

Sektion Physik der Wilhelm-Pieck-Universität Rostock

Thermodynamics and Nucleation

II. Adiabatic Nucleation in Finite Systems

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With 4 Figures

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Abstract

A thermodynamic analysis of the process of first-order phase transitions in finite systems under adiabatic conditions is given. It is shown, that similar to transitions under isothermal constraints depletion effects lead to the existence of an additional negative semidefinite term ΔW in the expression for the work of formation of the critical clusters.

Moreover, depletion or finite size effects result in variations of the parameters of the critical clusters which overcompensate the influence of the term ΔW and lead to an increase of the work of formation of the critical clusters. Again, there exists a lower limit of the total volume of the system for which transitions may proceed via the mechanism of homogeneous nucleation.

The general results are illustrated by the process of condensation of a gas in one-component systems. It is shown, in particular, that in contrast to the isothermal case variations of the temperature of the system due to the transition may result in the existence of an additional minimum of the thermodynamic potential also for one-component systems under a constant external pressure.

1. Introduction

The classical nucleation theory developed by VOLMER [1], KAISCHEW and STRANSKI [2], BECKER and DOERING [3], FRENKEL [4], ZELDOVICH [5] and others is based upon two results of thermodynamic investigations, the possibility to describe surface effects by the macroscopic value of the surface tension σ and the existence of a critical cluster size. As one main result of the theory the time-independent steady-state nucleation rate is derived.

This steady-state nucleation rate I is connected with the work of formation of the critical clusters W by eq. (1.1).

$$I = I_0 \exp\left(-\frac{W}{kT}\right) \quad (1.1)$$

k being the Boltzmann constant and T the absolute temperature. The exact value of the kinetic factor I_0 differs in dependence on what type of approximation was used in the derivation of eq. (1.1).

The general structure of eq. (1.1) is maintained also in modifications of the classical nucleation theory (see, e.g., [6-8, 23]), proposed in the last decades.

Non-stationary effects in nucleation arise from two sources. First of all, some period of time is needed to establish the stationary nucleation rate (time-lag in nucleation) and,

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second, the depletion of the medium surrounding the clusters of the new phase also affects the nucleation rate. Such a depletion could be neglected in the classical nucleation theory and a number of its modifications since as thermodynamic constraints constancy of the external pressure p and the temperature T were assumed. These constraints are equivalent to the consideration of nucleation in an infinite system.

In finite systems, however, the formation and growth of the clusters result in a depletion of the medium and the kinetics of the transition depends on the constraints chosen. Since different approaches to the description of nucleation lead qualitatively and in some cases quantitatively to the same results we study finite size effects based on a thermodynamic approach.

In a preceding paper [9] a thermodynamic analysis of the process of first-order phase transitions was given for isothermal constraints. It was shown, that the depletion of the medium leads to an additional negative semidefinite term ΔW in the expression for the work of formation of the critical clusters. It was discussed further, how the parameters of the critical clusters vary in dependence on depletion effects. In particular, it was shown, that in finite systems there exists a minimum value of the size of the system, for which a phase transition may proceed via the mechanism of homogeneous nucleation. This effect is equivalent to the dependence of the critical temperature on the volume of the system [10].

In a number of situations phase transitions proceed not under isothermal but adiabatic conditions. Therefore, it is of interest to prove, whether the conclusions derived in [9] are valid also, if instead of isothermal adiabatic constraints are assumed.

2. Work of Formation of Critical Clusters in Finite Systems

The minimum possible work which has to be supplied to a metastable homogeneous system to generate from outside a critical cluster, the work done in a reversible process, is called the work of formation of a critical cluster. But since reversible adiabatic processes are isentropic processes, the total entropy S of the system is constant

$$S \leq \text{const.} \quad (2.1)$$

and in a first approximation there is no need in a thermodynamic analysis of nucleation to divide between isentropic and adiabatic processes (for the details, see [24]).

In addition to the constraint (2.1) we assume that the total number of moles of the different components n_i , $i = 1, 2, \dots, k$ and either the pressure p or the total volume V of the system are kept constant. So, two different types of constraints are considered, expressed by eqs. (2.2) and (2.3), respectively.

$$n_i = \text{const}, \quad i = 1, 2, \dots, k; \quad V = \text{const.} \quad (2.2)$$

$$n_i = \text{const}, \quad i = 1, 2, \dots, k; \quad p = \text{const.} \quad (2.3)$$

For the two different constraints the work of formation of the critical clusters is equal either to the change of the inner energy U or to the change of the enthalpy $H = U + pV$

due to the formation of the cluster of the new phase [15]:

$$W = \begin{cases} \Delta U & n_i = \text{const}, \quad V = \text{const}. \\ \Delta H & n_i = \text{const}, \quad p = \text{const}. \end{cases} \quad (2.4)$$

Δ denotes here the difference between the heterogeneous state and the homogeneous metastable initial state.

The inner energy of the heterogeneous system, consisting of s clusters of the new phase in the otherwise homogeneous medium, can be expressed by [12, 16, 17]:

$$\begin{aligned} U_{\text{het}} = & \sum_{j=1}^r \left\{ T_{\alpha}^{(j)} S_{\alpha}^{(j)} - p_{\alpha}^{(j)} V_{\alpha}^{(j)} + \sum_{i=1}^k \mu_{i\alpha}^{(j)} n_{i\alpha}^{(j)} \right\} \\ & + \sum_{j=1}^r \left\{ T_0^{(j)} S_0^{(j)} + \sigma_{\alpha}^{(j)} A_{\alpha}^{(j)} + \sum_{i=1}^k \mu_{i0}^{(j)} n_{i0}^{(j)} \right\} \\ & + T_{\beta} S_{\beta} - p_{\beta} V_{\beta} + \sum_{i=1}^k \mu_{i\beta} n_{i\beta} \end{aligned} \quad (2.5)$$

μ is the chemical potential and A_{α} the surface area of the cluster. The subscript $\alpha(\beta)$ specifies the thermodynamic parameters of the clusters (surrounding medium), the subscript "o" the surface contributions to the thermodynamic functions. Parameters without a subscript refer, in general, to the homogeneous initial state.

To be definite we consider here condensation processes, the formation of clusters with a higher compared with the medium density. According to the postulate of an inner equilibrium underlying the thermodynamic description the variables $T_0^{(j)}$ and $\mu_{i0}^{(j)}$ can be set equal to $T_{\alpha}^{(j)}$ and $\mu_{i\alpha}^{(j)}$, then [12, 16, 17].

ΔU and ΔH are given by

$$\begin{aligned} \Delta U = & \sum_{j=1}^r \{ (T_{\alpha}^{(j)} - T_{\beta}) \tilde{S}_{\alpha}^{(j)} + (p_{\beta} - p_{\alpha}^{(j)}) V_{\alpha}^{(j)} + \sigma_{\alpha}^{(j)} A_{\alpha}^{(j)} \\ & + \sum_{i=1}^k (\mu_{i\alpha}^{(j)} - \mu_{i\beta}) \tilde{n}_{i\alpha}^{(j)} \} + S(T_{\beta} - T) + (p - p_{\beta}) V \\ & + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i, \end{aligned} \quad (2.6)$$

$$\begin{aligned} \Delta H = & \sum_{j=1}^r \{ (T_{\alpha}^{(j)} - T_{\beta}) \tilde{S}_{\alpha}^{(j)} + (p_{\beta} - p_{\alpha}^{(j)}) V_{\alpha}^{(j)} + \sigma_{\alpha}^{(j)} A_{\alpha}^{(j)} \\ & + \sum_{i=1}^k (\mu_{i\alpha}^{(j)} - \mu_{i\beta}) \tilde{n}_{i\alpha}^{(j)} \} + S(T_{\beta} - T) + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i \end{aligned} \quad (2.7)$$

where the notations (2.8) are used.

$$\tilde{n}_{i\alpha}^{(j)} = n_{i\alpha}^{(j)} + n_{i0}^{(j)} \quad \tilde{S}_{\alpha}^{(j)} = S_{\alpha}^{(j)} + S_0^{(j)}. \quad (2.8)$$

The change of the inner energy is given by

$$\begin{aligned} dU = \sum_{j=1}^r \left\{ (T_\alpha^{(j)} - T_\beta) d\tilde{S}_\alpha^{(j)} + \left(p_\beta - p_\alpha^{(j)} + \frac{2\sigma_\alpha^{(j)}}{r_\alpha^{(j)}} \right) dV_\alpha^{(j)} \right. \\ \left. + \sum_{i=1}^k (\mu_{i\alpha}^{(j)} - \mu_{i\beta}) d\tilde{n}_{i\alpha}^{(j)} \right\}. \end{aligned} \quad (2.9)$$

The same expression is obtained also for dH with the difference, that in the case of a constant external pressure p_β is equal to p .

The necessary thermodynamic equilibrium conditions read

$$\delta U = 0 \quad V = \text{const} \quad (2.10)$$

$$\delta H = 0 \quad p = p_\beta = \text{const} \quad (2.11)$$

resulting in

$$p_\alpha^{(j)} - p_\beta = \frac{2\sigma_\alpha^{(j)}}{r_\alpha^{(j)}}; \quad \mu_{i\alpha}^{(j)} = \mu_{i\beta}, \quad (2.12)$$

$$T_\alpha^{(j)} = T_\beta, \quad i = 1, 2, \dots, k; \quad j = 1, 2, \dots, r$$

δ denotes infinitesimal possible variations of the thermodynamic variables from the state considered, $r_\alpha^{(j)}$ is the radius of the j -th cluster.

States obeying the necessary thermodynamic equilibrium conditions (2.12) are either stable states or unstable states of saddle-point type (critical states) [11, 12, 18]. If additional assumptions concerning the thermodynamic properties of the two phases are made, resulting in a reduction of the number of degrees of freedom, saddle-points may degenerate into maxima.

A substitution of eqs. (2.12) into eqs. (2.6) and (2.7), respectively, leads to

$$\begin{aligned} \Delta U^{(e)} &= \sum_{j=1}^r \frac{1}{3} \sigma_\alpha^{(j)} A_\alpha^{(j)} + (T_\beta - T) S + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i + (p - p_\beta) V, \\ \Delta H^{(e)} &= \sum_{j=1}^r \frac{1}{3} \sigma_\alpha^{(j)} A_\alpha^{(j)} + (T_\beta - T) S + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i \end{aligned} \quad (2.13)$$

These equations are also valid, if clusters with a lower density compared with the medium are formed [12, 16].

The work of formation of critical states, in general, and one critical cluster ($r = 1$), in particular, can be expressed, therefore, as a sum of terms, derived already by GIBBS [19] and a correction term ΔW .

$$\begin{aligned} W^{(e)} &= W_{\text{Gibbs}} + \Delta W, \quad W_{\text{Gibbs}} = \sum_{j=1}^r \frac{1}{3} \sigma_\alpha^{(j)} A_\alpha^{(j)}, \\ \Delta W &= (T_\beta - T) S + (p - p_\beta) V + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i; \quad V = \text{const} \quad (2.13) \\ \Delta W &= (T_\beta - T) S + \sum_{i=1}^k (\mu_{i\beta} - \mu_i) n_i; \quad p = \text{const}. \end{aligned}$$

ΔW is different from zero only if the state of the medium changes due to the formation of clusters of the new phase.

By a Taylorexpansion of T_β , p_β and $\mu_{i\beta}$ with respect to the deviations of the parameters of the medium from the initial state it can be shown in the same way as discussed in detail for the isothermal case, that ΔW is a negative semidefinite quadratic form of the variations of the intensive variables describing the state of the medium (for the details see [9, 16]). Consequently, eq. (2.14) holds

$$\Delta W \leq 0 \quad (2.14)$$

3. Dependence of the Parameters of the Critical Clusters on Depletion Effects

In addition to the term ΔW depletion effects result in a variation of the parameters of the critical cluster, in particular, in a variation of its radius or surface area. Such variation can have also a significant influence on the nucleation rate (see, e.g., [9, 13]).

Since for a sufficiently large system depletion effects are negligible such effects can be studied considering the variation of the size of the system, the intensive variables of the initial state being kept constant.

The parameters of the critical cluster are determined by eqs. (2.12), which can be written in the following way:

$$\begin{aligned} f_i &= \mu_{i\alpha}(\bar{S}_\alpha, \varrho_{1\alpha}, \dots, \varrho_{k\alpha}) - \mu_{i\beta}(\bar{S}_\beta, \varrho_{1\beta}, \dots, \varrho_{k\beta}) = 0 \\ f_{k+1} &= T_\alpha(\bar{S}_\alpha, \varrho_{1\alpha}, \dots, \varrho_{k\alpha}) - T_\beta(\bar{S}_\beta, \varrho_{1\beta}, \dots, \varrho_{k\beta}) = 0 \\ f_{k+2} &= -p_\alpha(\bar{S}_\alpha, \varrho_{1\alpha}, \dots, \varrho_{k\alpha}) + p_\beta(\bar{S}_\beta, \varrho_{1\beta}, \dots, \varrho_{k\beta}) + \frac{2}{r_\alpha} \sigma_\alpha(\bar{S}_\alpha, \varrho_{1\alpha}, \dots, \varrho_{k\alpha}) = 0 \end{aligned} \quad (3.1)$$

As independent variables the entropy density S and the molar densities ϱ_i are chosen, determined by

$$\varrho_{i\alpha} = \frac{\tilde{n}_{i\alpha}}{V_\alpha} \quad \bar{S}_\alpha = \frac{\tilde{S}_\alpha}{V_\alpha} \quad \varrho_{i\beta} = \frac{n_{i\beta}}{V_\beta} \quad \bar{S}_\beta = \frac{S_\beta}{V_\beta} \quad (3.2)$$

Taking into account the constants (isochoric conditions)

$$\begin{aligned} n_i &= n_{i\beta} + \tilde{n}_{i\alpha} = \text{const} \quad S = S_\beta + \tilde{S}_\alpha = \text{const} \\ V &= V_\alpha + V_\beta = \text{const} \end{aligned} \quad (3.3)$$

eqs. (3.1) determine the independent parameters $\tilde{n}_{i\alpha}$, V_α , \tilde{S}_α as functions of the total volume V , the total entropy S and the total number of moles of the different components n_i . The change of the parameters of the critical clusters or clusters in stable equilibrium with the medium due to a variation of the size of the system, the intensive variables of the initial state being kept constant, can be expressed, therefore, by

$$\begin{aligned} \Delta \tilde{n}_{i\alpha} &= \Delta V \left\{ \frac{\partial \tilde{n}_{i\beta}}{\partial V} + \bar{S} \frac{\partial \tilde{n}_{i\alpha}}{\partial S} + \sum_{l=1}^k \varrho_l \frac{\partial \tilde{n}_{i\alpha}}{\partial n_l} \right\}, \\ \Delta \tilde{S}_\alpha &= \Delta V \left\{ \frac{\partial \tilde{S}_\alpha}{\partial V} + \bar{S} \frac{\partial \tilde{S}_\alpha}{\partial S} + \sum_{l=1}^k \varrho_l \frac{\partial \tilde{S}_\alpha}{\partial n_l} \right\}, \\ \Delta V_\alpha &= \Delta V \left\{ \frac{\partial V_\alpha}{\partial V} + \bar{S} \frac{\partial V_\alpha}{\partial S} + \sum_{l=1}^k \varrho_l \frac{\partial V_\alpha}{\partial n_l} \right\}. \end{aligned} \quad (3.4)$$

Applying the theory of implicate functions [20] to eqs. (3.1) the partial derivatives in eqs. (3.4) can be calculated and we obtain e.g., for $\Delta\tilde{n}_{1\alpha}$

$$\Delta\tilde{n}_{1\alpha} = -\frac{\Delta V}{J} \left\{ \frac{\partial(f_1, f_2, \dots, f_{k+1})}{\partial(V, \tilde{n}_{1\alpha}, \dots, V_\alpha)} + \bar{S} \frac{\partial(f_1, f_2, \dots, f_{n+2})}{\partial(S, \tilde{n}_{1\alpha}, \dots, V_\alpha)} + \sum_{l=1}^k \varrho_l \frac{\partial(f_1, f_2, \dots, f_{n+1}, f_{k+2})}{\partial(\tilde{n}_l, n_{l\alpha}, \dots, \bar{S}_\alpha, V_\alpha)} \right\}. \quad (3.5)$$

$$J = \frac{\partial(f_1, f_2, \dots, f_{k+1}, f_{k+2})}{\partial(\tilde{n}_{1\alpha}, \tilde{n}_{2\alpha}, \dots, \tilde{n}_{k\alpha}, \bar{S}_\alpha, V_\alpha)}. \quad (3.6)$$

Here by $\partial(y_1, y_2, \dots, y_n)/\partial(x_1, x_2, \dots, x_n)$ the Jacobideterminants are denoted (see [20]).

In a more extended form we can write also

$$\Delta\tilde{n}_{1\alpha} = -\frac{\Delta V}{J} \begin{vmatrix} \frac{\bar{S}_\beta - \bar{S}}{V_\beta} \frac{\partial\mu_{1\beta}}{\partial\bar{S}_\beta} + \sum_l \frac{\varrho_{l\beta} - \varrho_l}{V_\beta} \frac{\partial\mu_{1\beta}}{\partial\varrho_{l\beta}} \frac{\partial f_1}{\partial\tilde{n}_{2\alpha}} & \dots & \frac{\partial f_1}{\partial V_\alpha} \\ \frac{\bar{S}_\beta - \bar{S}}{V_\beta} \frac{\partial\mu_{2\beta}}{\partial\bar{S}_\beta} + \sum_l \frac{\varrho_{l\beta} - \varrho_l}{V_\beta} \frac{\partial\mu_{2\beta}}{\partial\varrho_{l\beta}} \frac{\partial f_2}{\partial\tilde{n}_{2\alpha}} & \dots & \frac{\partial f_2}{\partial V_\alpha} \\ \dots & \dots & \dots \\ \frac{\bar{S}_\beta - \bar{S}}{V_\beta} \frac{\partial T_\beta}{\partial\bar{S}_\beta} + \sum_l \frac{\varrho_{l\beta} - \varrho_l}{V_\beta} \frac{\partial\varrho_{l\beta}}{\partial T_\beta} \frac{\partial f_{k+1}}{\partial\tilde{n}_{2\alpha}} & \dots & \frac{\partial f_{k+1}}{\partial V_\alpha} \\ \frac{\bar{S}_\beta - \bar{S}}{V_\beta} \frac{\partial p_\beta}{\partial\bar{S}_\beta} + \sum_l \frac{\varrho_{l\beta} - \varrho_l}{V_\beta} \frac{\partial p_\beta}{\partial\varrho_{l\beta}} \frac{\partial f_{k+2}}{\partial\tilde{n}_{2\alpha}} & \dots & \frac{\partial f_{k+2}}{\partial V_\alpha} \end{vmatrix} \quad (3.7)$$

If instead of the first other columns of the determinant J are replaced by the first column of the determinant in eq. (3.7) then we get the expressions for $\Delta\tilde{n}_{i\alpha}$, $i \geq 2$, $\Delta\bar{S}_\alpha$ and ΔV_α , respectively.

If J is greater than zero, then the state determined by eqs. (3.1) is a stable equilibrium state, otherwise it is a critical state [12, 18]. Consequently, in general, the variation due to depletion effects of the parameters of the clusters will differ in dependence whether critical or stable states are considered.

Moreover, since the variations of the parameters of the critical clusters are linear functions of the changes of the state of the medium due to nucleation processes they and not the quadratic form ΔW determine the variation of the work of formation of the critical clusters. Consequently, the Gibbs expression $W = \sigma_\alpha A_\alpha/3$ is a good approximation for the work of formation of critical clusters also for finite systems under adiabatic conditions, if in the calculation of the surface area depletion effects are taken into account.

If instead of isochoric isobaric conditions are assumed the final results remain the same with the difference, that the following coefficients and their equivalent expressions are equal to zero

$$-\frac{\partial p_\beta}{\partial V_\beta} = \frac{\partial\mu_{i\beta}}{\partial V_\beta} = \frac{\partial p_\beta}{\partial n_{i\beta}} = \frac{\partial p_\beta}{\partial\bar{S}_\beta} = \frac{\partial T_\beta}{\partial V_\beta} = 0 \quad (3.8)$$

4. Special Cases

4.1. Adiabatic Condensation Under Isochoric Conditions

The general results outlined in the previous chapters are illustrated now by the process of formation of (incompressible) drops in a supersaturated metastable one-component vapour.

It was shown earlier [9, 11, 13] that for isothermal isochoric processes the work of formation W of a drop as a function of the radius shows a behaviour as presented in Fig. 1. The extrema of W ($W = \Delta F$, F - Helmholtz free energy)

$$\Delta F = (p - p_\beta) V + (\mu_\beta - \mu) n + V_\alpha(p_\beta - p' - \varrho_\alpha(\mu_\beta - \mu')) + \sigma_\alpha A_\alpha \quad (4.1)$$

are determined by

$$\frac{\partial \Delta F}{\partial r_\alpha} = -4\pi r_\alpha^2 \left\{ \varrho_\alpha(\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} = 0 \quad (4.2)$$

or by a generalized Gibbs-Thomson equation [12, 13]

$$\varrho_\alpha(\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} = 0 \quad (4.3)$$

p' and μ' are the values of the pressure and the chemical potential for a stable liquid-vapour coexistence at a planar interface and a given value of the temperature T .

The change of the position of the extrema with a decreasing total volume of the system is indicated in Fig. 1 by arrows. The decrease of the volume or the increase of the influence of depletion effects lead to an increase of r_{ac} and a decrease of r_{as} , an increase of the values of ΔF for the extrema. This type of behaviour is widely independent on the actual value of the temperature supposed the initial state is a metastable state.

Realizing, that the only difference resulting from adiabatic compared with isothermal constraints consists in an increase of the temperature of the system (latent heat of condensation), one can conclude, that qualitatively the variation of ΔU as a function of the radius is of the same type. There exists, of course, some change in the position of the extrema.

The direction of this variation can be obtained from eq. (4.3) by a derivation with respect to the temperature T , taking into account, that the positions of the extrema are also functions of T . We get

$$\frac{dr_\alpha}{dT} = \frac{\left(\frac{\partial}{\partial T} \left\{ \varrho_\alpha(\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} \right)_{V_\alpha}}{\frac{1}{4\pi r_\alpha^2} \left(\frac{\partial^2 \Delta F}{\partial r_\alpha^2} \right)_T} \quad (4.4)$$

But since the variation of the free energy due to the growth of an incompressible drop in a reversible process ($T_\alpha = T_\beta$) can be expressed by

$$dF = -S dT - \left\{ \varrho_\alpha(\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} dV_\alpha \quad (4.5)$$

it follows, that eq. (4.6) is fulfilled,

$$\left(\frac{\partial S}{\partial V_\alpha} \right)_T = \left(\frac{\partial}{\partial T} \left\{ \varrho_\alpha (\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} \right)_{V_\alpha} \quad (4.6)$$

The increase of the volume of the drop may proceed under isothermal conditions only if the latent heat of condensation is transferred to the surrounding medium. Therefore, the entropy of the system is decreased and we obtain

$$\left(\frac{\partial}{\partial T} \left\{ \varrho_\alpha (\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} \right)_{V_\alpha} < 0. \quad (4.7)$$

Together with eq. (4.2) eq. (4.7) leads to the conclusion, that in adiabatic processes the radius of the critical cluster is greater and the radius of the stable cluster is smaller compared with the isothermal case.

Moreover, a derivation of eq. (4.2) with respect to T for fixed values of r_α results in

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial \Delta F}{\partial r_\alpha} \right) \right)_{V_\alpha} = -4\pi r_\alpha^2 \left(\frac{\partial}{\partial T} \left\{ \varrho_\alpha (\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma_\alpha}{r_\alpha} \right\} \right)_{V_\alpha} > 0 \quad (4.8)$$

By the same arguments as applied earlier we may conclude, that for a defined initial state of the system and a fixed non-zero value of the radius r_α the work of formation W of a cluster is always greater for adiabatic compared with isothermal constraints (see Fig. 2).

A comparison of Figs. 1 and 2 indicates further, that the increase of temperature under adiabatic conditions due to the latent heat of condensation can be considered as a special type of depletion. Therefore, also for the adiabatic case variations of the positions of the extrema are found to proceed in agreement with the principle of le Chatelier-Braun.

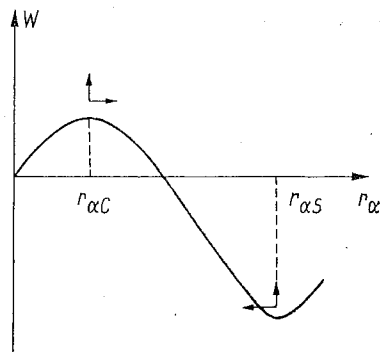


Fig. 1

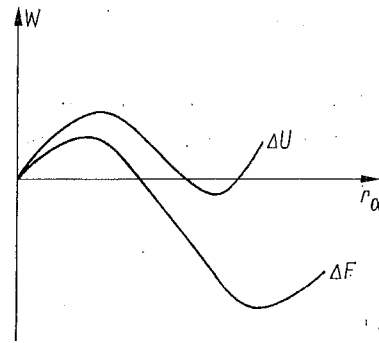


Fig. 2

Fig. 1. Work of formation of a drop as a function of its radius. The arrows indicate the change of the position of the extrema due to depletion effects

Fig. 2. Work of formation of a cluster of the new phase for adiabatic ($W = \Delta U$) and isothermal ($W = \Delta F$) conditions. The metastable initial state is assumed to be the same in both cases

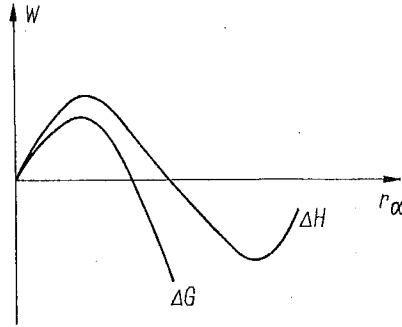


Fig. 3

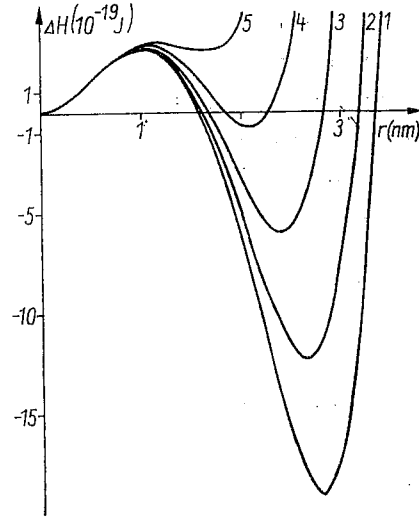


Fig. 4

Fig. 3. Work of formation of an incompressible drop for isobaric isothermal ($W = \Delta G$) and for isobaric adiabatic ($W = \Delta H$) conditions. The increase of temperature results in an increase of the critical radius and may lead to an additional extremum (minimum), which does not occur for isothermal conditions

Fig. 4. Change of the enthalpy ΔH due to the formation of a liquid drop under adiabatic isobaric conditions for different values of the initial volume of the system. The parameters are given by $q = 4 \times 10^4 \text{ J mol}^{-1}$, $C_p^v = 33.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $C_p^l = 75 \text{ J mol}^{-1} \text{ K}^{-1}$, $\rho_\alpha = 0.55 \times 10^5 \text{ mol m}^{-3}$, $\rho' = 0.97 \text{ mol m}^{-3}$, $T = 293 \text{ K}$, $p' = 2.34 \times 10^3 \text{ Pa}$, $\sigma = 0.073 \text{ Nm}^{-1}$, $p = 1.4 \times 10^4 \text{ Pa}$ reflecting in some idealization the process of condensation of water vapour [22].

It follows further, that, again, there exists a critical volume of the system V_c . If the total volume is less than V_c a phase transition cannot proceed via the mechanism of homogeneous nucleation [9, 10]. Moreover, V_c is for adiabatic conditions greater than the corresponding value for isothermal constraints.

4.2. Adiabatic Condensation Under Isobaric Conditions

The same analysis as outlined for isochoric conditions can be easily repeated for the isobaric case. As the result in eqs. (4.1)–(4.8) F has to be replaced by the Gibbs free energy G , μ_β and p_β by μ and p , respectively.

For isobaric isothermal conditions and one-components systems the work of formation of a cluster of a new phase ($W = \Delta G$) can be expressed by [21]

$$W = \Delta G_c \left\{ -2 \left(\frac{r_\alpha}{r_c} \right)^3 + 3 \left(\frac{r_\alpha}{r_c} \right)^2 \right\}. \quad (4.9)$$

The change of the Gibbs free energy as a function of the radius of the cluster is presented in Fig. 3. Since for isobaric isothermal conditions no depletion effects occur, a second extremum, a minimum of ΔG , does not exist.

For adiabatic processes, however, the growth of the drop is connected with an increase of temperature, with a depletion, and, in principle, a minimum of W ($W = \Delta H$) is to be expected for some values of the radius of the drop.

These expectations can be verified by a direct calculation of the change of the enthalpy connected with the formation of an incompressible drop. Hereby we consider a cut through the surface $\Delta H = \Delta H(\tilde{S}_\alpha, V_\alpha)$, which corresponds to a saddle-point approximation. It is defined by the additional condition $T_\alpha = T_\beta$. From eq. (2.7) we obtain then

$$\begin{aligned} \Delta H = & (p - p') V_\alpha + \sigma_\alpha A_\alpha + n_\alpha \{ \mu_\beta(p', T_\beta) - \mu_\beta(p, T_\beta) \} \\ & + S(T_\beta - T) + n \{ \mu_\beta(p, T_\beta) - \mu(p, T) \}. \end{aligned} \quad (4.10)$$

Qualitatively the variation of ΔH as a function of r_α is presented in Fig. 3. A minimum can be found always, if the increase of temperature leads to an increase of p' such, that $p'(T_\beta)$ becomes greater or equal to the external pressure.

In Fig. 4 the change of ΔH as a function of the radius of the drop is calculated for an idealized special case, the heat of vaporization q , the molar heat capacities of the liquid (C_p^l) and the gas (C_p^v) and the surface tension σ_α are assumed to be temperature independent, the vapour is considered as a perfect gas. The dependence of the saturation pressure p' on temperature is described by van't Hoff's law

$$p'(T_\beta) = p'(T) \exp \left\{ -\frac{q}{R} \left[\frac{1}{T_\beta} - \frac{1}{T} \right] \right\}. \quad (4.11)$$

From eq. (4.10) we obtain then

$$\begin{aligned} \Delta H = & \left\{ p - p'(T) \exp \left\{ -\frac{q}{R} \left[\frac{1}{T_\beta} - \frac{1}{T} \right] \right\} \right\} V_\alpha + \sigma_\alpha A_\alpha \\ & - n_\alpha RT \ln \frac{p}{p'(T)} + n_\alpha q \left[1 - \frac{T}{T_\beta} \right] - \frac{n}{2} \frac{C_p^v}{T} (T_\beta - T)^2 \end{aligned} \quad (4.12)$$

$$T_\beta = T + \frac{q}{C_p^l + \left(\frac{n}{n_\alpha} - 1 \right) C_p^v}.$$

Analogous curves are obtained, if for a constant volume of the system the number of clusters is increased, provided that all clusters are of nearly the same size.

5. Discussion

It was mentioned in the first part of these investigations [9] that the problem of the dependence of nucleation processes in finite systems on the type of thermodynamic constraints was formulated already by RUSANOV [14]. The new results outlined here are the following [9]):

- a strict proof is given, that independent on the thermodynamic constraints the cor-

rection term ΔW to the work of formation of the critical clusters is always less or equal to zero

- it is shown, that not the term ΔW but changes of the parameters of the critical clusters determine the variation of the work of formation of the critical clusters due to depletion effects
- necessary and sufficient conditions for the stability of heterogeneous systems—cluster in the otherwise homogeneous medium—are derived [12, 18]
- it is realized, that for the thermodynamic investigations of nucleation processes there is no need in a first approximation to differ between isentropic and adiabatic conditions
- the general results are applied to a number of special cases.

Moreover, for isothermal conditions based on the thermodynamic investigations a general scenario of first-order phase transitions in finite systems was proposed and a kinetic description of the different stages [11] and the transition as a whole [12, 13] was given.

A comparison of the results of the thermodynamic analysis for the both considered cases shows, that this general scenario remains valid. Also the methods used for a kinetic description can be applied with modifications to phase transitions under adiabatic conditions, as will be shown in a forthcoming paper [25].

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