly constant and, approximately, given by:

$$sn_\alpha = \frac{n_1 + n_2}{n_1 \dfrac{\partial \mu_2}{\partial x}} [\mu_2(P, x) - \mu_\alpha(P)] \, . \qquad (4.16)$$

This equation can be derived from (3.6) by a Taylor expansion of $\mu_{2\beta}$ viz.

$$\mu_{2\beta}(P, x_\beta) = \mu_2(P, x) + \frac{\partial \mu_2}{\partial x} \frac{\partial x_\beta}{\partial(sn_\alpha)}\bigg|_{sn_\alpha = 0} \cdot (sn_\alpha) + \dots \qquad (4.17)$$

taking further into account the additional relations

$$P_\alpha \approx P; \quad \frac{2\sigma_\alpha}{r_\alpha} \approx 0 \tag{4.18}$$

valid for sufficiently large bubbles.

A comparison of Eqs. (4.14) and (4.16) leads to the conclusion that in the a-symptotic region the number of bubbles decreases as

$$s \sim \frac{1}{t}. \tag{4.19}$$

Therefore, in the asymptotic region our analysis leads qualitatively to the same results as obtained first by Lifshitz and Slyozov [3]. This agreement confirms that the evolution of the ensemble of bubbles along the "valley" of the thermodynamic potential corresponds indeed to the process of Ostwald ripening.

To obtain also a quantitative agreement in the asymptotic region where the results of Lifshitz and Slyozov are exact, the parameter Q introduced in Equ. (4.4) is set equal to

$$Q = \frac{8}{27}. \tag{4.20}$$

4.4 Discussion of the kinetic equations

Introducing the notations

$$\tau \equiv \frac{1}{Q} \frac{\varrho_\alpha^2(P)RTr_k^3}{D\sigma_\alpha\varrho_{20}};$$

$$\bar{t} \equiv \frac{t}{\tau}; \quad \bar{r}_\alpha \equiv \frac{r_\alpha}{r_k}; \quad \bar{V}_\alpha = \frac{4\pi}{3}\bar{r}_\alpha^3, \tag{4.21}$$

where r_k is the critical bubble radius for a sufficiently large system ($x_\beta = x$) and Q is given by (4.20), Eq. (4.13) can be transformed into

$$\frac{d\bar{r}_\alpha}{dt} = \frac{\varrho_{2\beta}}{\varrho_{20}} \frac{\varrho_\alpha^2(P)}{\varrho_\alpha(P_\alpha)\left(\dfrac{dn_\alpha}{dV_\alpha}\right)} \frac{1}{r_\alpha^2} \frac{\left(1 + Z - \dfrac{2\sigma_\alpha}{3\varrho_\alpha r_\alpha} \dfrac{\partial\varrho_\alpha}{\partial P_\alpha}\right)}{Z}. \tag{4.22}$$

In Figs. 3–6 the mean radius $\bar{r}_\alpha$, the mean volume $\bar{V}_\alpha$ and the number s of the bubbles, the density of the bubbles ϱ_α, the overall volume of the gas phase V_{ov}, the overall surface area O_{ov}, of the bubbles and the quantities Z and x_β/x are presented as functions of time.

For the numerical calculations it was assumed, that the equation of state of the gas can be approximated by the ideal gas law and, further, that the liquid-gas solution is ideal:

$$P_\alpha = \varrho_\alpha RT; \quad \mu_{2\beta} = \mu_0 + RT \ln \frac{x_\beta \cdot P}{P_0} . \tag{4.23}$$

P_0 and μ_0 are the pressure and the chemical potential of the pure solute in a gas-liquid equilibrium at a planar interface. In this special case the critical radius r_k can be expressed by

$$r_k = \frac{2\sigma_\alpha}{P\left(\dfrac{x}{x_0} - 1\right)} . \tag{4.24}$$

The initial state is supposed to be located in the immediate neighbourhood of the critical state (4.1) along the "valley" of the Gibbs free energy.

In the first period of the ripening process the overall volume and the overall surface area of the ensemble of bubbles increases rapidly, while $\varrho_{2\beta}$ tends to the equilibrium value ϱ_{20}. The main thermodynamic driving force in this state of the ripening process is the decrease of G due to the growth of the volume of the new phase with lower bulk contributions to the thermodynamic potential.

After this initial period the evolution of the ensemble of bubbles is described by the asymptotic solutions (4.14) and (4.16). At this state the overall volume of the new phase is nearly constant, the overall surface area O_{ov} of the bubbles decreases as:

$$O_{ov} = \frac{3(n_1 + n_2)}{\dfrac{\partial \mu_2}{\partial x}} [\mu_2(P, x) - \mu_2(P)] \left(\frac{9RT}{8D\varrho_\alpha(P)\varrho_{20}\sigma_\alpha}\right)^{1/3} t^{-1/3} , \tag{4.25}$$

emphasizing that the main driving force of Ostwald ripening in this asymptotic state is the decrease of the surface contributions to the thermodynamic potential due to reduction of the total surface area. Equation (4.13) then simply reduces to:

$$\frac{d\bar{r}_\alpha}{d\bar{t}} = \frac{1}{\bar{r}_\alpha^2} . \tag{4.26}$$

This equation shows a that in the asymptotic region specific thermodynamic properties of the considered system influence only the time scale of the process and not the dynamics itself.
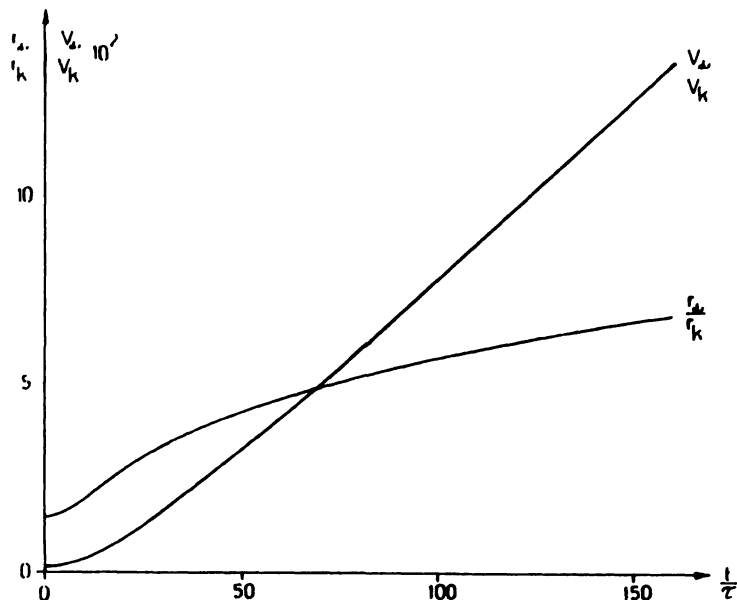
Fig. 3: The mean radius $\bar{r}_a$ and the mean volume $\bar{V}_a$ of the bubbles as a function of time (in reduced variables). The parameters are given by $n_1 = 5.43 \cdot 10^4$ mol, $n_2 = 2.512$ mol, $n_2 = 0.628$ mol, $V = 1$ m^3, $p = 101\,337$ N/m^2, $T = 298.15$ K, $D = 1.62 \cdot 10^{-9}$ m^2/s, $\sigma = 0.072$ N/m corresponding to a solution of nitrogen in water. Then τ and r_k are equal to $\tau = 0.02$ s, $r_k = 4.74 \cdot 10^{-7}$ m.
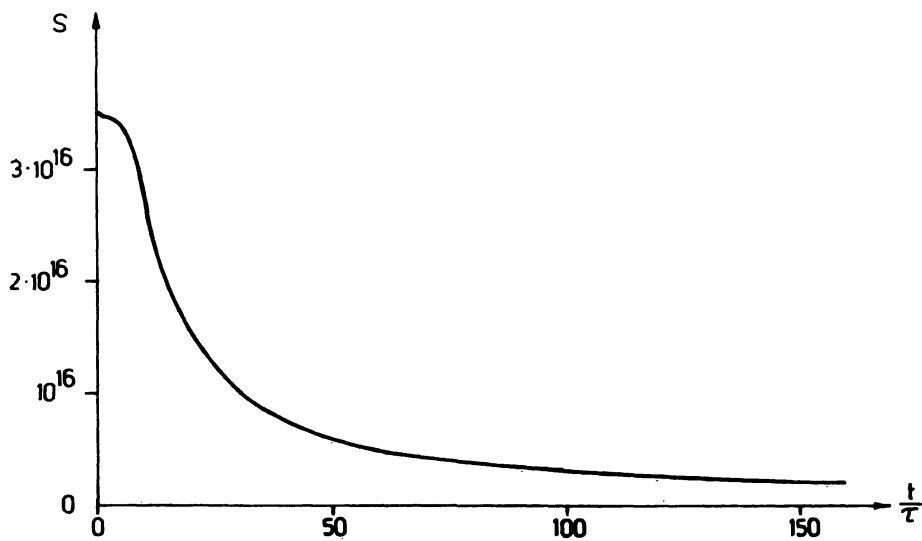

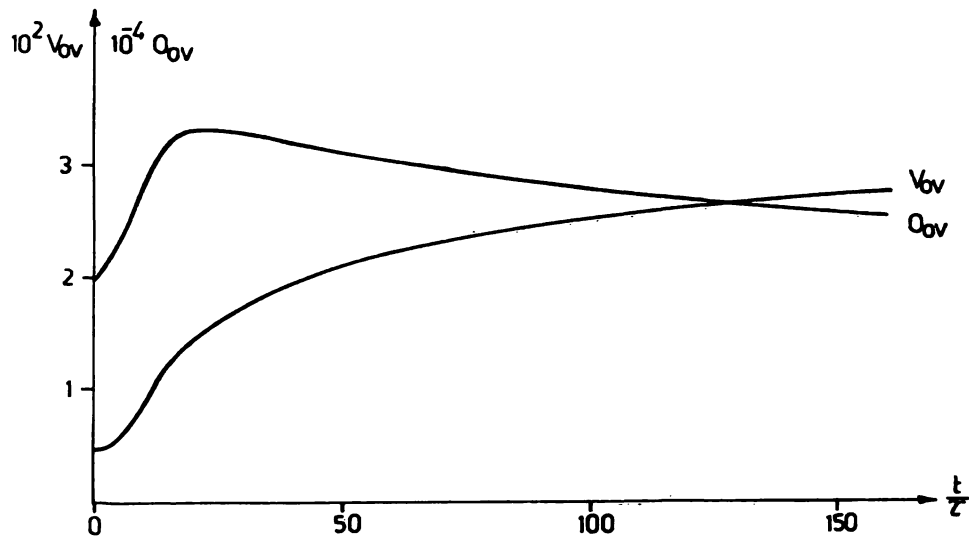Fig. 4: The number of bubbles as a function of time.

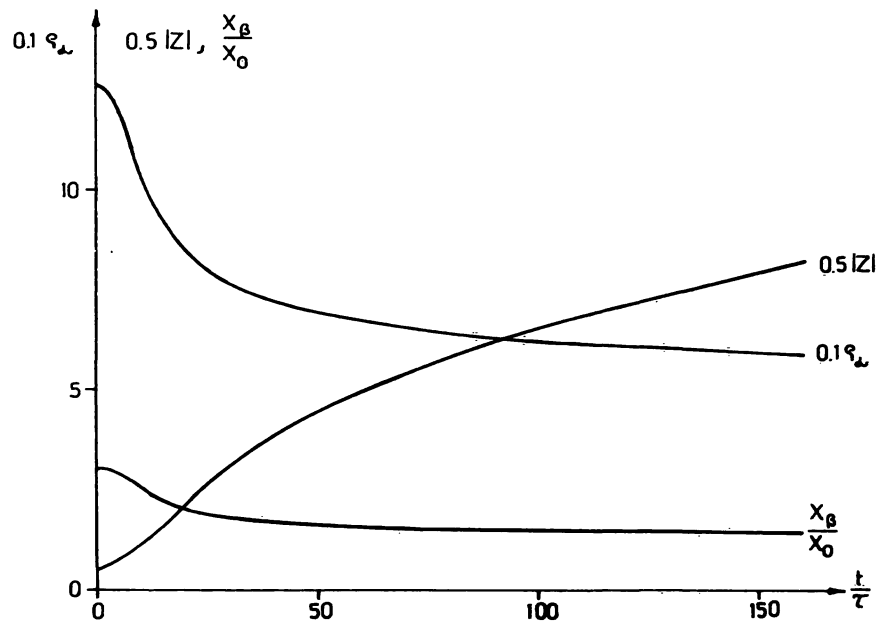Fig. 5: The overall volume V_{ov} and the total surface area O_{ov} of the bubbles as functions of time.

Fig. 6: The density ϱ_α of the gas in the bubble, the supersaturation x_β/x_0, x_0 being the mole fraction of the solute in equilibrium with the pure gas at a planar interface and the quantitity Z, defined by (4.12) as function of time.

5. Application to the growth of droplets in multi-component vapours

Though the derivations differ to some extent the results of the thermodynamic investigations, the kinetic equations also are valid for a description of the properties and the growth of droplets in a multi-component vapour. If in addition incompressibility of the liquid phase is assumed, i.e.

$$\varrho_\alpha = \text{const.} \,, \tag{5.1}$$

then in all equations $\dfrac{dn_\alpha}{dV_\alpha}$ has to be replaced by ϱ_α.

6. Conclusions

The main results of the present paper can be summarized as follows:

- In finite systems a cluster of the new phase, e.g. a bubble or a droplet, can exist in a stable thermodynamic equilibrium with the surrounding otherwise homogeneous medium. Under the thermodynamic constraints, assumed here and by Ward et al. [1], a stable coexistence of more than one cluster is excluded. From the thermodynamic point of view this instability is due to the decrease of the thermodynamic potential with a decreasing number of clusters.

- Thermodynamic considerations lead to the conclusion, that the process of Ostwald ripening can be interpreted as an evolution of clusters along a "valley" of the characteristic thermodynamic potential. A minimum value of the mean cluster radius and a corresponding maximum number of clusters are estimated, which can be considered as the initial point of the Ostwald ripening.

- While the first period of Ostwald ripening is dominated by the decrease of the characteristic thermodynamic potential due to the growth of the total volume of the new phase, in the asymptotic state the thermodynamic driving force of Ostwald ripening consists in the decrease of the surface contributions to the thermodynamic potential. In this asymptotic state the solutions are in agreement with the results of Lifshitz and Slyozov [3]. Moreover, it can be shown, that, again in agreement with Lifshitz and Slyozov, the mean cluster radius corresponds to a critical cluster size [6].

These conclusions remain valid for phase transitions in solids, if the surface contribution to the thermodynamic potential can be described by an effective value of a surface tension [13]. Therefore the equations can be applied to a description of the coalescence of vacancies in isotropic solids.

A behaviour, as obtained for the system analyzed here, is always to be expected, if the development of the new phase leads to a depletion of the surrounding medium (see, for example [4, 11]). Therefore, always in such cases, the methods outlined here, can be applied without principal difficulties.

The thermodynamic description is always valid, if the new phase adequately can

be described as an ensemble of clusters. The derivation of the kinetic equations (4.13) and (4.15) is based on the additional assumption that the growth of the clusters proceeds via diffusion-like processes. If other mechanisms of growth determine the time evolution, the kinetic equations may change, but the path of evolution defined by the dashed curve in Fig. 2 will remain the same.

Thermodynamic investigations of the type discussed in section 2 were earlier presented for a special case (isothermal-isochoric condensation in one-component closed systems) by Vogelsberger [9]. The results were applied to a reformulation of nucleation theory in application to finite systems while we could show, that the development along the "valley" corresponds not to nucleation but to the process of Ostwald ripening, or more general, to the further growth of the clusters. The conclusions which can be drawn from the thermodynamic analysis, concerning the whole process of first order phase transitions in finite systems and a detailed comparison with the results of Vogelsberger and earlier investigations by Rusanov [12], will be presented in a forthcoming paper.

Bibliography

[1] Ward, C. A., Tikuisis, P., Venter, R. D., Stability of bubbles in a closed volume of liquid-gas solution, J. Appl. Phys., 53 (1982), 6076.

[2] Ward, C. A., Levart, E., Conditions for stability of bubble nuclei in solid surfaces contacting a liquidgas solution, J. Appl. Phys., 56 (1984), 491.

[3] Lifshitz, I. M., Slyozov, V. V., The kinetics of precipitation from supersaturated solid solutions, J. Phys. Chem. Solids, 19 (1961), 35 and references cited therein.

[4] Schmelzer, J., On the kinetics of growth of clusters in solutions, Z. Phys. Chem. (Leipzig), 266 (1985), 1057.

[5] Gutzow, I., Schmelzer, J., Pascova, R., Popov, B., Crystallization in elastic and viscoelastic media, to be published; Nucleation and Crystal Growth in Viscoelastic Media, Rostocker Phys. Manuskr. H 8 (1985), 22; Schmelzer, J., Gutzow, I., On the kinetic description of Ostwald ripening in elastic media, Wiss. Z. WPU Rostock, in print (1986).

[6] Schmelzer, J., Schweitzer, F., On the kinetic description of condensation in binary vapours, Annalen der Physik, in print (1986).

[7] Landau, L. D., Lifshitz, I. M., Statistical Physics, Akademie-Verlag, Berlin, 1975.

[8] Schmelzer, J., Schweitzer, F., Thermodynamics and Nucleation, Z. Phys. Chem. (Leipzig), 266 (1985), 943.

[9] Vogelsberger, W., Thermodynamics of finite systems: A possibility for interpretation of nucleation and condensation experiments, J. Colloid and Interface Science, 88 (1982), 17; Theory of nucleation in finite systems-illustrated by ethanol condensation, J. Colloid and Interface Science, 103 (1985), 448; Thermodynamische Untersuchungen zur Stabilität kleiner Flüssigkeitstropfen in Kontakt mit ihrem Dampf, Z. Phys. Chem. (Leipzig), 258 (1977), 763.

[10] Defay, R., Prigogine, I., Bellemans, A., Everett, D. H., Surface Tension and Adsorption, London, 1966.

[11] Schmelzer, J., On the kinetics of growth of droplets in the gas phase, Comm. Department Chem., Bulgarian Acad. Sciences, Sofia, in press; Z. Phys. Chem. (Leipzig) 266 (1985), 1121.

[12] Rusanov, A. I., Phasengleichgewichte und Grenzflächenerscheinungen, Berlin, 1978.

[13] Woodruff, D. P., The Solid-Liquid Interface, Cambridge, Univ. Press, 1973.

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