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On the Nucleation Barrier in Finite Systems: an Investigation of the Thermodynamic Potential

1. Introduction

A number of important processes in chemistry, electronic sciences, or solid state physics, to name only some subjects, is based on the event that the system escapes a former filled stable state and crossover into another stable state, for instance in a trigger switching from the state 0 to the state 1.

From a physical point of view we have some questions about this system, e.g. how long does it remain at the stable state, how long does it take to leave the former stable state and arrive to the next stable state, what is the way for that transition and so on. It has been shown that the answers generally depend on the stability of the several states [1, 2], therefore we have the problem to know the potential of the system what determines the stability essentially.

We consider in the following a system with two relative stable states which are separated by an energy barrier. The state characterising the initial situation, is assumed to be metastable, that's why it will be left with a certain probability [2].

A concrete example of a bistable system is a supersaturated vapor. The initial metastable phase is then given by the supersaturated vapour phase only, but in the stable

state a coexistence of the liquid phase and the saturated vapour is found.

The transition from the metastable to the final stable state corresponds to a phase transition, given in this case by an condensation process. This condensation process can be well described by the model of nucleation. Generally the classical nucleation theory is known. There the nucleus or cluster is described as a droplet with an incompressible density and a constant surface tension. The free energy for the formation of the droplet is presented in Fig. 1.

The maximum of the energy corresponds to a critical droplet size, which the droplet has to reach at least to grow further. This maximum depends on the supersaturation of the vapour and characterizes the nucleation barrier what has to crossover during the phase transition.

The classical concept of nucleation is only valid for infinite systems where the pressure is constant. For a finite system with a constant volume and a constant overall particle number we find two extrema of the free energy determined by the thermodynamic constraints.

Except from the critical droplet state, given by the energy maximum, a stable state of the droplet exists, corresponding to a minimum of the energy. Such a model has been widely analyzed in recent time, for details, e.g. discussions of stability and equilibrium conditions, see [4-7] and references therein.

It was pointed out that a maximum of the energy is hold only for a droplet description with one variable, e.g. its particle number or its volume, presuming the incompressibility of the droplet. A more detailed description of the droplet by two variables leads to a thermodynamic saddle point instead of a maximum of the energy. Both thermodynamic equilibrium states, the saddle point and the minimum, are shown in Fig. 2 for one droplet characterized by two variables.

In this paper we further consider a model what describes the cluster only with one variable, that's the number of particles bound in the cluster. Instead of a single cluster we suppose a cluster distribution, which the thermodynamic potential is investigated for. We expect for this potential in dependence on the distribution regions of lower energy corresponding to relative stable states and a region of higher energy what separates this stable regions and can be interpreted as a barrier for the phase transition.

An analysis of the potential for some special cases is followed by conclusions for the probable course of the phase transition for the given model. We show that this model has the for bistable systems typical properties and discuss them in terms of the cluster distribution.

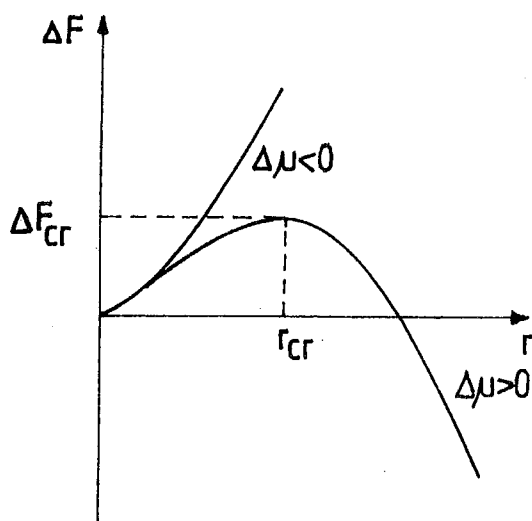


Fig. 1

Free energy of the formation of the droplet vs. droplet radius r (infinite system)
 $\Delta\mu$ — difference between the chemical potentials of the vapor and the liquid phase
 r_{cr} — critical droplet size

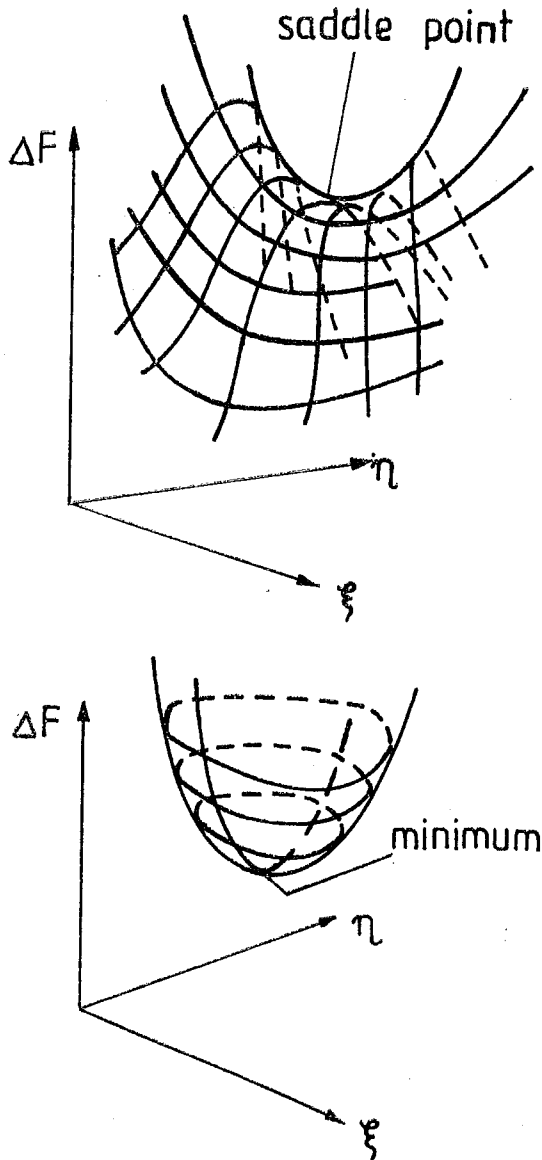


Fig. 2 (a + b)
Shape of the free energy vs. two coordinates of the cluster /3/
The saddle point (a) and the minimum (b) characterize the two equilibrium states (unstable and stable state) of the single cluster in the finite system.

2. The free energy of an ideal mixture of clusters and free particles

We consider a closed and finite system with N free particles and fix the thermodynamic constraints

$$N = \text{const.}, \quad V = \text{const.}, \quad T = \text{const.} \quad (2.1)$$

in such a way that the pressure of the supposed ideal vapour

$$p = \frac{N}{V} k_B T \quad (2.2)$$

is larger than the equilibrium $p_\infty(T)$ for the saturated vapour at a planar liquid interface.

Due to interactions between the particles a nucleation process can occur in the system, that means, the particles will bound in clusters, and a configuration of free particles (monomers), dimers (bound states of two particles), trimers ... is developed.

This configuration will be described by /8, 9/

$$N = \{N_1 N_2 N_3 \dots N_{n-1} N_n N_{n+1} \dots N_N\} \quad (2.3)$$

N_n is the number of clusters with n bound particles. Because of the conservation of the overall particle number (2.1) the relation holds:

$$N = \sum_{n=1}^N n N_n = \text{const.} \quad (2.4)$$

For the maximum number of clusters with n particles it follows:

$$0 \leq N_n \leq \frac{N}{n}, \quad n = 1, \dots, N \quad (2.5)$$

The configuration N can be interpreted as a discrete cluster distribution. The time evolution of this distribution from the supposed initial state of the N free particles to the stable state we former investigated by computer simulation techniques /9/.

Here we note only that first in a quasistationary time scale a distribution of some small (undercritical) clusters is developed what is related to the metastable state of the system. The escape of this metastable state is an intrinsic stochastic process which is characterized by overwhelming an activation barrier. After the crossover the relaxation to the stable state of the system in a stationary time scale can be described by a deterministic equation (see /9, 10, 12/ and references therein).

In this paper we are interested in the shape of the thermodynamic potential to discuss the extremum states for the given discrete cluster distribution.

Assuming that the cluster and the free particles are an ideal mixture we deduced in former investigations the free energy of the configuration (2.3) as:

$$F(T, V, N_1, N_2, \dots, N_N) = \sum_{n=1}^N N_n \left\{ f_n + k_B T \left(\ln \frac{N_n}{V} \lambda_n^3 - 1 \right) \right\} \quad (2.6)$$

For a detailed explanation of the given formula see originally ref. /8, 9/.

$F(T, V, N)$ (2.6) includes the contribution of the pressure p and the Gibbs potential G of the cluster distribution: $F = G - pV$.

The pressure

$$p = - \frac{\partial F}{\partial V} = \frac{k_B T}{V} \sum_{n=1}^N N_n \quad (2.7)$$

results from the partial pressures of the different kinds of clusters and the monomers.

The Gibbs potential is given by

$$G = \sum_{n=1}^N \mu_n N_n$$

where

$$\mu_n = f_n + k_B T \ln \frac{N_n}{V} \lambda_n^3 \quad (2.8)$$

is the chemical potential per cluster of size n . It consists of a potential term f_n discussed in the following and the contribution of the mixing entropy as the second term.

λ_n is the De Broglie wave length of a cluster with size n . F_n is related to the binding energy of the cluster. In a first approximation we choose the following ansatz with respect to the theory of atomic nuclei: /8, 9/

$$f_n = -A_n + B_n^{2/3} \quad (2.9)$$

The term A_n corresponds to the binding energy of the particles inside the cluster. The constant A can be calculated from the molar evaporation heat. Another, but quite equal estimation what is more convenient for analytical results is given in /11/ and leads to:

$$A = -k_B T \ln \frac{p_\infty}{k_B T} \lambda_1^3 \quad (2.10)$$

The term $B_n^{2/3}$ considers the surface energy of the cluster. We obtain for the constant B:

$$B = 4\pi\sigma \left(\frac{4\pi}{3} c_a \right)^{-2/3} \quad (2.11)$$

with σ being the surface tension and c_a being the particle density of an incompressible macroscopic liquid phase.

We note that the specific properties of the clusters are described similar to the droplet model of classical nucleation theory. The ansatz (2.9) for f_n is satisfied only for large clusters. For small clusters where interactions between all particles inside the cluster are yet possible we need another form of f_n /9/:

$$f_n = \frac{A}{2} n(n-1) \quad (2.12)$$

Thus it holds particularly:

$$f_1 = 0; f_2 = -A \quad (\text{two-particle binding energy})$$

In the following we use consequently the form (2.9) for f_n ($n=2, \dots, N$) and $f_1 = 0$, keeping in mind a certain inequality in the description of small clusters.

3. Discussion of the free energy

Now we investigate in a numerical analysis the free energy of the system in dependence on the cluster distribution. First we introduce a constant F_{id}

$$F_{id} = Nk_B T \left\{ \ln \frac{N}{V} \lambda_1^3 - 1 \right\} = \text{const.} \quad (3.1)$$

what represents the free energy of a system with the constraints (2.1), but N non-interacting free particles /9/. Calculating the value

$$\Delta F = F(T, V, N_1, N_2, \dots, N_N) - F_{id}(T, V, N) \quad (3.2)$$

with the restrictive condition

$$N_1 = N - \sum_{n=2}^N n N_n \quad (3.3)$$

following from the conversion of the overall particle number we receive for (3.2) with (2.9) and (2.10):

$$\begin{aligned} \frac{\Delta F}{k_B T} = & \left(N - N_1 \right) + N_1 \ln \frac{N_1 k_B T}{p_\infty V} \quad \left. \vphantom{\frac{\Delta F}{k_B T}} \right] F_1 \\ & + \frac{B}{k_B T} \sum_{n=2}^N n^{2/3} N_n \quad \left. \vphantom{\frac{\Delta F}{k_B T}} \right] F_2 \\ & + \sum_{n=2}^N N_n \left\{ \ln \frac{N_n}{V} \lambda_n^3 - 1 \right\} \quad \left. \vphantom{\frac{\Delta F}{k_B T}} \right] F_3 \\ & - N \ln \frac{N k_B T}{p_\infty V} \quad \left. \vphantom{\frac{\Delta F}{k_B T}} \right] F_4 \end{aligned} \quad (3.4)$$

In the formula (3.4) we distinguish four parts F_1, F_2, F_3, F_4 ; the last, F_4 , being a constant what further is ignored. F_1, F_2, F_3 represent the change of the free energy of the system caused by the establishment of the cluster distribution. F_1 considers the change of the monomer phase because the number of free particles diminishes due to the formation of clusters.

F_2 stands for the surface energy of the cluster distribution. F_3 corresponds to the mixing entropy and the partial pressure of the clusters.

Tab. 1:

Free energy (3.4) of the cluster distribution for a constant number of clusters $\sum_{n=2}^N N_n = 6$

cluster distribution	$\Delta F/k_B T$	$F_1/k_B T$	$F_2/k_B T$	$F_3/k_B T$
2^6	-106,59	-23,68	50,66	-133,58
4^6	-105,71	-46,32	80,43	-139,82
$2^3 3^1 4^1 5^1 6^1$	-115,76	-42,62	74,48	-147,61
$10^1 2^3 3^1 5^1 7^1$	-141,18	-172,02	183,62	-152,79

Tab. 2a

Free energy (3.4) of the cluster distribution for a constant number k of bound particles
a) $k=10$ b) $k=108$

cluster distribution	$\Delta F/k_B T$	$F_1/k_B T$	$F_2/k_B T$	$F_3/k_B T$
5^2	-38,17	-19,81	31,11	-49,47
2^5	-89,81	-19,81	42,44	-112,23
10^1	-21,58	-19,81	24,69	-26,46
$2^1 3^1 5^1$	-58,89	-19,81	35,06	-74,14

Tab. 2b

cluster distribution	$\Delta F/k_B T$	$F_1/k_B T$	$F_2/k_B T$	$F_3/k_B T$
54^2	-67,67	-163,07	152,01	-56,01
$80^1 20^1 8^1$	-87,05	-163,07	159,02	-83,23
108^1	-72,46	-163,07	120,65	-30,03
$106^1 2^1$	-89,53	-163,07	127,60	-54,06

If we would neglect F_3 in our theory and assume further that the clusters are all identical, a close connection to the results of a former thermodynamic analysis is obtained /5, 6/.

The different parts of ΔF are represented in Tab. 1, 2a, b for various cluster distributions. These distributions are chosen in such a way, that in Tab. 1 the whole number of clusters $\sum_{n=2}^N N_n$ is constant, but in Tab. 2a, b the whole

number of bound particles $\sum_{n=2}^N n N_n$ ist constant.

The numerical results are received for a system of ethanol vapour with the thermodynamic constraints:

$$N = 150, V = 2,0 \cdot 10^{-20} \text{m}^3, T = 290 \text{ K}$$

In this case we have $A/k_B T = 19,08$ and $B/k_B T = 5,32$.

To simplify the notation of the cluster distribution we use an abbreviation; the number of clusters of size n is written as an exponent. e. g. $2^3 3^1 108^1$ means that we have three clusters of size two, one of size three and one cluster of size 108 in the system. The number of free particles is given by (3.3). Tab. 1 demonstrates that the mixing entropy for different specieses of clusters has a greater value than those for the same number of identical clusters. The contribution of the parts F_1 and F_2 became apparent only in the case of clusters with great sizes, naturally. In this case the surface energy has an important amount but ΔF has a greater negative values because the influence of F_1 on ΔF increases.

Tab. 2a, b shows additionally that F_1 depends only from the whole number of bound particles and that the mixing entropy is mainly determined by the number of clusters instead of their sizes.

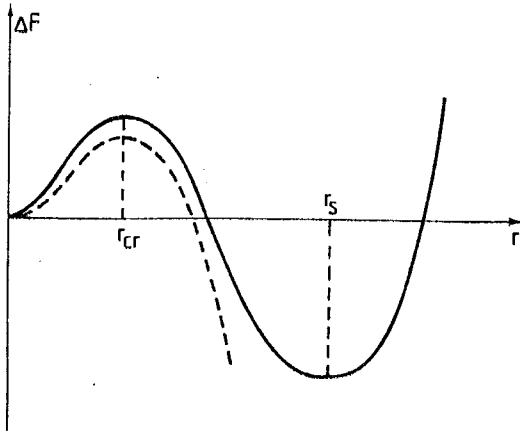


Fig. 3
Free energy of the formation of the cluster vs. cluster radius r (finite system)
 r_{cr} - critical cluster size
 r_{st} - stable cluster size
The dashed line gives the formation energy of the infinite system.

4. Extrema of the free energy

4.1. Analytical results

In the nucleation theory the extremum values of the potential require the main interest, because they define the equilibrium states, their location and stability.

A simple case is obtained for a system, which contains only one cluster in a bath of free particles. The thermodynamic potential in this case is schematically shown in Fig. 3. We have a maximum of ΔF corresponding to the instable state which represents the nucleation barrier, and, additionally, a minimum for large clusters in the system. The equilibrium condition in this case is given by the well known Kelvin equation [5, 11/:

$$\ln \frac{p(r)}{p_\infty} = d_0 \frac{1}{r} \quad (4.1)$$

r is the radius of the cluster, d_0 the capillary length, p_∞ the saturation pressure above a planar surface and $p(r)$ the equilibrium pressure above the curved surface of the cluster. In infinite system we get only one solution of (4.1) with respect to the critical radius (see Fig. 1 or 3), but in finite systems two solutions are held, corresponding to the critical and the stable radius of the cluster. For further discussions see ref. [5, 11/]. For a model considered in this paper we generally receive the extrema of the free energy (2.6) from the condition:

$$\frac{\partial F(T, V, N_1, \dots, N_N)}{\partial N_n} = 0 \quad (n = 2, \dots, N) \quad (4.2)$$

with the restrictive condition (3.3). With (2.6) and (2.9) we get from (4.2) the equilibrium cluster distribution [8, 9/:

$$N_n^0 = \frac{V}{\lambda_n^3} \exp \left\{ n \ln \frac{N_1 k_B T}{p_\infty V} - \frac{B}{k_B T} n^{2/3} \right\} \quad (4.3)$$

where N is the number of clusters of size n for the equilibrium state. With the expression for the chemical potential (2.8) and (2.9) the equilibrium condition is held in the known form of a mass action law

$$\mu_n^0 = n \mu_1^0 \quad (n = 2, \dots, N) \quad (4.4)$$

The eqs. (4.3) or (4.4) mean a system of $N-1$ equations which are to be solved simultaneously with respect to (3.3). It leads to a *continuous* distribution for the N_n^0 .

But in the considered model we are more interested in a *discrete* equilibrium distribution for the N_n^0 . That's a quite complicated problem. Mathematically $F(T, V, N_1, N_2, \dots, N_N)$ is a hyperplane in the space of the different kinds of clusters.

To get some information about the extrema of the free energy we investigate originally ΔF (3.4). We use a computer program for a KC 85/2 (see [13/]), what realizes a discrete search of the extremum values. The different cluster distributions are generated by hand, that means a purposeful search, instead of an automatic generation of the distributions which is more extensive in time, because most of the distributions generated in this way are not of interest.

The presentation of the free energy is given for two special cases corresponding to two cuts of the hyperplane of ΔF . We discuss the extrema of the free energy either for a constant number of clusters or for a constant number of bound particles in the clusters.

Our starting point for searching for the extrema are the extremum values of F in the case of only one cluster in the system, that means $\sum_{n=2} N_n = 1$.

4.2. Extrema for identical clusters

First we want to discuss the extremum values of ΔF for a constant number of clusters in the system. The results are demonstrated in Tab. 3 and Fig. 4.

Tab. 3:

Maximum values of the free energy (3.4) for a constant number of clusters. The related cluster distribution for the extremum value is given with an abbreviation, explained in chapter 3.

number of clusters	maximum of the free energy ($k_B T$)	related cluster distribution
1	-19,61	3
2	-37,77	3 ²
3	-55,35	3 ³
4	-72,53	3 ⁴
5	-89,30	4 ⁵
6	-105,77	4 ⁶

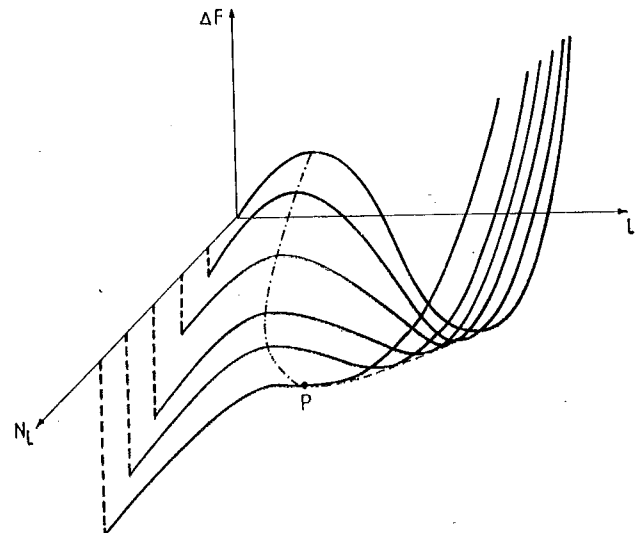


Fig. 4

Free energy of the formation of identical clusters n is the number of bound particles in the cluster, N_n is the number of clusters. The presentation considers the mixing entropy. P is the inflexion point hold for vanishing extrema at a critical number of clusters. The dashed line connects the minima, the dashed-dotted line the maxima of ΔF for different N_n .

For the given thermodynamic constraints the maximum of ΔF for one cluster is held for a cluster size of three particles. With an increasing number of clusters the free energy becomes more negative, as discussed before. But a maximum of ΔF for a constant number of clusters is obtained only for identical clusters. For distributions with clusters of different sizes smaller values of ΔF are found caused mainly by the influence of the mixing entropy.

To discuss further the extrema for a constant number of *identical* clusters we note that a true maximum of the free energy (extremum) is found only up to six clusters for $N = 150$ particles (see Tab.3). For seven or more clusters we obtain no true extremum in this case. The free energy then is a monoton increasing function of the cluster size.

In Fig. 4 the results are schematically represented for identical clusters. We also find a minimum of ΔF what is characteristic for the finite system only up to a certain number of clusters. Instead of true extrema, at a critical number of identical clusters only an inflexion point of the free energy exists. Starting with this point P we observe the known "valley of the free energy" consisting of the minima of the free energy for a decreasing number of identical clusters (dashed line in Fig. 4).

The results for a constant number of identical clusters are in complete comparison with those of the thermodynamic investigations /5, 6/ except for the fact that due to the mixing entropy a decrease of the maxima of ΔF (dashed-dotted line in Fig. 4) is obtained for an increasing number of clusters.

4.3. Extrema for cluster distributions

For a deeper inside into the shape of the potential plane of ΔF we now discuss the case that the number k of

bound particles in clusters $k = \sum_{n=2}^N n N_n$ is constant for different cluster distributions. The free energy of those distributions is demonstrated in a schematic plot (Fig. 5) explained as follows: On the left the distributions with small clusters are located. The left border line is given by distributions with dimers only. On the right we have distributions with small and large clusters. The separa-

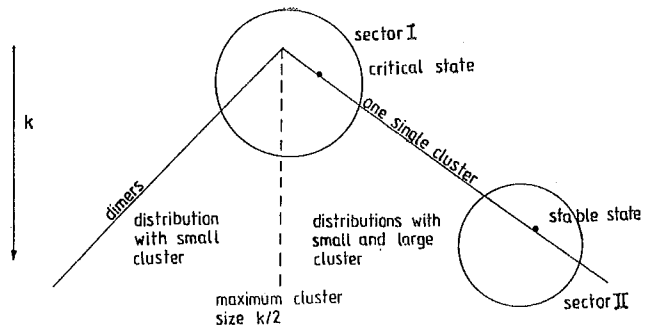


Fig. 5

Sketch of the presentation of the potential ΔF and the related cluster distributions for a constant number k of bound particles (explanation in the text).

Sector I and sector II are represented with numerical data.

ration between the left and the right is given by a maximum cluster size of $k/2$.

The case of only one cluster ($n \geq 2$) in the system as the limit of a cluster distribution is located on the total right.

With numerical data we represent only two sectors of this schema, one near the critical state (I) /Tab.4, the other near the stable state off the single cluster (II)/ Tab.5.

Sector I shows two limit cases. For the single cluster the free energy, has the greatest values because the mixing entropy is very small, but the lowest values of the free energy are hold for distributions with dimers only, the mixing entropy then has the greatest part and the surface energy is very small. We remark that the distinction of the dimer distribution is a consequence of the given model neglecting interactions between the clusters.

Between the two limit cases the other possible distributions of clusters are presented for a given value of k . The change from distributions with small clusters to those of large clusters is marked by distributions with a maximum cluster size of $k/2$. Among these such distributions are designated what contains of two nearly identical clusters because the free energy then attains its maximum value for a given value of k (except for the single cluster).

Tab. 4:

Free energy of the cluster distributions (section I of Fig. 5) for a given number k of bound particles.

k								
2					2^1			
					(-19,62)			
3							3^1	
							(-19,61)	
4				2^2			4^1	
				(-37,84)			(-19,69)	
5					$2^1 3^1$		5^1	
					(-39,15)		(-19,86)	
6		2^3			3^2	$2^1 4^1$	6^1	
		(-55,50)			(-37,77)	(-39,26)	(-20,10)	
7		$2^3 3^1$			$3^1 4^1$	$2^1 5^1$	7^1	
		(-57,37)			(-39,22)	(-39,52)	(-20,40)	
8	2^4	$2^1 3^2$	$2^2 4^1$		4^2	$3^1 5^1$	$2^1 6^1$	8^1
	(-72,79)	(-57,32)	(-57,42)		(-37,89)	(-39,37)	(-39,64)	(-20,75)
9 ...	$2^3 3^1$	3^3	$2^1 3^1 4^1$		$4^1 5^1$	$3^1 6^1$	$2^1 7^1$	9^1
	(-74,99)	(-55,35)	(-58,75)		(-39,42)	(-39,59)	(-39,93)	(-21,15)
10 ...	$2^3 4^1$	$3^2 4^1$	$2^1 4^1$	$2^1 3^1 5^1$	5^2	$4^1 6^1$	$3^1 7^1$	$2^1 8^1$
	(-75,03)	(-57,30)	(-57,41)	(-58,89)	(-38,17)	(-39,63)	(-39,87)	(-40,27)

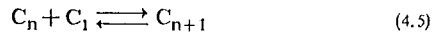
Tab. 5:

Free energy of the cluster distributions (section II of Fig. 5) for a given number k of bound particles.

k					
106				106 ¹ (-72,39)	
107		4 ¹ 103 ¹ (-87,08)	3 ¹ 104 ¹ (-88,24)	2 ¹ 105 ¹ (-89,52)	107 ¹ (-72,44)
108	2 ² 104 ¹ (-105,239)	4 ¹ 104 ¹ (-87,09)	3 ¹ 105 ¹ (-86,26)	2 ¹ 106 ¹ (-89,53)	108 ¹ (-72,463)
109	2 ² 105 ¹ (-105,230)	4 ¹ 105 ¹ (-87,08)	3 ¹ 106 ¹ (-88,25)	2 ¹ 107 ¹ (-89,53)	109 ¹ (-72,463)
110	2 ² 106 ¹ (-105,19)	4 ¹ 106 ¹ (-87,05)	3 ¹ 107 ¹ (-88,22)	2 ¹ 108 ¹ (-89,50)	110 ¹ (-72,44)
111	2 ² 107 ¹ (-105,14)	4 ¹ 107 ¹ (-87,00)	3 ¹ 108 ¹ (-88,17)	2 ¹ 109 ¹ (-89,45)	111 ¹ (-72,39)
112	2 ² 108 ¹ (-105,06)	4 ¹ 108 ¹ (-86,92)	3 ¹ 109 ¹ (-88,10)	2 ¹ 110 ¹ (-89,38)	112 ¹ (-72,32)

These distributions characterize, for this particular presentation, an energy barrier what has to crossover when a transition from distributions of small clusters to those with large clusters occurs.

Let us discuss this fact in more detail and therefore remember the mechanism of the phase transition by nucleation. We choose the following kinetic ansatz:



It means a cluster of size n grows up only by an attachment of a free particle. Interactions between clusters of different sizes are excluded.

If we consider an initial state of N free particles, then in the first step a dimer is created due to the reaction (4.5). During the next step this dimer is able to tend to be a trimer or splits into two monomers again, or a second dimer will be created. Caused by the stochastic nature the selection of one these reactions is determined by a random process. After every realization new possibilities for the dynamic process of phase transition arise due to the reaction (4.5) (see sector I) (Tab. 4).

But from an energetic point of view such reactions are preferred which lead to a decrease of the energy of the system. This means the system will relax from the initial state first to such states what are presented on the left hand in section I. The case that only a single cluster is created in the system growing further is on principle not so probable than the establishment of a certain number of small clusters, because the free energy in this case is more decreased. Distributions of only dimers in the given model are energetically more favourable indeed, but the fluctuations in the system prevent it.

It is notable that for different distributions of small clusters only small energy differences exist that's why transitions between these distributions are possible.

The phase transition in the system is now characterized by the establishment of a large cluster inside the metastable vapour phase consisting of small clusters and free particles only. This cluster grows further until a coexistence of the liquid phase with the surrounding vapour is hold in the final state.

To built up such large clusters ($n > k/2$) in the system of course the energy barrier in the middle region has to crossover. This process cannot be described in a determini-

stic model but only in a stochastic model considering the influence of fluctuations in the system /9, 10, 12/.

The phase transition in this model is interpreted as an stochastic tunnel process through unprobable (that means energetically unfavourable) states.

After the crossover the large cluster has an overcritical size and grows up to its final stable state. In sector II (Tab. 5) we represent some distributions of large and small clusters for $k = \text{const.}$ near the stable state of the single cluster ($n = 108$).

In agreement with former discussions of the free energy it is to be seen that the stable state in fact is given by a distribution of small clusters and free particles with one large cluster, instead of a single large cluster, because of the more decreasing energy. This fact confirms with results of a stochastic simulation of the nucleation process for the given model /9/.

5. Conclusions

In the present paper we investigate the thermodynamic potential of a system where a discrete distribution of clusters of different kinds and free particles exists. Because of the complicated structure of the potential the analysis is obtained only for some special cases corresponding to certain cuts of the hyperplane of this potential. The results show the properties of the potential in agreement with those expecting for typical bistable systems.

We find for the considered cuts of the hyperplane a potential barrier consisting of the maxima of the free energy. This energy barrier separate two regions with lower energy given by states of a larger stability. In the discussed model the metastable state is hold for distributions with small clusters, on the other side of the barrier the stable state is characterized by distributions with small and large clusters. A phase transition only occurs if the metastable state will be escaped by crossover the potential barrier.

For the relative stable states a multitude of different distributions is possible, but the energy of the distributions for a given stable state differs only slightly. That's why transitions between similar distribution are quite possible. But for the transition between the metastable

and the stable state a rather large energy barrier must be crossed over.

Finally we remark that some slight uncertainties, e. g. the energetically favourable state of distributions with dimers only, are involved by the character of the given model. The term f_2 was not exact considered, moreover all interactions between the clusters are neglected.

Zusammenfassung

In der Arbeit wird die freie Energie einer idealen Mischung von Clustern und freien Teilchen untersucht. Dieses thermodynamische Potential bildet die Grundlage für die Beschreibung von Keimbildungsprozessen in finiten Systemen. Die verschiedenen Anteile der freien Energie werden in Abhängigkeit von der Clusterverteilung berechnet und diskutiert.

Nach allgemeinen Ausführungen über die Extrema des thermodynamischen Potentials werden die Bereiche extremer Energie für Spezialfälle berechnet und diskutiert. Diese Spezialfälle entsprechen zwei Schnitten durch die Hyperfläche des Potentials. Es wird deutlich gezeigt, daß die freie Energie des Systems Eigenschaften eines bistabilen Potentials besitzt. In Abhängigkeit von der Cluster-Verteilung werden Bereiche kleiner Energie gefunden, die dem metastabilen bzw. dem stabilen Zustand des Systems entsprechen. Diese Bereiche sind durch eine Energiebarriere getrennt. Der Phasenübergang durch Keimbildung wird als Durchtunnelung dieser Energiebarriere erklärt.

Резюме

В статье описаны исследования свободной энергии идеальной смеси состоящей из сгустков и свободных частиц. Этот термодинамический потенциал образует основу для описания процессов образования ростков в финитных системах. Различные части свободной энергии рассчитаны в зависимости от распределения сгустков и обсуждены в статье.

Сообразно с общими изложениями о экстремах термодинамического потенциала определены и обсуждены диапазоны экстремальной энергии для специальных случаев. Эти специальные случаи соответствуют двум срезам через гиперповерхность потенциала. В статье отчетливо показано, что свободная энергия системы обладает свойствами бистабильного потенциала. В зависимости от сгустков найдены диапазоны малой энергии, которые соответствуют метастабильному или стабильному состоянию системы. Эти диапазоны разделены барьером энергии. Фазовый переход путем образования ростков объясняется как прорыв этого барьера энергии.

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But the meaning result, that's the confirmation of the bistable character of the given model, therefore is not restricted in any sense.

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Summary

The contribution deals with the free energy in an ideal mixture of nuclei and free particles. This thermodynamic potential forms the basis for a description of the nucleation process in finite systems. The different fractions of the free energy are calculated from the nucleus distributions and discussed.

After a general discussion regarding the extreme values of thermodynamic potentials, the regions of extreme energies are calculated and discussed for special cases corresponding to two cross sections through the hypersurface of the potential. It is shown clearly that the free energy of the system possesses properties of a bistable potential. Regions of lower energy are found, depending on the nucleus distribution, which correspond to the metastable and stable states of the system respectively. These regions are separated by an energy barrier. The phase transition by nucleation is discussed in terms of a tunneling through this barrier.

Résumé

L'article a pour objet l'étude de l'énergie libre d'un mélange idéal d'essaims et de particules libres. Ce potentiel thermodynamique est la base de la description des processus de germination caractérisant les systèmes finis. Le calcul et la discussion des différentes parts de l'énergie libre se font suivant la répartition des essaims.

Après des considérations de caractère général sur les valeurs extrêmes du potentiel thermodynamique, les auteurs calculent et discutent les domaines d'énergie extrême dans des cas spéciaux qui répondent à deux coupes par l'hypersurface du potentiel. Ils mettent en évidence que l'énergie libre du système présente des propriétés d'un potentiel bistable. En fonction de la répartition des essaims, ils découvrent des domaines de faible énergie répondant à l'état métastable ou stable du système. Les domaines sont séparés l'un de l'autre par une barrière énergétique. La transition de phase par germination est expliquée par l'intermédiaire de tunnels passant par la barrière énergétique.

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