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Thermodynamics of Heterogeneous Systems: Stability Analysis

1. Introduction

Based on Gibbs' approach /1/ in preceding papers /2, 3/ a thermodynamic theory of heterogeneous systems was developed, which allows a description of heterogeneous systems not only in equilibrium but also in non-equilibrium states. The outlined theory is more general compared with the theory of Defay et al. /4/, where from the very beginning a mechanical and thermal equilibrium between the different phases is assumed.

The developed by us theory was applied to the calculation of the change of the thermodynamic potentials describing the system of interest due to the formation of clusters of a new phase in thermodynamic phase transitions of first order /3, 5/. Based on these calculations a general scenario of first-order phase transitions in finite systems was proposed and a kinetic description of this process was given /3, 6, 7/.

One main problem in the application of the theory to the investigation of first-order phase transitions consists in the analysis of the type of extrema (stable or unstable states) of the thermodynamic potential describing the heterogeneous system consisting of s clusters in the otherwise homogeneous medium. For special cases such a stability analysis was carried out in /5, 7, 8/. These investigations are generalized here and extended to a number of practically important situations (see also /3/).

2. Derivation of auxiliary relations

If the formation of clusters with a higher molar density compared with the surrounding medium is considered, the Gibbs adsorption equation reads

$$S_0 dT_\alpha + A d\sigma + \sum_{i=1}^{k} n_{i0} d\mu_{i\alpha} = 0 \qquad (2.1)$$

S_0 and n_{i0} are the superficial entropy and mole numbers, T the temperature, A the surface area of the cluster, σ the surface tension and μ_i the chemical potential of the different components.

According to the postulate of an inner equilibrium /2, 3/ the intensive variables T and μ_{i0} of the surface phase are determined by the corresponding quantities of the phase with a higher molar density, in this case of the cluster phase (specified by a subscript α). It follows, that σ can be considered as a function of T_α and the molar densities $\varrho_{i\alpha}$ of the different components in the cluster phase.

Introducing the notations

$$\Gamma_{i0} = \frac{n_{i0}}{A} \qquad \bar{S}_0 = \frac{S_0}{A} \qquad (2.2)$$

eq. (2.1) yields

$$\frac{\partial \sigma}{\partial T_\alpha} = -\bar{S}_0 - \sum_{i=1}^{k} \Gamma_{i0} \frac{\partial \mu_{i\alpha}}{\partial T_\alpha} \qquad (2.3)$$

$$\frac{\partial \sigma}{\partial \varrho_{j\alpha}} = -\sum_{i=1}^{k} \Gamma_{i0} \frac{\partial \mu_{i\alpha}}{\partial \varrho_{j\alpha}} \qquad (2.4)$$

The change of the free energy of a heterogeneous system (one cluster in the homogeneous medium) for isothermal reversible processes is given in the considered case by /2, 3/:

$$dF_{het} = \left(p_\beta - p_\alpha + \frac{2\sigma}{r_\alpha}\right) dV_\alpha + \sum_{i=1}^{k} (\mu_{i\alpha} - \mu_{i\beta}) d\tilde{n}_{i\alpha} \qquad (2.5)$$

p is the pressure, r_α and V_α are the radius and the volume of the spherical cluster, $\tilde{n}_{i\alpha}$ is determined by $\tilde{n}_{i\alpha} = n_{i\alpha} + n_{i_0}$. The subscript β specifies the thermodynamic parameters of the medium.

According to eq. (2.5) the following relations hold

$$\frac{\partial}{\partial \tilde{n}_{i\alpha}} \left(p_\beta - p_\alpha + \frac{2\sigma}{r_\alpha}\right) = \frac{\partial}{\partial V_\alpha} (\mu_{i\alpha} - \mu_{i\beta}) \qquad (2.6)$$

Taking into account in addition

$$\frac{\partial p_\beta}{\partial n_{i\beta}} = -\frac{\partial \mu_{i\beta}}{\partial V_\beta} \qquad (2.7)$$

we obtain

$$\left(\frac{\partial \mu_{i\alpha}}{\partial V_\alpha}\right)_{\tilde{n}_{j\alpha}} = \left(\frac{\partial \mu_{i\alpha}}{\partial V_\alpha}\right)_{n_{j\alpha}} + \sum_{l=1}^{k} \left(\frac{\partial \mu_{i\alpha}}{\partial n_{l\alpha}}\right)_{V_\alpha} \left(\frac{\partial n_{l\alpha}}{\partial V_\alpha}\right)_{\tilde{n}_{j\alpha}} \qquad (2.8)$$

$$\left(\frac{\partial p_\alpha}{\partial \tilde{n}_{i\alpha}}\right)_{V_\alpha} = \sum_{l=1}^{k} \left(\frac{\partial p_\alpha}{\partial n_{l\alpha}}\right)_{V_\alpha} \left(\frac{\partial n_{l\alpha}}{\partial \tilde{n}_{i\alpha}}\right)_{V_\alpha} \qquad (2.9)$$

$$\left(\frac{\partial}{\partial \tilde{n}_{i\alpha}} \frac{2\sigma}{r_\alpha}\right)_{V_\alpha} = \frac{2}{r_\alpha} \sum_{l=1}^{k} \left(\frac{\partial \sigma}{\partial n_{l\alpha}}\right)_{V_\alpha} \left(\frac{\partial n_{l\alpha}}{\partial \tilde{n}_{i\alpha}}\right)_{V_\alpha} \qquad (2.10)$$

Here $\mu_{l\alpha}$, σ and p_α are considered as functions of $n_{l\alpha}$, $l = 1, 2, \ldots, k$ and V_α.

A substitution of these equations into eq. (2.6) yields

$$\sum_{l=1}^{k} \left(\frac{\partial n_{l\alpha}}{\partial \tilde{n}_{i\alpha}}\right)_{V_\alpha} \left\{ -\left(\frac{\partial p_\alpha}{\partial n_{l\alpha}}\right)_{V_\alpha} + \frac{2}{r_\alpha} \left(\frac{\partial \sigma}{\partial n_{l\alpha}}\right)_{V_\alpha} \right\} =$$

$$= \left(\frac{\partial \mu_{i\alpha}}{\partial V_\alpha}\right)_{n_{j\alpha}} + \sum_{l=1}^{k} \left(\frac{\partial \mu_{i\alpha}}{\partial n_{l\alpha}}\right)_{V_\alpha} \left(\frac{\partial n_{l\alpha}}{\partial V_\alpha}\right)_{\tilde{n}_{j\alpha}} \qquad (2.11)$$

This equation must be equivalent to eq. (2.4). To guaranty this the following relations have to be fulfilled:

$$\left(\frac{\partial n_{j\alpha}}{\partial \tilde{n}_{j\alpha}}\right)_{V_\alpha} = \delta_{ij} \qquad \left(\frac{\partial n_{i\alpha}}{\partial V_\alpha}\right)_{\tilde{n}_{j\alpha}} = -\frac{2\Gamma_{i0}}{r_\alpha} \qquad (2.12)$$

All the partial derivatives are to be calculated here under the additional assumption of a constant value of the temperature.
In the same way we obtain for isentropic processes

$$\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{\tilde{S}_\alpha,\,\tilde{n}_{i\alpha}} = -\frac{2\bar{S}_0}{r_\alpha} \qquad \left(\frac{\partial S_\alpha}{\partial \tilde{n}_{i\alpha}}\right)_{V_\alpha,\,\tilde{S}_\alpha} = 0 \tag{2.13}$$

$$\left(\frac{\partial S_\alpha}{\partial \tilde{S}_\alpha}\right)_{V_\alpha,\,\tilde{n}_{i\alpha}} = 1 \qquad \left(\frac{\partial n_{j\alpha}}{\partial \tilde{n}_{i\alpha}}\right)_{\tilde{S}_\alpha,\,V_\alpha} = \delta_{ij} \tag{2.14}$$

$$\left(\frac{\partial n_{i\alpha}}{\partial V_\alpha}\right)_{\tilde{S}_\alpha,\,\tilde{n}_{i\alpha}} = -\frac{2\Gamma_{i0}}{r_\alpha} \qquad \left(\frac{\partial n_{i\alpha}}{\partial \tilde{S}_\alpha}\right)_{V_\alpha,\,\tilde{n}_{i\alpha}} = 0 \tag{2.15}$$

where $\tilde{S}_\alpha$ is defined by $\tilde{S}_\alpha = S_\alpha + S_0$.

3. Stability analysis for isothermal constraints

The necessary and sufficient conditions for stability of a heterogeneous system consisting of s clusters in the otherwise homogeneous medium for the constraints:

$$V = \text{const.} \quad T = \text{const.} \quad n_i = \text{const.}, \quad i = 1,2,\dots,k \tag{3.1}$$

can be formulated as /9/

$$\delta F_{het} = 0 \tag{3.2}$$

$$\delta^2 F_{het} > 0 \tag{3.3}$$

Here only the case of formation of clusters with a higher molar density compared with the medium is considered, the opposite case can be analyzed in the same way with the same final results.
For s clusters in the medium the free energy of the heterogeneous system (s clusters in the medium) can be written as /2, 3/:

$$F_{het} = \sum_{j=1}^{s} \tilde{F}_\alpha^{(j)} + \sum_{j=1}^{s} F_0^{(j)} + F_\beta \qquad F_0^{(j)} = \sigma^{(j)} A^{(j)}$$
$$\tilde{F}_\alpha^{(j)} = -p_\alpha^{(j)} V_\alpha^{(j)} + \sum_{i=1}^{k} \mu_{i\alpha}^{(j)} \tilde{n}_{i\alpha}^{(j)} \qquad F_\beta = -p_\beta V_\beta + \sum_{i=1}^{k} \mu_{i\beta} n_{i\beta} \tag{3.4}$$

Taking into account the constraints (3.1) the following expressions for F_{het} and δF_{het} are obtained

$$F_{het} = \sum_{j=1}^{s} \left\{ \left(p_\beta - p_\alpha^{(j)}\right) V_\alpha^{(j)} + \sigma^{(j)} A^{(j)} + \sum_{i=1}^{k} \left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right) \tilde{n}_{i\alpha}^{(j)} \right\} - p_\beta V + \sum_{i=1}^{k} \mu_{i\beta} n_i \tag{3.5}$$

$$\delta F_{het} = \sum_{j=1}^{s} \left\{ \left(p_\beta - p_\alpha^{(j)}\right) \delta V_\alpha^{(j)} + \sigma^{(j)} \delta A^{(j)} + \sum_{i=1}^{k} \left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right) \delta \tilde{n}_{i\alpha}^{(j)} \right\} \tag{3.6}$$

The necessary equilibrium conditions are determined, therefore, by

$$\mu_{i\alpha}^{(j)} = \mu_{i\beta} \qquad p_\alpha^{(j)} - p_\beta = \frac{2\sigma^{(j)}}{r_\alpha^{(j)}} \qquad \begin{matrix} i = 1,2,\dots,k \\ j = 1,2,\dots,s \end{matrix} \tag{3.7}$$

The type of equilibrium state is determined by eq. (3.3). In the subsequent discussion necessary and sufficient conditions for the stability of the equilibrium state determined by eqs. (3.2) or (3.7) are derived.

Taking as the point of departure eq. (3.6) $\delta^2 F_{het}$ can be expressed as

$$\delta^2 F_{het} = \sum_{j=1}^{s} \left[\delta^2 \tilde{F}_\alpha^{(j)} + \sigma^{(j)} \delta^2 A^{(j)} + \delta\sigma^{(j)} \delta A^{(j)} \right] + \delta^2 F_\beta \tag{3.8}$$

and applying the constraints

$$\delta V_\beta = -\sum_{j=1}^{s} \delta V_\alpha^{(j)} \qquad \delta n_{i\beta} = -\sum_{j=1}^{s} \delta \tilde{n}_{i\alpha}^{(j)} \tag{3.9}$$

by

$$\begin{aligned}
\delta^2 F_{het} = \sum_{j=1}^{s} \Bigg\{ & \sum_{i,l}^{k} \left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} + \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j)} - \\
& - \sum_{l=1}^{k} \left(\frac{\partial p_\alpha^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} + \frac{\partial p_\beta}{\partial n_{l\beta}} - \frac{2}{r_\alpha^{(j)}} \frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} \right) \delta \tilde{n}_{l\alpha}^{(j)} \delta V_\alpha^{(j)} + \\
& + \sum_{i=1}^{k} \left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_\alpha^{(j)}} + \frac{\partial \mu_{i\beta}}{\partial V_\beta} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta V_\alpha^{(j)} - \left(\frac{\partial p_\alpha^{(j)}}{\partial V_\alpha^{(j)}} + \frac{\partial p_\beta}{\partial V_\beta} + \frac{\sigma^{(j)}}{2\pi r_\alpha^{(j)4}} - \right. \\
& \left. - \frac{2}{r_\alpha^{(j)}} \frac{\partial \sigma^{(j)}}{\partial V_\alpha^{(j)}} \right) \delta V_\alpha^{(j)^2} + \\
& + \sum_{j'=1}^{s} \left(1 - \delta_{jj'}\right) \Bigg\{ \sum_{i,l}^{k} \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j')} - \sum_{i=1}^{k} \frac{\partial p_\beta}{\partial n_{i\beta}} \delta \tilde{n}_{i\alpha}^{(j)} \delta V_\alpha^{(j')} + \\
& + \sum_{i=1}^{k} \frac{\partial \mu_{i\beta}}{\partial V_\beta} \delta \tilde{n}_{i\alpha}^{(j)} \delta V_\alpha^{(j')} - \frac{\partial p_\beta}{\partial V_\beta} \delta V_\alpha^{(j)} \delta V_\alpha^{(j')} \Bigg\} \Bigg\}
\end{aligned} \tag{3.10}$$

δ_{ij} is the Kronecker symbol.
The inequality (3.3) has to be fulfilled for any possible deviations of the independent variables from the equilibrium state (3.2) or (3.7). Consequently, we obtain as one group of necessary stability conditions

$$\begin{aligned}
& \sum_{i,l}^{k} \left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} + \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j)} - \\
& - \sum_{l=1}^{k} \left(\frac{\partial p_\alpha}{\partial \tilde{n}_{l\alpha}^{(j)}} + \frac{\partial p_\beta}{\partial n_{l\beta}} - \frac{2}{r_\alpha^{(j)}} \frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} \right) \delta n_{l\alpha}^{(j)} \delta V_\alpha^{(j)} + \\
& + \sum_{i=1}^{k} \left(\frac{\partial \mu_{i\alpha}}{\partial V_\alpha^{(j)}} + \frac{\partial \mu_{i\beta}}{\partial V_\beta} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta V_\alpha^{(j)} - \\
& - \left(\frac{\partial p_\alpha^{(j)}}{\partial V_\alpha^{(j)}} + \frac{\partial p_\beta}{\partial V_\beta} + \frac{\sigma^{(j)}}{2\pi r_\alpha^{(j)4}} - \frac{2}{r_\alpha^{(j)}} \frac{\partial \sigma^{(j)}}{\partial V_\alpha^{(j)}} \right) \delta V_\alpha^{(j)^2} > 0
\end{aligned} \tag{3.11}$$

This conditions has to be fulfilled for each of the clusters. The inquality (3.11) is equivalent to the demand that the matrix (3.12), formed by the coefficients of the quadratic form (3.11), is positive definite /10/. This is the case, if all major subdeterminants and the determinant J of the matrix (3.12) itself are positive.
The chemical potentials, the pressure and the surface tension can be considered also as functions of the molar densities and the temperature. Consequently, the partial derivatives in the matrix (3.12) can be expressed by eqs. (3.13).

$$
\begin{bmatrix}
\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}}+\frac{\partial \mu_{1\beta}}{\partial n_{1\beta}} & \cdots & \frac{\partial \mu_{1\alpha}^{(j)}}{\partial \tilde{n}_{k\alpha}^{(j)}}+\frac{\partial \mu_{1\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{1\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}+\frac{\partial \mu_{1\beta}}{\partial V_{\beta}} \\
\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}}+\frac{\partial \mu_{2\beta}}{\partial n_{1\beta}} & \cdots & \frac{\partial \mu_{2\alpha}^{(j)}}{\partial \tilde{n}_{k\alpha}^{(j)}}+\frac{\partial \mu_{2\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{2\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}+\frac{\partial \mu_{2\beta}}{\partial V_{\beta}} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}}+\frac{\partial \mu_{k\beta}}{\partial n_{1\beta}} & \cdots & \frac{\partial \mu_{k\alpha}^{(j)}}{\partial \tilde{n}_{k\alpha}^{(j)}}+\frac{\partial \mu_{k\beta}}{\partial n_{k\beta}} & \frac{\partial \mu_{k\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}+\frac{\partial \mu_{k\beta}}{\partial V_{\beta}} \\
-\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}}-\frac{\partial p_{\beta}}{\partial n_{1\beta}}+\frac{2}{r_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} & \cdots & -\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{k\alpha}^{(j)}}-\frac{\partial p_{\beta}}{\partial n_{k\beta}}+\frac{2}{r_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{k\alpha}^{(j)}} & a_{k+1,k+1}
\end{bmatrix} \tag{3.12}
$$

$$
a_{k+1,k+1}=-\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}-\frac{\partial p_{\beta}}{\partial V_{\beta}}-\frac{\sigma^{(j)}}{2\pi r_{\alpha}^{(j)4}}+\frac{2}{r_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}}
$$

$$
\begin{aligned}
&\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}=\frac{1}{V_{\alpha}^{(j)}}\sum_{r=1}^{k}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \varrho_{r\alpha}^{(j)}}\left(\frac{\partial n_{r\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)_{V_{\alpha}} && \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}}=\frac{1}{V_{\beta}}\frac{\partial \mu_{i\beta}}{\partial \varrho_{l\beta}} \\
&\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}=\frac{1}{V_{\alpha}^{(j)}}\sum_{r=1}^{k}\frac{\partial p_{\alpha}^{(j)}}{\partial \varrho_{r\alpha}^{(j)}}\left(\frac{\partial n_{r\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)_{V_{\alpha}} && \frac{\partial p_{\beta}}{\partial n_{l\beta}}=\frac{1}{V_{\beta}}\frac{\partial p_{\beta}}{\partial \varrho_{l\beta}} \\
&\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}=\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\left(\frac{\partial n_{l\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)_{\tilde{n}_{r\alpha}^{(j)}}-\varrho_{l\alpha}^{(j)}\right] && \frac{\partial \mu_{i\beta}}{\partial V_{\beta}}=-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial \mu_{i\beta}}{\partial V_{\beta}} \\
&\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}=\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial p_{\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\left(\frac{\partial n_{l\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)_{\tilde{n}_{r\alpha}^{(j)}}-\varrho_{l\alpha}^{(j)}\right] && \frac{\partial p_{\beta}}{\partial V_{\beta}}=-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial p_{\beta}}{\partial \varrho_{l\beta}} \\
&\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}}=\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\left(\frac{\partial n_{l\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)_{\tilde{n}_{r\alpha}^{(j)}}-\varrho_{l\alpha}^{(j)}\right] && \frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}=\sum_{r=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial \varrho_{r\alpha}^{(j)}}\left(\frac{\partial n_{r\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)_{V_{\alpha}}
\end{aligned} \tag{3.13}
$$

With the auxiliary relations (2.12) and eq. (2.4) we obtain the following expression for the matrix (3.12):

$$
\begin{bmatrix}
\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{1\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{1\beta}}{\partial \varrho_{k\beta}} & -\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\frac{2\Gamma_{l0}^{(j)}}{r_{\alpha}^{(j)}}+\varrho_{l\alpha}^{(j)}\right]-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial \mu_{1\beta}}{\partial \varrho_{l\beta}} \\
\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{2\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{2\beta}}{\partial \varrho_{k\beta}} & -\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\frac{2\Gamma_{l0}^{(j)}}{r_{\alpha}^{(j)}}+\varrho_{l\alpha}^{(j)}\right]-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial \mu_{2\beta}}{\partial \varrho_{l\beta}} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{k\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_{\beta}}\frac{\partial \mu_{k\beta}}{\partial \varrho_{k\beta}} & -\sum_{l=1}^{k}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left[\frac{2\Gamma_{l0}^{(j)}}{r_{\alpha}^{(j)}}+\varrho_{l\alpha}^{(j)}\right]-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial \mu_{k\beta}}{\partial \varrho_{l\beta}} \\
a_{k+1,1} & \cdots & a_{k+1,k} & a_{k+1,k+1}
\end{bmatrix} \tag{3.14}
$$

$$
a_{k+1,i}=-\sum_{l=1}^{k}\frac{\varrho_{l\beta}^{(j)}}{V_{\alpha}^{(j)}}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}+\frac{2}{r_{\alpha}^{(j)}}\frac{1}{V_{\alpha}^{(j)}}\frac{\partial \sigma^{(j)}}{\partial \varrho_{i\alpha}^{(j)}}-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_{\beta}}\frac{\partial \mu_{i\beta}}{\partial \varrho_{l\beta}} \qquad i=1,2,\ldots,k
$$

$$
a_{k+1,k+1}=\frac{1}{V_{\alpha}^{(j)}}\sum_{l=1}^{k}\sum_{i=1}^{k}\left[\frac{2\Gamma_{l0}^{(j)}}{r_{\alpha}^{(j)}}+\varrho_{l\alpha}^{(j)}\right]\left[\frac{2\Gamma_{i0}^{(j)}}{r_{\alpha}^{(j)}}+\varrho_{i\alpha}^{(j)}\right]\frac{\partial \mu_{l\alpha}^{(j)}}{\partial \varrho_{i\alpha}^{(j)}}-\frac{\sigma^{(j)}}{2\pi r_{\alpha}^{(j)4}}+\frac{1}{V_{\beta}}\sum_{l=1}^{k}\sum_{i=1}^{k}\varrho_{l\beta}\varrho_{i\beta}\frac{\partial \mu_{l\beta}}{\partial \varrho_{i\beta}}
$$

The conditions for an intrinsic stability of both bulk phases (which are the basis of the thermodynamic description) can be expressed as

$$\delta^2 F_\alpha > 0 \qquad \delta^2 F_\beta > 0 \tag{3.15}$$

It follows immediately from these conditions, that all major subdeterminants of the matrix (3.14) are positive. Therefore, equilibrium states of a heterogeneous system described by eq. (3.5) are either stable states or unstable states of saddle-point type. The necessary conditions for stability can be formulated, therefore, as $J > 0$, where J is the determinant of the matrix (3.14).

If only one cluster is present in the system, $J > 0$ is the necessary and sufficient stability condition. In particular, for one-component systems, we get

$$\frac{\sigma}{2\pi r_\alpha^4} < \frac{\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\left(\frac{2\Gamma_0}{r_\alpha}+\varrho_\alpha-\varrho_\beta\right)^2}{V_\alpha V_\beta\left(\frac{1}{V_\alpha}\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}+\frac{1}{V_\beta}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\right)} \tag{3.16}$$

If more than one cluster is formed in the system $J > 0$ is necessary but not sufficient for stability (compare, in contrast /11/). E. g., in one-component systems eq. (3.7) has solutions, corresponding to states consisting of s identical clusters in the homogeneous medium. Considering simultaneous variations of the parameters of two of the clusters from eq. (3.3) in addition to eq. (3.16) the following inequalities are derived

$$\frac{\sigma}{2\pi r_\alpha^4} < \frac{\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\left(\frac{2\Gamma_0}{r_\alpha}+\varrho_\alpha-\varrho_\beta\right)^2}{V_\alpha V_\beta\left(\frac{1}{V_\alpha}\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}+\frac{2}{V_\beta}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\right)} \tag{3.17}$$

$$\frac{\sigma}{2\pi r_\alpha^4} > 2\,\frac{\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\left(\frac{2\Gamma_0}{r_\alpha}+\varrho_\alpha-\varrho_\beta\right)^2}{V_\alpha V_\beta\left(\frac{1}{V_\alpha}\frac{\partial\mu_\alpha}{\partial\varrho_\alpha}+\frac{2}{V_\beta}\frac{\partial\mu_\beta}{\partial\varrho_\beta}\right)} \tag{3.18}$$

This set of inequalities cannot be fulfilled simultaneously. Consequently, in one-component closed isochoric systems heterogeneous states consisting of s identical clusters ($s \geqq 2$) in the otherwise homogeneous medium are always unstable.

If instead of the constraints (3.1) isobaric isothermal conditions are assumed

$$p = p_\beta = \text{const.} \qquad n_i = \text{const.} \qquad T = \text{const.} \tag{3.19}$$

then the characteristic thermodynamic potential is the Gibbs free energy G. As it was shown earlier /2, 3/, the expressions for G_{het} and δG_{het} have the form

$$G_{het} = \sum_{j=1}^{s}\left\{\left(p_\beta - p_\alpha^{(j)}\right)V_\alpha^{(j)} + \sigma^{(j)}A^{(j)} + \sum_{i=1}^{k}\left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right)\tilde{n}_{i\alpha}^{(j)}\right\} + \sum_{i=1}^{k} n_i\mu_{i\beta} \tag{3.20}$$

$$\delta G_{het} = \sum_{j=1}^{s}\left\{\left(p_\beta - p_\alpha^{(j)} + \frac{2\sigma^{(j)}}{r_\alpha^{(j)}}\right)\delta V_\alpha^{(j)} + \sum_{i=1}^{k}\left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right)\delta\tilde{n}_{i\alpha}^{(j)}\right\} \tag{3.21}$$

δG_{het} has the same structure as δF_{het} (see eq. (3.6)), the only difference is that p_β is equal here to the constant external pressure p.

It follows, that also $\delta^2 G_{het}$ has the same form as eq. (3.10) but some of the partial derivatives in eq. (3.10) and the subsequent expressions are equal to zero, now.

$$\frac{\partial\mu_{i\beta}}{\partial V_\beta} = \frac{\partial p_\beta}{\partial n_{j\beta}} = \frac{\partial p_\beta}{\partial V_\beta} = \sum_{l=1}^{k}\varrho_{l\beta}\frac{\partial\mu_{i\beta}}{\partial\varrho_{l\beta}} = 0 \tag{3.22}$$

In particular, for one-component systems the necessary equilibrium condition (3.16) is reduced to $\sigma < 0$. This relation cannot be fulfilled, since the surface tension must be positive. Consequently, in one-component systems under the constraints (3.19) no stable heterogeneous state can be formed.

4. Stability under isentropic constraints

First, again, isochoric isentropic processes in closed systems are considered. The constraints are given by

$$V = \text{const.} \qquad S = \text{const.} \qquad n_i = \text{const.} \tag{4.1}$$

The characteristic thermodynamic potential is now the inner energy U and the necessary and sufficient conditions for a stable equilibrium state read

$$\delta U_{het} = 0 \tag{4.2}$$

$$\delta^2 U_{het} > 0 \tag{4.3}$$

The inner energy of the heterogeneous system U_{het} can be expressed by /2, 3/

$$U_{het} = \sum_{j=1}^{s}\tilde{U}_\alpha^{(j)} + \sum_{j=1}^{s}U_0^{(j)} + U_\beta \qquad U_0^{(j)} = \sigma^{(j)}A^{(j)}$$

$$U_\alpha^{(j)} = T_\alpha^{(j)}\tilde{S}_\alpha^{(j)} - p_\alpha^{(j)}V_\alpha^{(j)} + \sum_{i=1}^{k}\mu_{i\alpha}^{(j)}\tilde{n}_{i\alpha}^{(j)} \tag{4.4}$$

$$U_\beta = T_\beta S_\beta - p_\beta V_\beta + \sum_{i=1}^{k}\mu_{i\beta}n_{i\beta}$$

and taking into account the constraints (4.1) we get

$$U_{het} = \sum_{j=1}^{s}\left\{\left(T_\alpha^{(j)} - T_\beta\right)\tilde{S}_\alpha^{(j)} + \left(p_\beta - p_\alpha^{(j)}\right)V_\alpha^{(j)} + \sigma^{(j)}A^{(j)} + \sum_{i=1}^{k}\left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right)\tilde{n}_{i\alpha}^{(j)}\right\} + T_\beta S - p_\beta V + \sum n_i\mu_{i\beta} \tag{4.5}$$

$$\delta U_{het} = \sum_{j=1}^{s}\left\{\left(p_\beta - p_\alpha^{(j)} + \frac{2\sigma^{(j)}}{r_\alpha^{(j)}}\right)\delta V_\alpha^{(j)} + \left(T_\alpha^{(j)} - T_\beta\right)\delta\tilde{S}_\alpha^{(j)} + \sum_{i=1}^{k}\left(\mu_{i\alpha}^{(j)} - \mu_{i\beta}\right)\delta\tilde{n}_{i\alpha}^{(j)}\right\} \tag{4.6}$$

From eqs. (4.2) and (4.4) in addition to eq. (3.7) the necessary equilibrium conditions

$$T_\alpha^{(j)} = T_\beta \qquad j = 1, 2, \ldots, s \tag{4.7}$$

are obtained.

$\delta^2 U_{het}$ reads

$$\delta^2 U_{het} = \sum_{j=1}^{s}\left\{\delta^2 U_\alpha^{(j)} + \delta\sigma^{(j)}\delta A^{(j)} + \sigma^{(j)}\delta^2 A^{(j)}\right\} + \delta^2 U_\beta \tag{4.8}$$

and taking into account the constraints

$$S = \sum_{j=1}^{s}\tilde{S}_\alpha^{(j)} + S_\beta \qquad V = \sum_{j=1}^{s}V_\alpha^{(j)} + V_\beta \qquad n_i = \sum_{j=1}^{s}\tilde{n}_{i\alpha}^{(j)} + n_{i\beta} \tag{4.9}$$

we get

$$
\begin{aligned}
\delta^2 U_{\mathrm{het}} = \sum_{j=1}^{s} \Bigg\{ & \sum_{i,l}^{k} \left(\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} \right) + \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j)} \\
& + \sum_{i=1}^{k} \left(\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{i\beta}}{\partial S_{\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta S_{\alpha}^{(j)} + \sum_{i=1}^{k} \left(\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{i\beta}}{\partial V_{\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta V_{\alpha}^{(j)} \\
& + \sum_{i=1}^{k} \left(\left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{n}_{i\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial n_{i\beta}} \right) \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{S}_{\alpha}^{(j)} + \left(\left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial S_{\beta}} \right) \delta \tilde{S}_{\alpha}^{(j)2} + \\
& + \left(\left(\frac{\partial T_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial V_{\beta}} \right) \delta \tilde{S}_{\alpha}^{(j)} \delta V_{\alpha}^{(j)} + \sum_{l=1}^{k} \left(-\left(\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial \tilde{n}_{l\beta}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial n_{l\alpha}^{(j)}} \right) \right) \delta V_{\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j)} \\
& + \left(-\left(\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial S_{\beta}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) \right) \delta V_{\alpha}^{(j)} \delta \tilde{S}_{\alpha}^{(j)} \\
& + \left(-\left(\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial V_{\beta}} - \frac{\sigma^{(j)}}{2\pi r_{\alpha}^{(j)4}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}} \right) \right) \delta V_{\alpha}^{(j)2} \qquad (4.10) \\
& + \sum_{j'=1}^{s} \left(1 - \delta_{jj'} \right) \Bigg\{ \sum_{i,l} \frac{\partial \mu_{i\beta}}{\partial n_{l\beta}} \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{n}_{l\alpha}^{(j')} + \sum_{i} \frac{\partial \mu_{i\beta}}{\partial S_{\beta}} \delta \tilde{S}_{\alpha}^{(j)} \delta \tilde{n}_{i\alpha}^{(j')} \\
& + \sum_{i=1}^{k} \frac{\partial \mu_{i\beta}}{\partial V_{\beta}} \delta \tilde{n}_{i\alpha}^{(j)} \delta V_{\alpha}^{(j')} + \sum_{i=1}^{k} \frac{\partial T_{\beta}}{\partial n_{i\beta}} \delta \tilde{n}_{i\alpha}^{(j)} \delta \tilde{S}_{\alpha}^{(j')} \\
& + \frac{\partial T_{\beta}}{\partial S_{\beta}} \delta \tilde{S}_{\alpha}^{(j)} \delta S_{\alpha}^{(j')} + \frac{\partial T_{\beta}}{\partial V_{\beta}} \delta \tilde{S}_{\alpha}^{(j)} \delta V_{\alpha}^{(j')} - \sum_{i=1}^{k} \frac{\partial p_{\beta}}{\partial n_{i\beta}} \delta V_{\alpha}^{(j)} \delta \tilde{n}_{i\alpha}^{(j')} \\
& - \frac{\partial p_{\beta}}{\partial S_{\beta}} \delta V_{\alpha}^{(j)} \delta \tilde{S}_{\alpha}^{(j')} - \frac{\partial p_{\beta}}{\partial V_{\beta}} \delta V_{\alpha}^{(j)} \delta V_{\alpha}^{(j')} \Bigg\} \Bigg\}
\end{aligned}
$$

The brackets () in the partial derivatives indicate, that in the derivation with respect to one of the variables $\tilde{n}_{i\alpha}^{(j)}$, $V_{\alpha}^{(j)}$ or $S_{\alpha}^{(j)}$ the others are held constant.

As a set of necessary conditions for stability we can formulate, again, that for all s clusters the major subdeterminants and the determinant J of the matrix (4.11) have to be positive.

With eqs. (2.13)–(2.15) the partial derivatives in eq. (4.11) are determined by eq. (4.12). Going over to the molar densities and the entropy densities $S = S/V$ as independent variables the matrix (4.11) is transformed into expression (4.14).

From the condition of an intrinsic equilibrium of the bulk phases it follows, again, that all major subdeterminants of the matrix (4.14) are greater than zero. So the necessary stability conditions are given by $J > 0$, again. For one cluster in the medium this condition is necessary and sufficient for stability.

$$
\begin{bmatrix}
\left(\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) + \frac{\partial \mu_{1\beta}}{\partial n_{1\beta}} & \cdots & \left(\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{1\beta}}{\partial S_{\beta}} & \left(\frac{\partial \mu_{1\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{1\beta}}{\partial V_{\beta}} \\
\left(\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) + \frac{\partial \mu_{2\beta}}{\partial n_{1\beta}} & \cdots & \left(\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{2\beta}}{\partial S_{\beta}} & \left(\frac{\partial \mu_{2\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{2\beta}}{\partial V_{\beta}} \\
\cdots & \cdots & \cdots & \cdots \\
\left(\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) + \frac{\partial \mu_{k\beta}}{\partial n_{1\beta}} & \cdots & \left(\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{k\beta}}{\partial S_{\beta}} & \left(\frac{\partial \mu_{k\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial \mu_{k\beta}}{\partial V_{\beta}} \\
\left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial n_{1\beta}} & \cdots & \left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial S_{\beta}} & \left(\frac{\partial T_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) + \frac{\partial T_{\beta}}{\partial V_{\beta}} \\
-\left(\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial n_{1\beta}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{1\alpha}^{(j)}} \right) & \cdots & -\left(\frac{\partial \tilde{p}_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial S_{\beta}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}} \right) & -\left(\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}} \right) - \frac{\partial p_{\beta}}{\partial V_{\beta}} - \frac{\sigma^{(j)}}{2\pi r_{\alpha}^{(j)4}} + \frac{2}{r_{\alpha}^{(j)}} \left(\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}} \right)
\end{bmatrix} \qquad (4.11)
$$

$$\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)=\frac{\partial \mu_{i\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}} \qquad \left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}}\right)=\frac{\partial \mu_{i\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}}$$

$$\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)=\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}-\frac{2}{r_{\alpha}^{(j)}}\left[\sum_{l=1}^{k}\Gamma_{l0}^{(j)}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}}+\bar{S}_{0}^{(j)}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}}\right] \qquad \left(\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)=\frac{\partial p_{\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}}$$

$$\left(\frac{\partial p_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}}\right)=\frac{\partial p_{\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}} \qquad \left(\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)=\frac{\partial p_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}-\frac{2}{r_{\alpha}^{(j)}}\left[\sum_{l=1}^{k}\Gamma_{l0}^{(j)}\frac{\partial p_{\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}}+\bar{S}_{0}^{(j)}\frac{\partial p_{\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}}\right]$$

$$\left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)=\frac{\partial T_{\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}} \qquad \left(\frac{\partial T_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}\right)=\frac{\partial T_{\alpha}^{(j)}}{\partial V_{\alpha}^{(j)}}-\frac{2}{r_{\alpha}^{(j)}}\left[\sum_{l=1}^{k}\Gamma_{l0}^{(j)}\frac{\partial T_{\alpha}^{(j)}}{\partial n_{l\alpha}^{(j)}}+\bar{S}_{0}^{(j)}\frac{\partial T_{\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}}\right]$$

$$\left(\frac{\partial T_{\alpha}^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}}\right)=\frac{\partial T_{\alpha}^{(j)}}{\partial S_{\alpha}^{(j)}} \qquad \left(\frac{\partial \sigma^{(j)}}{\partial \tilde{n}_{l\alpha}^{(j)}}\right)=\frac{\partial \sigma^{(j)}}{\partial n_{l\alpha}^{(j)}} \qquad \left(\frac{\partial \sigma^{(j)}}{\partial \tilde{S}_{\alpha}^{(j)}}\right)=\frac{\partial \sigma^{(j)}}{\partial S_{\alpha}^{(j)}}$$

$$\left(\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}}\right)=\frac{\partial \sigma^{(j)}}{\partial V_{\alpha}^{(j)}}-\frac{2}{r_{\alpha}^{(j)}}\left[\sum_{l=1}^{k}\Gamma_{l0}^{(j)}\frac{\partial \sigma^{(j)}}{\partial n_{l\alpha}^{(j)}}+\bar{S}_{0}^{(j)}\frac{\partial \sigma^{(j)}}{\partial S_{\alpha}^{(j)}}\right] \tag{4.12}$$

Moreover, it follows that the equilibrium states correspond either to stable states or to unstable states of saddle-point type. Only if additional assumptions concerning the thermodynamic properties of the different phases are made, the number of degrees of freedom of the system is decreased and saddle-points can degenerate into maxima.

If instead of isochoric isobaric conditions are assumed, the characteristic thermodynamic potential is the enthalpy H. For $\delta^2 H_{het}$ the same expression as for $\delta^2 U_{het}$ is obtained, again, with the difference, that p_β is determined by the constant external pressure p. So, again, the necessary stability conditions are given by $J > 0$, where the following terms in the matrix (4.14) are equal to zero, now:

$$-\frac{\partial p_\beta}{\partial V_\beta}=\frac{\partial \mu_{i\beta}}{\partial V_\beta}=\frac{\partial p_\beta}{\partial n_{i\beta}}=\frac{\partial p_\beta}{\partial S_\beta}=\frac{\partial T_\beta}{\partial V_\beta}=0 \tag{4.13}$$

The conclusions concerning the possible types of equilibrium states hold also for this case.

5. Concluding remarks

The present paper completes the series of studies dealing with the thermodynamic description of three-dimensional heterogeneous systems in non-equilibrium states. The same approach can be used also for the thermodynamic description of two-dimensional systems, e. g., adsorbed layers. A detailed study will be presented later.

$$\begin{bmatrix}
\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{1\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{1\beta}}{\partial \varrho_{k\beta}} & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{1\beta}}{\partial \bar{S}_\beta} & \left(\frac{\partial \mu_{1\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial \mu_{1\beta}}{\partial V_\beta} \\
\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{2\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{2\beta}}{\partial \varrho_{k\beta}} & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{2\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{2\beta}}{\partial \bar{S}_\beta} & \left(\frac{\partial \mu_{2\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial \mu_{2\beta}}{\partial V_\beta} \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \varrho_{1\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{k\beta}}{\partial \varrho_{1\beta}} & \cdots & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \varrho_{k\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{k\beta}}{\partial \varrho_{k\beta}} & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{k\beta}}{\partial \bar{S}_\beta} & \left(\frac{\partial \mu_{k\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial \mu_{k\beta}}{\partial V_\beta} \\
\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{1\alpha}^{(j)}}{\partial \bar{S}_{\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{1\beta}}{\partial \bar{S}_{\beta}} & \cdots & \frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{k\alpha}^{(j)}}{\partial \bar{S}_{\alpha}^{(j)}}+\frac{1}{V_\beta}\frac{\partial \mu_{k\beta}}{\partial \bar{S}_{\beta}} & \frac{1}{V_\alpha^{(j)}}\frac{\partial T_{\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}+\frac{1}{V_\beta}\frac{\partial T_{\beta}}{\partial \bar{S}_\beta} & \left(\frac{\partial T_{\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial T_{\beta}}{\partial V_\beta} \\
a_{k+2,1} & \cdots & a_{k+2,k} & a_{k+2,k+1} & a_{k+2,k+2}
\end{bmatrix} \tag{4.14}$$

$$a_{k+2,i}=\left(\frac{\partial \mu_{i\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial \mu_{i\beta}}{\partial V_\beta}=-\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}\left(\bar{S}_\alpha^{(j)}+\frac{2\bar{S}_0^{(j)}}{r_\alpha^{(j)}}\right)-\sum_{l=1}^{k}\frac{1}{V_\alpha^{(j)}}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left(\varrho_{l\alpha}^{(j)}+\frac{2\Gamma_{l0}^{(j)}}{r_\alpha^{(j)}}\right)-\frac{\bar{S}_\beta}{V_\beta}\frac{\partial \mu_{i\beta}}{\partial \bar{S}_\beta}-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_\beta}\frac{\partial \mu_{i\beta}}{\partial \varrho_{l\beta}}$$

$$a_{k+2,k+1}=\left(\frac{\partial T_{\alpha}^{(j)}}{\partial V_\alpha^{(j)}}\right)+\frac{\partial T_{\beta}}{\partial V_\beta}=-\frac{1}{V_\alpha^{(j)}}\frac{\partial T_{\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}\left(\bar{S}_\alpha^{(j)}+\frac{2\bar{S}_0^{(j)}}{r_\alpha^{(j)}}\right)-\sum_{l=1}^{k}\frac{1}{V_\alpha^{(j)}}\frac{\partial T_{\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left(\varrho_{l\alpha}^{(j)}+\frac{2\Gamma_{l0}^{(j)}}{r_\alpha^{(j)}}\right)-\frac{\bar{S}_\beta}{V_\beta}\frac{\partial T_{\beta}}{\partial \bar{S}_\beta}-\sum_{l=1}^{k}\frac{\varrho_{l\beta}}{V_\beta}\frac{\partial T_{\beta}}{\partial \varrho_{l\beta}}$$

$$\begin{aligned}
a_{k+2,k+2}=&\frac{1}{V_\alpha^{(j)}}\left\{\left(\bar{S}_\alpha^{(j)}+\frac{2\bar{S}_0^{(j)}}{r_\alpha^{(j)}}\right)\left[\frac{\partial T_\alpha^{(j)}}{\partial \bar{S}_\alpha^{(j)}}\left(\bar{S}_\alpha^{(j)}+\frac{2\bar{S}_0^{(j)}}{r_\alpha^{(j)}}\right)+\sum_{i=1}^{k}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \bar{S}_\alpha^{(j)}}\left(\varrho_{i\alpha}^{(j)}+\frac{2\Gamma_{i0}^{(j)}}{r_\alpha^{(j)}}\right)\right]+\right.\\
&\left.+\sum_{l=1}^{k}\left(\varrho_{l\alpha}^{(j)}+\frac{2\Gamma_{l0}^{(j)}}{r_\alpha^{(j)}}\right)\left[\frac{\partial T_\alpha^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left(\bar{S}_\alpha^{(j)}+\frac{2\bar{S}_0^{(j)}}{r_\alpha^{(j)}}\right)+\sum_{i=1}^{k}\frac{\partial \mu_{i\alpha}^{(j)}}{\partial \varrho_{l\alpha}^{(j)}}\left(\varrho_{i\alpha}^{(j)}+\frac{2\Gamma_{i0}^{(j)}}{r_\alpha^{(j)}}\right)\right]\right\}\\
&+\frac{1}{V_\beta}\left\{\bar{S}_\beta\left(\bar{S}_\beta\frac{\partial T_\beta}{\partial \bar{S}_\beta}+\sum_{i=1}^{k}\varrho_{i\beta}\frac{\partial \mu_{i\beta}}{\partial \bar{S}_\beta}\right)+\sum_{l=1}^{k}\varrho_{l\beta}\left(\bar{S}_\beta\frac{\partial T_\beta}{\partial \varrho_{l\beta}}+\sum_{i=1}^{k}\varrho_{i\beta}\frac{\partial \mu_{i\beta}}{\partial \varrho_{l\beta}}\right)\right\}\\
&-\frac{\sigma^{(j)}}{2\pi r_\alpha^{(j)4}}
\end{aligned}$$

Zusammenfassung

Eine Analyse der Stabilität heterogener Systeme, bestehend aus s Clustern einer neuen Phase im ansonsten homogenen Medium, wird vorgenommen für eine Reihe praktisch relevanter thermodynamischer Randbedingungen. Notwendige und hinreichende Bedingungen für Stabilität werden abgeleitet. Es wird gezeigt, daß die Gleichgewichtszustände entweder stabil sind oder instabilen Zuständen vom Sattelpunktstyp entsprechen unabhängig von den Randbedingungen und der Zahl der Komponenten im System. Nur wenn zusätzliche Annahmen über die thermodynamischen Eigenschaften der beiden Phasen gemacht werden, die die Zahl der thermodynamischen Freiheitsgrade einschränken, können Sattelpunkte zu Maxima entarten.

Резюме

В статье описывается анализ стабильности гетерогенных систем состоящих из s сгустков (гластерн) новой фазы в в остальном гомогенном медиуме. Этот анализ произведен для ряда практически релевантных термодинамических граничных условий. В статье отводятся необходимые и достаточные условия для стабильности. Показано, что состояния равновесия являются стабильными или соответствуют нестабильным состояниям типа перевала независимо от граничных условий и числа компонентов в системе. Только если производятся дополнительные предложения о термодинамических качествах обеих фаз, которые ограничивают число термодинамических степеней свободы, перевалы могут выраждатся до максимума.

Summary

An analysis of the stability of heterogeneous systems consisting of a nuclei of a new phase in an otherwise homogeneous medium is developed for a number of practically relevant thermodynamic constraints. It is shown that the equilibrium states are either stable states or non-stable states of the saddle-point type regardless of the thermodynamic constraints or the number of components in the system. Saddle points can degenerate into maxima only if additional assumptions concerning the thermodynamic properties of the two phases reduce the number of thermodynamic degrees of freedom of the system.

Résumé

Les auteurs analysent la stabilité de systèmes hétérogènes constitués de « s » essaims d'une nouvelle phase dans un milieu généralement homogène, pour une série de conditions marginales thermodynamiques d'intérêt pratique. Ils formulent les conditions de stabilité nécessaires et suffisantes. Ils montrent que les états d'équilibre sont soit stables soit instables au point de répondre à des états du type de points de selle, quels que soient les conditions marginales et le nombre des composants du système. Ce n'est qu'en posant des hypothèses supplémentaires pour les propriétés thermodynamiques des deux phases, limitant le nombre des degrés de liberté thermodynamiques, qu'il est possible que les points de selle dégénèrent en points maximaux

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