

Sektion Physik der Wilhelm-Pieck-Universität Rostock

Thermodynamic Limitations for Homogeneous Nucleation in Pores

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With 5 Figures and 1 Table

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Abstract

The boundaries for phase transformations in capillaries or pores deviate from the macroscopic ones. This effect is usually contributed to the interactions with the walls (capillary condensation).

In the present study it is shown that the depletion of the medium due to the phase transformation may significantly influence the process of condensation also in the absence of interactions with the walls. In particular, the depletion results in the existence of a critical system volume V_c . While for $V > V_c$ a transition may proceed by homogeneous nucleation, this is excluded for $V \leq V_c$.

The dependence of the critical volume V_c on temperature is discussed analytically and numerically for water both for a constant initial density or a constant initial supersaturation and isothermal and adiabatic constraints, respectively. Conclusions, concerning the kinetics of phase transitions in pores, are verified by calculations of the mean first passage time for the formation of a supercritical drop in dependence on the size of the pore.

1. Introduction

The analysis of the properties of small clusters, of matter in small cavities is an intensively developing area of research, both from experimental and theoretical points of view (see, e.g. [1–6]). Hereby it is found, that the behaviour of matter may change significantly in dependence on the size of the object of interest, the size of the capillary or pore, where the process takes place.

A problem of particular interest is the investigation of phase transformations in small cavities, realized, e.g., in zeolites [5] and porous glasses [7–9]. The degree, to which extent the phase transformation proceeds for a given size distribution of the pores in dependence on the chosen boundary conditions, influences significantly the properties of the material. Thus, the investigation of the influence of the system size on the course of the phase transition is of immediate technological relevance.

As a part of such investigations here the process of condensation of a supersaturated vapour in pores is analyzed from a thermodynamic point of view. The object of the analysis consists in the following problem.

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As it has been mentioned already in preceding papers [10–12] for a given temperature T and a given initial supersaturation y (or initial molar density ρ) a lower critical volume V_c of the pore exists. While for $V > V_c$ a phase transition may proceed by homogeneous nucleation, this is excluded for $V \leq V_c$. The actual value of V_c depends hereby on T and y (or ρ), thus resulting in a functional dependence $V_c = V_c(T, y)$ or $V_c = V_c(T, \rho)$, respectively.

The estimation and general discussion of this dependence for isothermal isochoric constraints and one-component systems is one main aim of the present paper (chapters 2–3). However, since in a number of practical situations the process of condensation proceeds rapidly, compared with processes of heat conduction, instead of isothermal adiabatic conditions may be more appropriate. Therefore, in chapter 4 variations of the critical volume V_c are analyzed, which are due to the switch from isothermal to adiabatic constraints.

2. Thermodynamic Analysis. General Aspects

We consider a one-component closed isochoric system first at a constant temperature T . For the chosen constraints the Helmholtz free energy is the appropriate thermodynamic potential and thermodynamic investigations on processes of the phase transformation have to be based on calculations of variations of F due to the formation of clusters of the new phase.

Assuming the parameters of the initial gas phase are chosen in such a way that a transition to the liquid may proceed, the variation of the free energy ΔF due to the formation of one drop with the radius r_α is given by [10a, 11, 12]

$$\Delta F = (p_\beta - p') V_\alpha + n_\alpha (\mu' - \mu_\beta) + \sigma A + V(p - p_\beta) + n(\mu_\beta - \mu) \quad (2.1)$$

p is the pressure, n is the mole number, V the volume, μ the chemical potential, σ the surface tension and A the surface area of the drop. The subscripts $\alpha(\beta)$ specify the parameters of the cluster (vapour), parameters without a subscript refer, in general, to the homogeneous metastable initial state. μ' and p' are the values for μ and p for a stable coexistence of both phases at a planar interface.

It is assumed here that the liquid can be considered as an incompressible one. This implies that the surface tension may depend only on temperature but not on the size of the drop [12, 15].

For a sufficiently large size of the system the function $\Delta F = \Delta F(r_\alpha)$ shows a behaviour as presented in Fig. 1. It has two extrema for $r_\alpha = r_c$ and $r_\alpha = r_{st}$, respectively. The position and character of the extrema (maximum or minimum) are determined by

$$\frac{\partial \Delta F}{\partial r_\alpha} = -4\pi r_\alpha^2 \left\{ \rho_\alpha (\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma}{r_\alpha} \right\} = 0, \quad (2.2)$$

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = -8\pi\sigma(1 + Z) \quad Z = -3 \frac{\partial \mu_\beta}{\partial \rho_\beta} \frac{r_\alpha (\rho_\alpha - \rho)^2 V_\alpha}{2\sigma \left(1 - \frac{V_\alpha}{V}\right)^3 V} \quad (2.3)$$

ρ being the molar density.

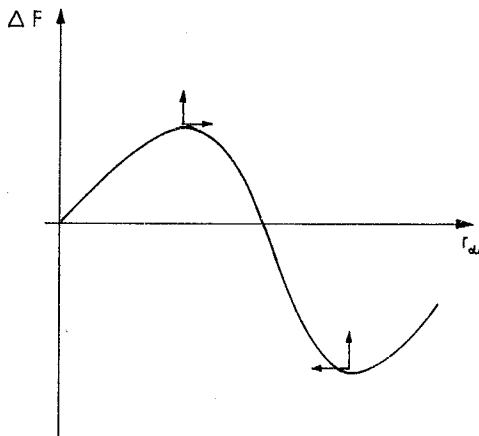


Fig. 1. Dependence of the change of the free energy ΔF , due to the formation of a drop with the radius r_α , on the size of the drop. The arrows indicate the change of the position of the extrema with a decreasing volume of the system for a constant initial supersaturation and a constant temperature

It can be obtained from eqs. (2.1) and (2.2) that the change of the position of the extrema with an increasing size of the system, the initial supersaturation being constant is given by

$$\frac{dr_\alpha}{dV} = \frac{r_\alpha}{3V} \frac{Z}{1+Z}, \tag{2.4}$$

$$\frac{d\Delta F}{dV} = -(\langle\rho_\beta\rangle - \rho)(\mu_\beta - \mu) < 0, \tag{2.5}$$

$\langle\rho_\beta\rangle$ is some intermediate value of the molar density of monomers in the vapour in the course of formation of the drop, it is less than its initial value ρ and greater than the equilibrium density ρ' .

Taking into account the extremum conditions and eqs. (2.4), (2.5), the variation of the position of the extrema with a decreasing volume V , the initial supersaturation and temperature being constant, is directed as indicated in Fig. 1 by arrows. Consequently, with a decreasing system size both extrema coincide in a point of inflexion, characterized by a common radius r_α^c . The corresponding value of the volume of the system we denote by V_c . However, to avoid unnecessary complications the subscript "c" is omitted, in general, if this cannot lead to confusion.

The values of r_α^c and V_c are determined by eq. (2.2) and $(1+Z) = 0$ (see, eq. (2.3)) or by

$$f_1 = \rho_\alpha(\mu_\beta - \mu') - (\rho_\beta - \rho') - \frac{2\sigma}{r_\alpha} = 0 \tag{2.6}$$

$$f_2 = 1 - 3 \frac{\partial\mu_\beta}{\partial\rho_\beta} \frac{r_\alpha(\rho_\alpha - \rho)^2 V_\alpha}{2\sigma \left(1 - \frac{V_\alpha}{V}\right)^3 V} = 0.$$

The indication of the existence and numerical estimations of the dependence $V_c = V_c(T, y)$ or $V_c = V_c(T, \rho)$ for special cases are given already in previous papers [10–12]. The existence of such a size effect was verified also by computer simulations of the processes of formation of a drop in finite systems (e.g. [16, 17]).

But since the equations (2.6) are highly nonlinear, the derivation of general conclusions concerning this dependence has not been carried out until now. This will be done in the next chapter.

3. Critical Values for the Size of the System in Isothermal-Isochoric Condensation

Taking into account the additional conditions $y = \text{const.}$ (or $\rho = \text{const.}$), which correspond to definite values of the initial supersaturation (initial density), and $\rho_\alpha = \rho_\alpha(T)$ (incompressibility of the liquid) it becomes evident, that the functions f_i , defined by eqs. (2.6), depend on V_α , T and V , only. Consequently, the two equations (2.6) determine V_α^c , the value of the volume of the drop corresponding to the point of inflexion of the curve $\Delta F = \Delta F(r_\alpha)$, and V_c as a function of the temperature T .

Applying the theory of implicate functions [18] we may write

$$\frac{dV_\alpha^c}{dT} = -\frac{1}{D} \begin{vmatrix} \left(\frac{\partial F_1}{\partial T}\right)_{V_\alpha, V} & \left(\frac{\partial F_1}{\partial V}\right)_{T, V_\alpha} \\ \left(\frac{\partial F_2}{\partial T}\right)_{V_\alpha, V} & \left(\frac{\partial F_2}{\partial V}\right)_{T, V_\alpha} \end{vmatrix} \quad (3.1)$$

$$\frac{dV_c}{dT} = -\frac{1}{D} \begin{vmatrix} \left(\frac{\partial f_1}{\partial V_\alpha}\right)_{T, V} & \left(\frac{\partial f_1}{\partial T}\right)_{V_\alpha, V} \\ \left(\frac{\partial F_2}{\partial V_\alpha}\right)_{T, V} & \left(\frac{\partial F_2}{\partial T}\right)_{V_\alpha, V} \end{vmatrix} \quad (3.2)$$

$$D = \left(\frac{\partial F_1}{\partial V_\alpha}\right)_{T, V} \left(\frac{\partial F_2}{\partial V}\right)_{T, V_\alpha} - \left(\frac{\partial F_1}{\partial V}\right)_{T, V_\alpha} \left(\frac{\partial F_2}{\partial V_\alpha}\right)_{T, V} \quad (3.3)$$

The partial derivatives with respect to T are different in dependence on whether the initial supersaturation y or the initial density ρ is kept constant.

An application of the Clausius-Clapeyron equation [19]

$$\frac{1}{p'} \frac{dp'}{dT} = \frac{q}{RT^2} \quad (3.4)$$

(q being the molar heat of the transition, R the universal gas constant), the perfect gas law for the vapour

$$\mu_\beta = \mu' + RT \ln \frac{p_\beta}{p'} \quad p_\beta = \rho_\beta RT \quad (3.5)$$

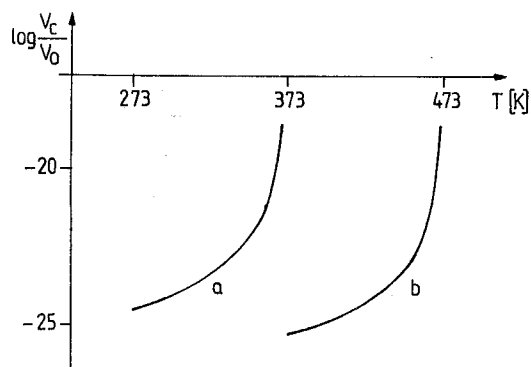


Fig. 2. The critical volume V_c as a function of temperature for two different constant values of the initial density of the vapour ($a: \rho = 33 \text{ mol} \cdot \text{m}^{-3}$; $b: 440 \text{ mol} \cdot \text{m}^{-3}$). As an example water vapour was taken. For the values of the parameters see, e.g. [21, 22]

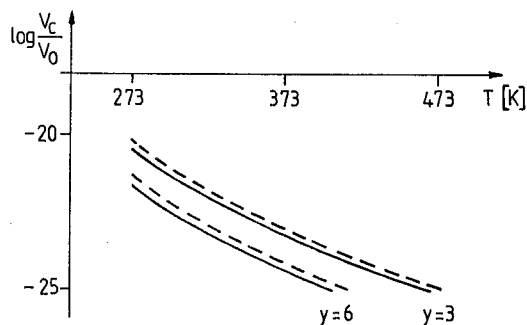


Fig. 3. Absolute (full curves) and effective (dashed curves) limits for homogeneous nucleation of water vapour as a function of temperature for different constant values of the initial supersaturation

and the relation

$$\rho_\beta = \rho \frac{1 - \frac{n_\alpha}{n}}{1 - \frac{V_\alpha}{V}} \quad (3.6)$$

we arrive after a neglect of, in general, small terms at

$$\left(\frac{dV_c}{dT} \right)_{\rho = \text{const.}} \approx \frac{3 V_c r_\alpha^c (\rho_\alpha - \rho') q}{2 \sigma T} \quad (3.7)$$

$$\left(\frac{dV_c}{dT} \right)_{y = \text{const.}} \approx - \frac{3 r_\alpha^c n_\alpha^c (\rho_\alpha - \rho') q}{2 \sigma (n - n_\alpha^c) T} \quad (3.8)$$

Results of numerical calculations, based on eqs. (2.6), (3.5), (3.6), for water are shown in Figs. 2 and 3. In agreement with the approximative analytic result (3.7) the critical volume increases with an increasing temperature, provided that the initial density is kept constant (see

Fig. 2). This increase is due mainly to the dependence of the saturation pressure on temperature (cf. eq. (3.4)).

Though the condition $\rho = \text{const.}$ can be realized easier in experiments, a more significant characteristic of the temperature dependence of phase transitions in finite systems is the dependence of the critical volume V_c on T for constant values of the initial supersaturation (see Fig. 3). Again in agreement with the analytic result (3.8) $V_c = V_c(T, y = \text{const.})$ is a monotonously decreasing function of T .

For selected values of the temperature the total number N_c of particles in the system and the number of particles N_α^c in the cluster with the volume V_α^c are given in the table. The values for $T = 473 \text{ K}$ and $y = 6$ are left open since the number of particles becomes too small to allow for a satisfactory macroscopic description.

Till now the analysis was confined to an estimation of the limiting values of the volume for which the formation of a drop is excluded, in principle. In practice, however, the system will be found in the heterogeneous state only, if the second extremum of ΔF (minimum) is sufficiently deep.

From a thermodynamic point of view it is appropriate to suggest, that the transition takes place if the minimum of $\Delta F = \Delta F(r_\alpha)$ corresponds to the same or to lower values of the thermodynamic potential compared with the metastable homogeneous initial state. Otherwise, the system will return to and be found most of the time in the homogeneous gas phase (compare [20]).

Starting with these arguments the effective or practical boundaries for a phase transition in a pore can be determined by

$$\Delta F = \left(\frac{\partial \Delta F}{\partial r_\alpha} \right) = 0 . \quad (3.9)$$

Curves, calculated based on these equations, are shown in Fig. 3 by dashed lines. They deviate only slightly from the curves, calculated via eqs. (2.6).

4. Extension to Other Types of Constraints

Since the formation of a drop is a stochastic process, it may take a long time until a sufficiently large fluctuation results in the formation of a two-phase system. The duration of this special fluctuation, leading to the formation of a drop, is, however, relatively short. Thus, processes of heat conduction are negligible and, instead of isothermal conditions, the assumption of an adiabatically closed system is more appropriate.

A general thermodynamic analysis of the process of cluster formation under adiabatic conditions was given elsewhere [14, 23, 24]. For the considered case ($U = \text{const.}$, $n = \text{const.}$, $V = \text{const.}$) the characteristic potential is the entropy S and the process of cluster formation is to be analyzed from a thermodynamic point of view by a calculation of S .

For the homogeneous initial state the entropy can be written as

$$S_{\text{hom}} = \frac{1}{T} (U + pV - \mu n) \quad (4.1)$$

while we obtain for the heterogeneous state [12, 24]

$$S_{\text{het}} = \frac{\bar{U}_\alpha + p_\alpha V_\alpha - \mu_\alpha \bar{n}_\alpha}{T_\alpha} + \frac{U_\beta + p_\beta V_\beta - \mu_\beta n_\beta}{T_\beta} \quad (4.2)$$

$$\bar{U}_\alpha = U_\alpha + U_s \quad \bar{n}_\alpha = n_\alpha + n_s .$$

U_s and n_s are the surface contributions to the inner energy U and the number of moles n [25].

Calculating $\Delta S = S_{\text{het}} - S_{\text{hom}}$ and proceeding in the same way as described for the isothermal case, we obtain, instead of eqs. (2.6), the following expressions for the size dependence of the critical volume V_c

$$\rho_\alpha (\mu_\beta - \mu') - (p_\beta - p') - \frac{2\sigma}{r_\alpha} = 0$$

$$1 - \frac{3r_\alpha}{2\sigma} \left\{ \frac{\partial \mu_\beta}{\partial \rho_\beta} \frac{(\rho_\alpha - \rho)^2 V_\alpha}{\left(1 - \frac{V_\alpha}{V}\right)^3 V} + \frac{C_V \rho (T_e - T)^2 V}{T_e V_\alpha} \right\} = 0 \quad (4.3)$$

$$T_e = T + \int_0^{n_\alpha} \frac{q dn_\alpha}{C_L n_\alpha + C_V (n - n_\alpha)} .$$

C_L and C_V are the molar heat capacities of the liquid and the vapour.

It can be seen from Fig. 4 by a comparison with Figs. 2–3 that for a given value of the initial temperature T the increase of T due to the latent heat of condensation ($T_e > T$) results in higher values of the critical volume V_c . This conclusion is generally valid and not restricted to some special choice of the parameters (compare [23]). In the limit $q \rightarrow 0$ eqs. (4.3) are reduced to eqs. (2.6), again.

In general, a behaviour as shown in Fig. 1 (the existence of a minimum) will always be found, if the phase transition is accompanied by a depletion of the mother phase. Thus the discussed effect, the existence of a critical volume V_c , always occurs in such situations and can be analyzed by the same method.

5. Discussion

The presented analysis shows in agreement with experimental investigations and results of computer simulations that the boundaries for phase transformations in small volumes are modified compared with macroscopic systems also in the case of negligible interactions with the walls. This can be verified by calculations of the mean first passage time for a formation of a supercritical drop in dependence on the actual value of the system size [11, 12].

Results, obtained for the isothermal case, are shown in Fig. 5. For volumes, comparable with the critical volume V_c the average time interval τ for the formation of a supercritical drop increases significantly compared with the macroscopic value τ_∞ and diverges as V trends to V_c .

It follows as a conclusion that for $V \simeq V_c$ an additional decrease of the temperature for fixed values of the density of monomers is needed to initiate condensation. Thus, in small cavities

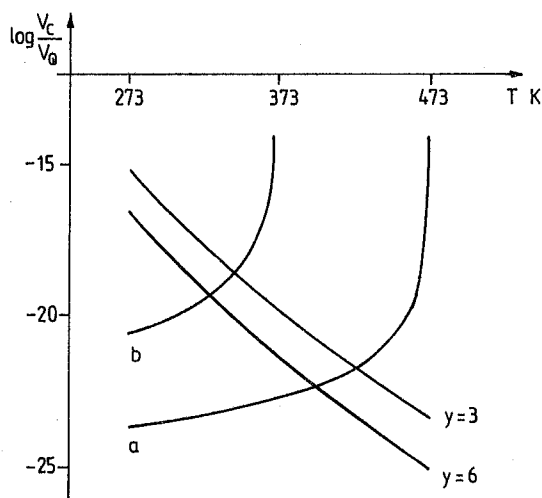


Fig. 4. Dependence of the critical volumes for constant initial densities and constant initial supersaturations, respectively, in adiabatically closed systems on temperature. T is here the initial temperature of the vapour

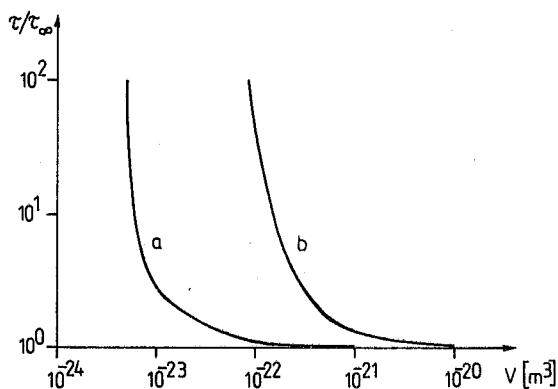


Fig. 5. Ratio of the mean first passage times for the formation of a supercritical cluster in a finite (τ) and infinite (τ_∞) system as a function of the volume of the system for two different initial supersaturations and isothermal conditions ($T = 323$ K). (a : $y = 6$; $y = 3$)

phase transitions proceed for higher undercoolings compared with macroscopic systems, if in both cases impurities or interactions with the walls may be excluded.

Besides the assumption of the absence of heterogeneities and the neglect of possible interactions with the walls another restriction of the outlined method of analysis exists. It is assumed always that the heterogeneous system consists of one cluster and monomers only. However, besides monomers and the drop also dimers, trimers and so on will be formed, in general, resulting in finite systems in an additional depletion and, consequently, in an increase

Table 1. Total number of particles N_c in the critical volume V_c and number of particles N_α^c in a cluster with the volume V_α^c for different values of the initial supersaturation and isothermal conditions

T [K]	$y = 3$		$y = 6$	
	N_c	N_α^c	N_c	N_α^c
273	1786	394	271	87
323	796	176	120	39
373	359	79	55	17
423	155	34	23	8
473	58	13	—	—

of the critical volume (see also [28]). In principle, it is possible to incorporate such effects into the thermodynamic description.

For a first qualitative understanding and a first quantitative estimation of the critical volumes for different systems the applied method seems to be more appropriate. Quantitatively exact studies require a microscopic approach (e.g. [26, 27]) taking into account explicitly also the interactions with the walls.

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