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Thermodynamic Aspects of Nucleation in Finite Systems

This paper deals with a short summary of thermodynamic aspects of the nucleation process in finite systems. For detailed explanations see the given references and literature therein.

1. Description of the two-phase system

The phase transition in a metastable system, e.g. in a super-saturated vapor, leads to a heterogeneous system (Fig. 1). The new phase α consists of the spatially distributed nuclei, e.g. the droplets. The phase β is given by the surrounding medium, e.g. the vapor. The droplet is characterized by its particle number N_α and its volume V_α . If we assume the droplet to be spherical ($V_\alpha \rightarrow r_\alpha$) and incompressible ($c_\alpha = N_\alpha/V_\alpha = \text{const.}$), only one variable is needed for the droplet description. The droplet surface is approximated by the Gibbsian surface of tension /1/. A thermodynamic analysis shows that the surface tension σ depends on the curvature of the droplet /2,3/. A general formulae for $\sigma(r)$ which includes well known formulae of $\sigma(r)$ by several authors as special cases is given in /4,5/.

The phase β contains a vapor mixture, which is approximately described as an ideal gas with only free particles. From an experimental point of view a carrier gas is used which is not condenserable but able to change the special properties of the liquid drop (e.g. the saturation pressure p_∞ , the surface tension σ or the sticking coefficient X at the droplet surface).

For a theoretical description in the given sense p_∞ , σ , c_α are expressed by the parameters of the flat macroscopic liquid phase (droplet model).

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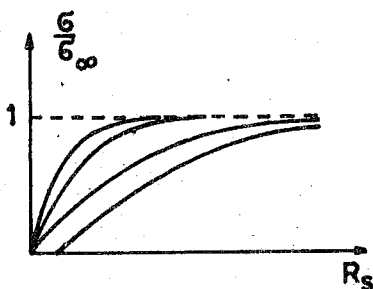


Fig. 1: Curvature dependence of the surface tension of droplets in the gas phase

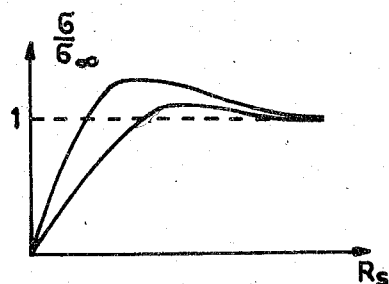


Fig. 2: Curvature dependence of the surface tension of bubbles in the liquid phase

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2. Thermodynamic constraints

The thermodynamic constraints, e.g. system volume V , overall particle number N , temperature T , pressure p , are represented by the supersaturation of the initial vapor state. Considering in the following an ideal one-component vapor, the initial supersaturation is given by:

$$y_0(N, V, T) = \frac{Nk_b T}{P_{\infty} V} = \frac{P}{P_{\infty}(T)} \quad (1)$$

Here we assume an initial state with N free particles. Further in this paper only isothermal processes are supposed ($T = \text{const.}$). In general cooling rates change the supersaturation rapidly. The classical nucleation theory has been worked out for a constant pressure of the system, that means the actual supersaturation is always equal to the initial supersaturation.

Instead of this in finite systems the constraints

$$N, V, T = \text{const.} \quad (2)$$

are hold. Here the actual supersaturation y changes because the number of free particles and thus the vapor pressure decreases by the formation of droplets. Such depletion effects lead to a new stable state of the droplets in finite systems /6,7/.

3. Thermodynamic potential

For the given thermodynamic constraints (2) the free energy is the thermodynamic potential to describe the heterogeneous system. It consists of three parts, which represent the free energy of the droplet phase (F_{α}) respectively of the vapor phase (F_{β}) and the surface energy (F_0):

$$F_{\text{het}} = F_{\alpha} + F_{\beta} + F_0 \quad (3)$$

The droplet phase is spatially distributed, that means

$$V_{\alpha} = \sum_{l=1}^s V_{\alpha}^{(l)} ; N_{\alpha} = \sum_{l=1}^s N_{\alpha}^{(l)} ; O_{\alpha} = \sum_{l=1}^s O_{\alpha}^{(l)} \quad (4)$$

where $V_{\alpha}^{(l)}$, $N_{\alpha}^{(l)}$ and $O_{\alpha}^{(l)}$ are the volume, the particle number and the surface area of a given droplet (1).

Generally the potential difference $\Delta F = F_{\text{het}} - F_{\text{hom}}$ is

discussed, where F_{hom} means the free energy of the initial homogeneous system: $F_{\text{hom}} = -pV + \mu N$ with μ being the chemical potential. Considering the relations $V = V_\alpha + V_\beta = \text{const.}$, $N = N_\alpha + N_\beta = \text{const.}$ we receive from thermodynamics /7/:

$$\Delta F = (p - p_\beta) V + (\mu_\beta - \mu) N + \sum_{l=1}^s \left\{ (p_\beta - p_\alpha^{(l)}) V_\alpha^{(l)} + (\mu_\alpha^{(l)} - \mu_\beta) N_\alpha^{(l)} + \sigma O_\alpha^{(l)} \right\} \quad (5)$$

F is interpreted as the reversible work of formation of the given droplet distribution. Eq. (5) can be calculated with the assumptions for the phases α and β given in section 1.

From a statistical point of view another form of the free energy is obtained if we consider the droplets of different sizes and free particles as an ideal gas mixture. Then the partial pressure and the mixing entropy of the droplets give a part to the free energy /8,15/.

4. Equilibrium conditions and stability

The equilibrium conditions are obtained from $d\Delta F = 0$. A minimum of ΔF corresponds to a stable state of the heterogeneous system (coexistence of droplets and vapor), but a maximum or an extremum of a saddle-point type is due to an instable equilibrium state. General investigations on equilibrium and stability conditions for a k -component system under different thermodynamic constraints are given in /7,9/. Here the discussion is hold for an one-component system with only one droplet.

Because the droplet is described by two independent variables, N_α and V_α , we have two equilibrium conditions:

$$\begin{aligned} f_1 &= \mu_\alpha(N_\alpha, V_\alpha) - \mu_\beta(N_\beta, V_\beta) = 0 \\ f_2 &= p_\alpha(N_\alpha, V_\alpha) - p_\beta(N_\beta, V_\beta) - \frac{2\sigma}{r_\alpha} = 0 \end{aligned} \quad (6)$$

with $N_\beta = N - N_\alpha$ and $V_\beta = V - V_\alpha$.

f_1 and f_2 define implecietely two functions $N_\alpha^{(1)}(V_\alpha)$ and $N_\alpha^{(2)}(V_\alpha)$ /10/, which represents the equilibrium conditions. A schematically plot of them is shown in Fig. 2. The points of

intersection of both functions give the equilibrium states of the droplet with the equilibrium values $N_{\alpha eq}$ and $V_{\alpha eq}$. One can prove /10/ that for isothermal-isochoric conditions two points of intersection exist (Fig. 2a), but for isothermal-isobaric conditions only one point is found (Fig. 2b).

A stability analysis leads to the sufficient stability condition /10/:

$$\frac{\partial N_{\alpha}^{(2)}}{\partial V_{\alpha}} > \frac{\partial N_{\alpha}^{(1)}}{\partial V_{\alpha}} \quad (7)$$

In Fig. 2 it is to be seen that we have only one stable equilibrium state obtained under isochoric conditions. The other equilibrium state for lower values of $N_{\alpha eq}$ and $V_{\alpha eq}$ is an instable one because of (7). It has a saddle-point type /7,9, 10/. If we use the approximation of an incompressible droplet it can be characterized by the droplet radius r_{α} only. The free energy in this case is shown in Fig. 3. Now only one equilibrium condition is hold similar to the known Kelvin equation /11/

$$\ln \frac{p_A}{p_{\infty}} - \frac{p_{\infty}}{c_{\alpha} k_B T} \left(\frac{p_A}{p_{\infty}} - 1 \right) = \frac{2\sigma}{c_{\alpha} k_B T} \frac{1}{r_{\alpha}} \quad (8)$$

p_A is the vapor pressure

$$p_A = \frac{N_A k_B T}{V} = \frac{(N - N_{\alpha}) k_B T}{V}$$

and the ratio p_A/p_{∞} gives the actual supersaturation instead of the initial supersaturation (1). Eq. (8) has two solutions /11/ (Fig. 4). The lower value of r_{α} is the critical radius, where the free energy (Fig. 3) has its maximum, the greater value of r_{α} gives the radius of the stable droplet. Both solutions are determined by the thermodynamic constraints. For larger initial supersaturations the critical radius becomes smaller and the stable radius becomes larger /12/.

5. Finite size effects

The thermodynamic behaviour of the system is influenced by the system size. Here we note only some aspects of this:

(1) The work of formation of equilibrium droplets is obtained

from (5) and (6) as follows /7/:

$$\Delta F_{eq} = \frac{1}{3} \sigma_0 \sigma_\alpha + (p - p_\beta) V + (\mu_\beta - \mu) N \quad (9)$$

The first term on r.h.s. is denoted as W_{Gibbs} , because Gibbs has found $W = \frac{1}{3} \sigma_0$ as the work of formation of a critical droplet in an infinite system. The second term gives corrections to the Gibbsian work, because the medium is changed in the finite system when a droplet will be formed. This term, denoted as $\Delta W(V)$, is always negative but only of second order in the density changes /7/. Both terms depend on the system volume, but their behaviour is characteristically determined by the stability of the equilibrium state /7/.

(ii) The equilibrium values $N_{\alpha eq}$ and $V_{\alpha eq}$ of the droplet depend on the system size too. If we diminish the system volume ($V \rightarrow V - \Delta V$) and the overall particle number ($N \rightarrow N - \Delta N$) in such a way that the overall density $c = N/V = (N - \Delta N)/(V - \Delta V)$ is constant then we find a change of $N_{\alpha eq}$ and $V_{\alpha eq}$ which also depends on the stability /7/. E.g. for a stable droplet $N_{\alpha eq}$ and $V_{\alpha eq}$ decreases with a decreasing system size, but for a critical droplet $V_{\alpha eq}$ increases.

(iii) In finite systems critical thermodynamic parameters exist for the formation of a stable respectively an overcritical droplet /12,13/. So we find a critical system volume V_c or a critical particle number N_c or a critical temperature T_c for the phase transition by nucleation. The critical parameters can be discussed in terms of a critical initial supersaturation y_c /12/

$$y_c = \exp \left\{ \left(\frac{4}{N} \left(\frac{4\pi}{3} c_\alpha \right) \right)^{1/4} \left(\frac{4}{3} \frac{2\sigma}{c_\alpha k_B T} \right)^{3/4} \right\} \quad (10)$$

y_c has to reach at least to realize a certain probability to find a thermodynamically stable droplet. In fact only for supersaturations larger than y_c a stable droplet is really existing in the system over a long time /14/.

6. Applications

The existence of critical parameters for a nucleation process

should be of practical importance for phase transitions in small systems. Moreover, a thermodynamic analysis allows to predict the critical and stable droplet sizes and the height of the activation barrier what has to cross over when a phase transition occurs /15/.

The thermodynamic results have been used to derive a growth equation /16/

$$\frac{dN_\alpha}{dt} = - \frac{c_B D}{k_B T} \frac{1}{L} 4\pi r_\alpha^2 \frac{\partial \Delta \phi}{\partial N_\alpha} \quad (11)$$

which describes the deterministic growth or shrinkage of the droplet size. $\Delta \phi$ is the thermodynamic potential what considers the critical radius and the depletion of the medium when the droplet grows.

The thermodynamic concept has been applied also to the formation of bubbles in a metastable liquid /17/, further the thermodynamics of nucleation under adiabatic constraints is investigated recently /18/.

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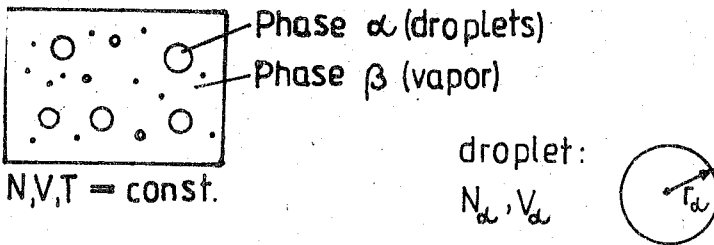


Fig. 1: The finite heterogeneous system for the condensation process in a supersaturated vapor.

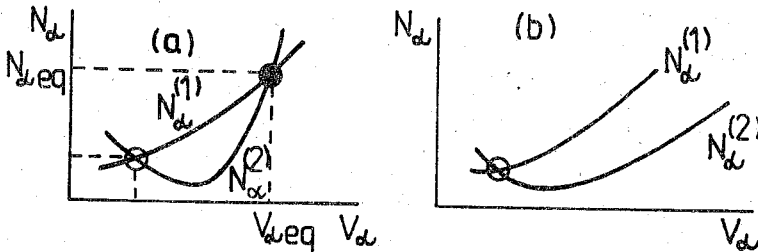


Fig. 2: Sketch of the functions $N_{\alpha}^{(1)}(V_{\alpha})$ and $N_{\alpha}^{(2)}(V_{\alpha})$ representing the equilibrium conditions (6). The points of intersections give the equilibrium states $(N_{\alpha,eq}, V_{\alpha,eq})$.
 (a) $N, V, T = \text{const.}$, (b) $N, P, T = \text{const.}$ /10/

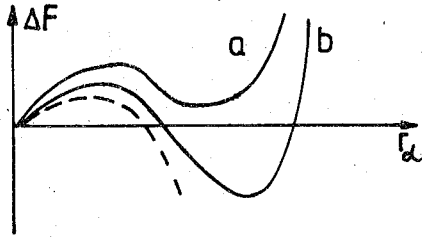


Fig. 3: Schematic plot of the free energy vs. droplet radius r_α . The initial supersaturation of plot (b) is larger than this of plot (a). The dashed line gives the free energy for the droplet formation in an infinite system.

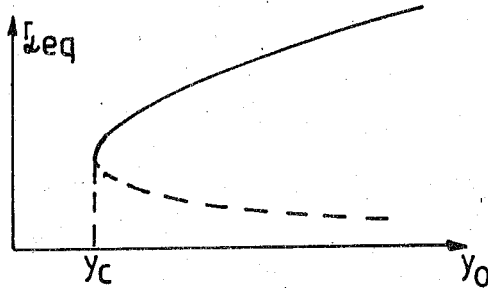


Fig. 4: Equilibrium droplet size ($r_{\alpha,eq}$) vs. initial supersaturation y_0 . The solid line gives the stable droplet radius, the dashed line the critical radius. An overcritical droplet is found only for initial supersaturations larger than y_c (eq. (10) /12/).

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Thermodynamic Description of Ferrofluids: Dissipated Mechanisms
in Micropolar Ferrohydrodynamics

1. Introduction

In the simplest mathematical models of ferrofluid as a media with intrinsic moment of momentum /1/ assignment of internal energy of unite mass V is postulated depending on constituent parameters: mass density ρ , entropy of unite mass S , magnetic field strength \vec{H} , magnetization \vec{M} and intrinsic moment of momentum \vec{k} - in the following form:

$$V = V_0(\rho, S, \vec{k}, \frac{\vec{M}}{\rho}) + \frac{H^2}{8\pi\rho} \quad (1)$$

The basic equations of continuum mechanics and electrodynamics are completed by constitutive relations using equation (1) and nonequilibrium thermodynamic methods. Thus a differential equations of the relaxation type is obtained for \vec{M} .

Such approach to getting equations of ferrohydrodynamics is somewhat limited because there are more basic differential equations than equations of variations in integral form. Hence, in particular it follows that system of jump conditions on discontinuity surfaces in ferrohydrodynamics with internal rotation appears to be not completed.

Besides, dissipated mechanisms playing significant role in large gradients regions of constitutive parameters appear not to be taking into account in the obtained equations.

2. The General System of Equations in Integral Form and Jump Conditions

In quasistationary magnetic field the following laws of changing mass, momentum, moment of momentum and energy of closed thermodynamic system "medium, electromagnetic field" hold /2/: