

Critical Parameters for Nucleation in Finite Systems

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We consider a supersaturated vapor in a closed and finite system. The conditions for the existence of a stable droplet of the liquid phase in this system are in principle determined by the thermodynamic parameters (N , V , T). It is shown that in deviation from the nucleation theory of infinite systems the nucleation in finite systems occurs in a smaller region of thermodynamic values. We investigate critical values of this parameters, e.g., the critical system size, the critical overall particle number, and the critical temperature, where it becomes impossible for a stable droplet to exist in the finite system. The critical parameters are discussed in terms of the initial supersaturation. © 1987 Academic Press, Inc.

1. INTRODUCTION

The behavior of systems which can initiate a phase transition is mainly determined by thermodynamic constraints like temperature, volume, pressure, and particle density. Thus, as is well known growing droplets may be developed in infinite systems under isobaric conditions for a fixed region of thermodynamic parameters only (1). Nucleation is possible if the pressure is larger than the equilibrium pressure p_∞ defined by the Maxwell rule. We consider a supersaturated vapor in a finite thermodynamic system with a fixed particle number. The phase transition is assumed to be preceded by the formation of a single droplet which is surrounded by the free particles of the vapor.

We note the simplicity of this supposed kinetic ansatz. In fact a cluster distribution which evolves due to a stochastic process is established (6). But in this paper we are mainly interested in critical values of the nucleation process which can be described sufficiently by the given model.

A thermodynamic analysis of the establishment of droplets in the initially metastable vapor can lead to a deeper insight into the late stage of this process (2, 3). In particular it gives

results for the existence of stable droplets in principle (4). In this paper the investigations are based on the consideration of a Markovian process for the growth and decay of the droplet. The condition for the existence of a stable droplet is found from the modality of its equilibrium probability distribution. Distributions with two maxima (bimodal) in the space of the spatial range of the droplet describe situations where the equilibrium state of the system is attainable by a nucleation process and a stable droplet is found. The conditions of bimodal distributions are given as dependent on the thermodynamic parameters. Therefore we find critical values of the system volume, the particle number, and the temperature for the existence of a stable droplet in finite systems.

We obtain a critical upper temperature dependent on the system size which is lower than the critical temperature for an infinite system.

It turns out in our investigations that the region for the nucleation process depends strongly on the system size. This region lessens for finite systems.

The critical parameters are discussed in terms of the initial supersaturation of the finite system where critical values are found.

2. KINETIC DESCRIPTION OF THE DROPLET EVOLUTION AND EQUILIBRIUM DISTRIBUTION

We consider a closed system with N free particles an ideal gas mixture in a finite volume V at temperature T . The thermodynamic constraints

$$N = \text{const}, \quad V = \text{const}, \quad T = \text{const} \quad [1]$$

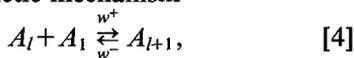
are chosen in such a way that the pressure of the supposed ideal vapor

$$p = \frac{N}{V} k_B T \quad [2]$$

is larger than the equilibrium pressure $p_\infty(T)$ of the saturated vapor coexisting with the planar interface of the liquid phase. That means that the system is in a supersaturated state. We define the initial supersaturation y as

$$y = \frac{p}{p_\infty} = \frac{N k_B T}{p_\infty V} \quad [3]$$

To reach the equilibrium state the supersaturated system will be able to initiate a first-order phase transition. In a certain region of the supersaturation the initial state is a metastable one and the phase separation takes place by a nucleation process. We suppose that a single droplet forms in the system and evolves due to the kinetic mechanism



where l is the number of particles bound in the droplet ($l \leq N$). Because of the limitation of the fixed overall particle number, the number of free particles changes with the given process. The droplet evolution [4] is assumed to be a Markovian birth and death process. If we define $P(l, t)$ to be the probability to find the droplet with l particles at time t , then the following master equation for the growth and decay of the droplet is found,

$$\begin{aligned} \frac{\partial}{\partial t} P(l, t) &= w^+(l-1)P(l-1, t) + w^-(l+1)P(l+1, t) \\ &\quad - [w^+(l) + w^-(l)]P(l, t), \quad [5] \end{aligned}$$

where w^+ and w^- are the transition probabilities per unit time as also introduced in [4]. We define them as (5, 6)

growth:

$$l \rightarrow l+1: \quad w^+(l) = \alpha l^{2/3} \frac{N-l}{V} \quad [6.1]$$

decay: $l \rightarrow l-1$:

$$w^-(l) = \alpha l^{2/3} \lambda_1^{-3} \exp\left(\frac{f_l - f_{l-1}}{k_B T}\right), \quad [6.2]$$

where λ_1 is the de Broglie wavelength of a free particle: $\lambda_1 = h(2\pi m_l k_B T)^{-1/2}$; α is a constant with respect to the special properties of the droplet like the liquid density c_α [particles/m³], the surface tension σ , the temperature, and the sticking coefficient. Equation [6.1] gives that the probability of an attachment of a free particle from the vapor to the droplet of size l increases with the surface of the droplet ($\sim l^{2/3}$) and with the density of the free particles. The term $(N-l)$ includes the finiteness of the system caused by the limitation of the overall particle number. The probability of the evaporation of a free particle from the droplet given by Eq. [6.2] is also determined by the surface of the droplet and further by an exponential term which contains the change of a potential function f_l defined by (6)

$$f_l = -Al + Bl^{2/3}. \quad [7]$$

This expression is valid only for large droplets. The constant A corresponds to the binding energy of a particle in the droplet and can be estimated from the molar evaporation heat. Later it is approximated from expressions for the stable droplet size. The second term of Eq. [7] is proportional to the surface area and the surface tension of the droplet. It reads

$$B = 4\pi\sigma(4\pi c_\alpha/3)^{-2/3}. \quad [8]$$

Computer simulations with the given transition probabilities demonstrate the several stages of the stochastic evolution of the droplet during the phase transition (7, 8). In this paper we are interested only in the equilibrium probability distribution $P^0(l)$. It follows from the condition of detailed balance that

$$P(l, t)w^+(l) = P(l + 1, t)w^-(l) \quad [9]$$

which is an inherent property of the assumed transition probabilities.

We find for $P^0(l)$

$$P^0(l) = P_N \prod_{j=2}^l \frac{w^+(j-1)}{w^-(j)} \quad [10]$$

with the normalization

$$P_N = \left(\sum_{n=1}^N P^0(n) \right)^{-1} = \left(1 + \sum_{n=2}^N \prod_{j=2}^n \frac{w^+(j-1)}{w^-(j)} \right)^{-1}.$$

We underline that $P^0(l)$ is the equilibrium probability distribution to find the droplet with l particles. It contains the main information concerning the stability of the droplet.

Due to the thermodynamic parameters, $P^0(l)$ can be a bimodal or a unimodal distribution. The maxima of $P^0(l)$ define the stable equilibrium states. A maximum of $P^0(l)$ in the range of large l characterizes the existence of a stable droplet in the system, while a maximum in the range of small l ($l \leq l_0$; l_0 is of molecular range order) means that the droplet has with a certain probability such a minor size that it is considered to be a part of the vapor.

If $P^0(l)$ is a bimodal distribution, transitions between the two stable states are possible (7, 8). The maxima are separated by a minimum of $P^0(l)$ that is relative to the critical droplet size caused by the nucleation barrier for the formation of the critical surface of the droplet.

Figure 1 shows $P^0(l)$ dependent on the thermodynamic constraints. If the only maximum of $P^0(l)$ exists for the state $l = 1$ no stable droplet can be found (Fig. 1a). To expect a stable droplet in the system we are therefore interested in a maximum of $P^0(l)$ for large l .

3. CONDITION FOR THE STABLE EXISTENCE OF A DROPLET

The extremum condition for the equilibrium probability distribution can be written approximately as

$$P^0(l^E) = P^0(l^E + 1). \quad [11]$$

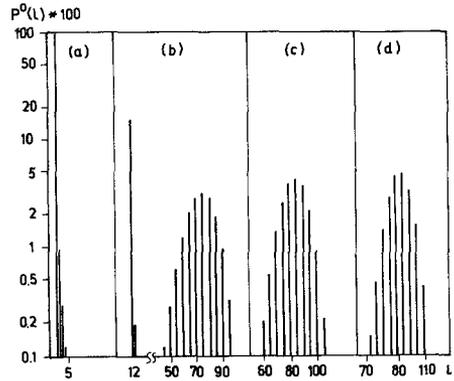


FIG. 1. Equilibrium distribution $P^0(l)$ of the droplet for various values of the system volume V or the initial supersaturation y , respectively. The maximum states are relative to the stable states of the droplet. A large stable droplet is found only for larger supersaturations. The first maximum of (c) and (d) is smaller than 0.1 but has not vanished yet. Vapor: ethanol, $T = 290$ K, $N = 150$. (a) $V = 2.75 \times 10^{-23}$ m³, $y = 3.86$. (b) $V = 2.5 \times 10^{-23}$ m³, $y = 4.63$. (c) $V = 2.25 \times 10^{-23}$ m³, $y = 5.15$. (d) $V = 2.0 \times 10^{-23}$ m³, $y = 5.79$.

With the condition of detailed balance [9] we get the extremum condition

$$w^+(l^E) = w^-(l^E + 1). \quad [12]$$

With Eq. [6] it results in

$$\ln \left(\frac{l^E}{l^E + 1} \right)^{2/3} + \ln \frac{N - l^E}{V} \lambda_1^3 = \frac{1}{k_B T} (f_{l^E+1} - f_{l^E}). \quad [13]$$

The first term of Eq. [13] is small and can be neglected except for very small clusters. The right-hand side of Eq. [13] is transformed into

$$f_{l+1} - f_l = -A + B((l+1)^{2/3} - l^{2/3}) \approx -A + \frac{2}{3} B l^{-1/3}.$$

Thus we get

$$\ln \frac{N - l^E}{V} \lambda_1^3 + \frac{A}{k_B T} = \frac{2}{3} \frac{B}{k_B T} (l^E)^{-1/3}. \quad [14]$$

If instead of the bound particle number l the radius of the droplet is introduced,

$$r^3 = \left(\frac{4}{3} c_\alpha \right)^{-1} l, \quad [15]$$

then Eq. [14] leads to

$$\ln \frac{N - (4\pi/3)c_\alpha r_E^3}{V} \lambda_1^3 + \frac{A}{k_B T} = d_0 \frac{1}{r_E}, \quad [16]$$

where d_0 is the capillary length: $d_0 = 2\sigma \times (c_\alpha k_B T)^{-1}$. Now we must determine the constant A in such a way that in the limit of large droplets Eq. [16] must agree for the stable droplet radius with the Kelvin equation (10), well known from equilibrium thermodynamics:

$$\ln \frac{p(r)}{p_\infty} = d_0 \frac{1}{r}. \quad [17]$$

Equation [17] gives a relation between the equilibrium pressure $p(r)$ above a curved surface and the curvature of this surface for small departures from planarity. In the case considered the equilibrium pressure for the vapor coexisting with the stable droplet is given by

$$p(r_s) = \frac{N - (4\pi/3)c_\alpha r_s^3}{V} k_B T,$$

where r_s is the radius of the stable droplet. Thus it follows that

$$A = -k_B T \ln \frac{p_\infty}{k_B T} \lambda_1^3. \quad [18]$$

Inserting A in Eq. [16] the extremum condition reads

$$\ln \frac{(N - (4\pi/3)c_\alpha r_E^3)k_B T}{p_\infty V} = d_0 \frac{1}{r_E}. \quad [19]$$

Thus we obtain a relation between our kinetic ansatz [6] and the equilibrium thermodynamics in the limit of large droplets.

A truncated Taylor expansion of the logarithm in Eq. [19] leads to

$$r_E^4 + Rr_E + S = 0 \quad [20]$$

with

$$R = -N \ln \frac{Nk_B T}{p_\infty V} \left(\frac{4\pi}{3} c_\alpha \right)^{-1} < 0$$

$$S = Nd_0 \left(\frac{4\pi}{3} c_\alpha \right)^{-1} > 0. \quad [21]$$

Equation [20] possesses only two positive solutions dependent on the thermodynamic pa-

rameters (11) and gives the extremum droplet sizes. The smaller value of r_E corresponds to the critical droplet size, the greater value to the stable droplet size, respectively. Figure 2 shows the two solutions of Eq. [20] dependent on the system size.

Two solutions of Eq. [20] can be observed only if the inequality holds:

$$\left(\frac{R}{4} \right)^4 - \left(\frac{S}{3} \right)^3 > 0. \quad [22]$$

It is a condition to find a stable droplet in the system. When both solutions coincide the stable droplet loses its stability and becomes part of the vapor. By the equality of [22]

$$\left(\frac{R}{4} \right)^4 = \left(\frac{S}{3} \right)^3, \quad [23]$$

the second maximum of the probability distribution vanishes. This case defines the critical thermodynamic parameters for the existence of a stable droplet.

4. DETERMINATION OF THE CRITICAL THERMODYNAMIC PARAMETERS

Equation [23] allows the investigation of the critical values N_c , V_c , and T_c . We get the relation

$$N \left(\ln \frac{Nk_B T}{p_\infty V} \right)^4 = 4 \left(\frac{4\pi}{3} c_\alpha \right) \left(\frac{4}{3} d_0 \right)^3. \quad [24]$$

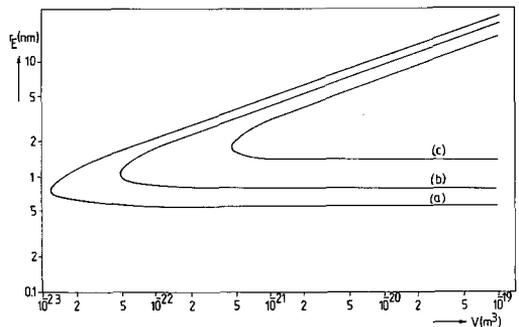


FIG. 2. Solutions of Eq. [20] dependent on the system volume V . r_E is the extremum droplet size. The smaller value of r_E corresponds to the critical droplet size, the greater value to the stable droplet size. Vapor: Ethanol, $N/V = 4 \times 10^{24} \text{ m}^{-3}$. (a) $T = 280 \text{ K}$. (b) $T = 290 \text{ K}$. (c) $T = 300 \text{ K}$.

Let us first discuss this condition for a given temperature $T = \text{const}$. For a given system size V , a critical overall particle number N_c results from Eq. [24] which must at least exist in the system to find a stable droplet in it.

For a given value of N we get a critical volume V_c of the system which does not permit it to cross over when expecting a stable droplet state. The critical values N_c and V_c are represented in Fig. 3, which gives for $T = \text{const}$ the region of the thermodynamic parameters N and V where a nucleation process in a finite system may lead to an overcritical droplet. This is the bistable region of the system; outside this region of the N, V, T space the initial vapor phase is the only stable state of the system. In a second point of discussion of the critical parameters we want to consider the relation between the critical temperature T_c and the system size V . T_c is that temperature where for given parameters N and V the coexistence between droplet phase and vapor phase vanishes because a stable droplet is not able to exist. That is why T_c is the limiting upper temperature for a possible phase separation. It is implicitly defined by Eq. [24], but we must take into account that the equilibrium pressure p_∞ , the surface tension σ , and the particle density c_α in the droplet depend on

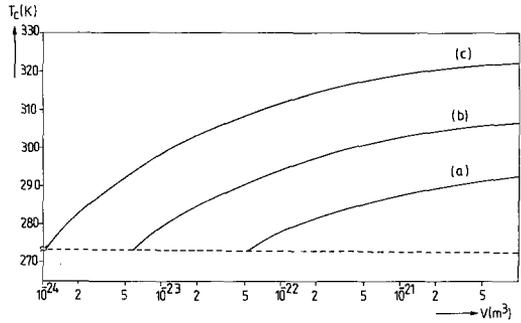


FIG. 4. Critical temperature T_c versus system volume V . If $T > T_c$ the binodal region of the finite system is left and no nucleation can be obtained. T_c is plotted for various overall particle densities. (a) $N/V = 2 \times 10^{24} \text{ m}^{-3}$, (b) $N/V = 4 \times 10^{24} \text{ m}^{-3}$, (c) $N/V = 8 \times 10^{24} \text{ m}^{-3}$. Vapor: ethanol.

the temperature, too. For numerical calculations and also to receive the given figures, we use well-confirmed temperature dependences for these parameters (12).

For an analytical result we set $\sigma = \text{const}$ and $c_\alpha = \text{const}$ in a first approximation. The temperature dependence of p_∞ can be estimated in a simple way by van't Hoff's law,

$$p_\infty(T) = p_\infty^0 \exp\left(-\frac{1}{k_B T} q\right) \quad [25]$$

with

$$p_\infty^0 = p_\infty(T_0) \exp\left(\frac{q}{k_B T_0}\right) = \text{const},$$

where q is the evaporation heat per particle and is assumed to be constant. With the ansatz [25] we get from Eq. [24] a differential equation for the change of the critical temperature T_c with varying system size V , where V_c is given by Eq. [24]:

$$\frac{dT_c}{dV} = \frac{T_c}{V_c} \left\{ 1 - \frac{4}{\ln(Nk_B T/p_\infty^0 V)} \right\}^{-1} \quad [26]$$

For the metastable region the term in brackets is greater than zero. Thus the critical temperature of a finite system becomes smaller than the critical temperature of an infinite system. A decrease in the system size leads to a diminution of the critical temperature which gives the upper limit for a stable phase separation by nucleation. In Fig. 4 the critical temperature

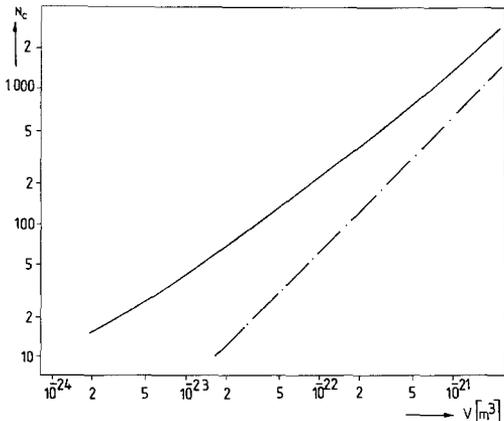


FIG. 3. Critical overall particle number N_c versus system volume V . Only for $N > N_c$ is a coexistence of the droplet in the vapor possible. The dashed-dotted line gives the saturation particle number $N_0 = p_\infty V/k_B T$. Vapor: ethanol, $T = 280 \text{ K}$.

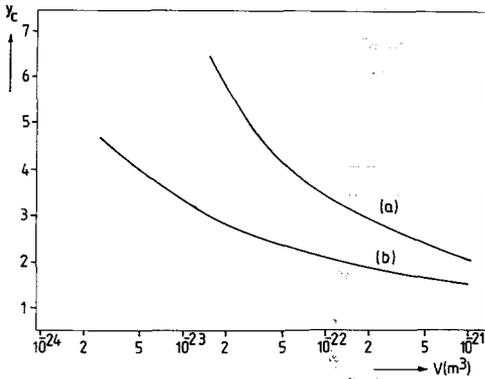


FIG. 5. Critical supersaturation y_c versus system volume V . For $y < y_c$ an overcritical droplet cannot be established. (a) $T = 280$ K. (b) $T = 312.15$ K. Vapor: ethanol.

T_c is calculated by means of Eq. [24] dependent on the system size. Asymptotically T_c must tend to the critical temperature for macroscopic systems. As is shown in Fig. 2 and pointed out in former investigations (3), a decrease in the volume of the system leads to a decrease in the size of the stable droplet. Thus a relation between a decreasing volume of the stable droplet and a decreasing critical temperature exists that can be noted to be in agreement with molecular dynamics simulations of small drops (see, e.g. (13, 14)).

5. DISCUSSION

The existence of critical thermodynamic parameters for the nucleation in finite systems should have practical importance in phase transitions in small systems, particularly in porous media. The finite size effects discussed

in Section 4 can be summarized by a discussion of the supersaturation y defined by Eq. [3]. From Eq. [24], a critical supersaturation y_c follows for the initial system:

$$y_c = \exp\left\{\left(\frac{(4\pi/3)c_\alpha}{N/4}\right)^{1/4} \left(\frac{4}{3}d_0\right)^{3/4}\right\}. \quad [27]$$

For the initial supersaturation $y < y_c$ the system possesses only one stable state, which is the vapor phase. No overcritical droplet can be formed because the pressure of the system decreases faster than the droplet reaches the overcritical size, due to the attachment of free particles by the droplet. This effect is caused by the finiteness of the system.

For $y > y_c$ it is possible for a stable droplet to exist. That means that y_c must be reached at least initially to insert the nucleation process in the finite system (see Fig. 5).

For $y = y_c$, Eq. [23] is held and the critical and the stable droplet sizes coincide. In this case the droplet is not really stable; as pointed out in thermodynamic investigations (4, 15) we obtain a saddle point-type state.

It is seen in Fig. 1 that with an increasing supersaturation the equilibrium probability to find a stable droplet with a large size is also increasing. In fact the probability to find the droplet as a part of the vapor diminishes. For a big supersaturation this probability vanishes. Thermodynamically it means that for this supersaturation the nucleation barrier disappears and a critical droplet size does not exist. In this case the nucleation process is converting into a spinodal decomposition, which means

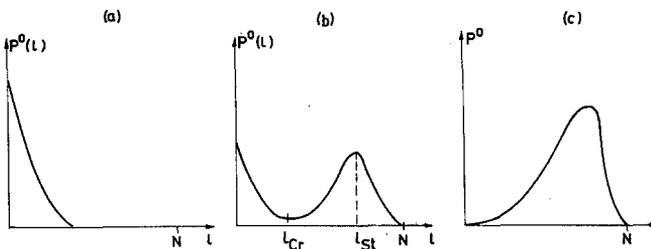


FIG. 6. Schematic plot of the equilibrium probability distribution $P^0(l)$ dependent on the initial supersaturation y . (a) $y < y_c$. (b) $y_c < y < y_{sd}$. (c) $y > y_{sd}$.

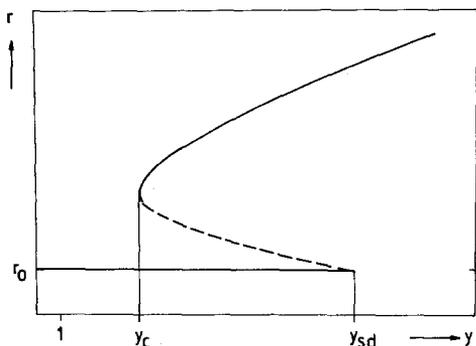


FIG. 7. Stable and critical droplet radius as a function of the initial supersaturation (schematic plot). A phase transition by nucleation occurs only in the range $y_c < y < y_{sd}$.

in our consideration that the droplet reaches its stable spatial range explosively fast.

We can estimate this critical value of the supersaturation by means of the extremum condition Eq. [19]. We assume in this case that the critical droplet radius is of molecular size r_0 . Thus it holds that $N - (4\pi/3)c_\alpha r_E^3 \approx N$. In a raw approximation we get the supersaturation for the conversion into spinodal decomposition:

$$y_{sd} \approx \exp\left(\frac{d_0}{r_0}\right). \quad [28]$$

Let us note again that in the case of big supersaturations the kinetics of phase transition may be quite different from the given model. But we are interested in y_{sd} only to discuss approximately the range of bistable behavior of the system.

The results of Section 5 are concluded in Figs. 6 and 7. There the shape of the equilibrium distribution is plotted dependent on the initial supersaturation (Fig. 6). It shows clearly the close relation between the thermodynamic parameters and the existence of a stable vapor or a stable droplet.

In Fig. 7 we show the extremal values of the probability distribution dependent on the

initial supersaturation. The bistability of the considered system for $y_c < y < y_{sd}$ is demonstrated. The phase transition by a nucleation process takes place only for a supersaturation between y_c and y_{sd} .

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