Heinz Ulbricht Frank Schweitzer

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Thermodynamics and Kinetics of First-Order Phase Transitions

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Selected lectures of the first autumn school on "Theory of homogeneous nucleation in first-order phase transitions"

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Wilhelm-Pieck-Universität Rostock
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Preface

In autumn 1986 a school on the theory of homogeneous nucleation and phase transitions was organized by the Department of Physics of the Wilhelm Pieck University Rostock, German Democratic Republic. This school was devoted to the following three topics in the field of phase transitions:

- thermodynamics of heterogeneous systems and problems of surface tension
- theory of the kinetics of first-order phase transitions, deterministic and stochastic description and computer simulations
- practical experiences with known nucleation theories and relations to experimental necessities.

We were very glad to welcome 25 participants who are interested in an intensive interchange of ideas. Thus a lot of valuable suggestions could be given and many remarkable results have been discussed.

Our thank goes to all who supported this school with suggestions and collaboration in the organization.

This booklet contains a selection of papers presented at the autumn school.

We thank R. Mahnke and A. Budde for their help in the preparation of the manuscripts and last but not least, we thank Mrs. Hiltrud Bahlo, who typed the whole manuscript, and Mrs. Renate Nareyka for preparing the figures.

H. Ulbricht F. Schweitzer

Program of the Autumn School

Thuesday, 14. 10. 1086

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2. Adsorption of binary liquids on solids

W. Vogelsberger (Jena):
Considerations on the correct interpretation of the derivative $[\partial\gamma/\partial r]$ in the theory of interface of liquids

Wednesday, 15. 10. 1986

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Thermodynamic analysis of nucleation processes for different constraints

F. Siegmann, H. Ulbricht, F. Schweitzer (Rostock):
Thermodynamics of nucleation in binary mixtures

D. Stock, H. Geiler (Jena):
Deterministic description of laser-induced nucleation and growth processes in silicon

U. Lembke (Rostock):
Experimental investigations of nucleation, growth processes and Ostwald ripening of metal halogenide phases in photochromic model glasses

H. Linck (Wolfen):
Precipitation of silverhalogenide for producing photographic emulsions

H. Ulbricht (Rostock):
Nucleation in porous media

A. Hoell (Rostock):
On the influence of elastic strains on growth processes in solids and on a solid surface

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J. Barthels (Rostock), A. Richter (Dresden):
Kinetics of nucleation for isothermal processes

F. Schweitzer (Rostock):
Stochastic description of nucleation in finite systems: theory and results of computer simulations

H. Tietze, F. Schweitzer (Rostock):
The nucleation barrier in finite systems: an investigation of the thermodynamic potential

R. Mahnke (Rostock):
On the kinetics of Ostwald ripening in finite systems

A. Budde (Rostock):
On the kinetics of nucleation in finite and isolated systems

N. F. Patsegon (Kharkov, USSR):
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Quantum statistical approach to cluster formation and phase transition in dense systems

B. Lorenz (Potsdam):
Theory of grain size distribution in nucleation and growth processes

T. Boseniuk, R. Feistel (Berlin):
Nucleation in bistable reaction-diffusion systems

L. Schimansky-Geier (Berlin):
Nucleation and activation

H. Ulbricht (Rostock): Conclusions

Rostocker Physikalische Manuskripte, Heft 10 (1987)

Peter Bräuer; Matthias Heuchel

Thermodynamics of Sorption Processes on the Basic of Excess Values

1. Introduction

In our lectures we try to develop an uniform thermodynamic description of various problems concerning systems with interfaces /1/. We want to start always from the given experimental situation. This will be shown mostly by means of problems of adsorption.

At least two homogeneous parts of a heterogeneous system are necessary for an interface. That is the reason why interfaces are not independent objects. A usual thermodynamic description can not give exact results for this isolated unstable region. The correct approach is to treat the interface on the basis of excess values. An excess means an accumulation or a diminution of any component of the system in the interfacial region with respect to the homogeneous parts of the system. From this point of view the thermodynamic formalism is treatable in an uniform way. It must specialized for all physically different interfacial systems (i.e. liquid-liquid, liquid-gas, solid-gas, solid-liquid) and also for the different experimental situations (e.g. either volumetric or gravimetric method in gas adsorption). The thermodynamic description of interfaces has a long history. It has started with the famous pioneer work of Gibbs /2/. The following derivation given here bases on the generalized results of Lopatkin and Vernov /3,4/. For our own contributions to the following representation the reader is refered to page 1 in our detailed paper /1/. In case of gas adsorption we refer also to /1/.

2. Basic Equations

For simplicity we consider a heterogeneous system consisting only of two homogeneous parts α and β and one interface (for detail see /1/). Usual thermodynamics of heterogeneous systems neglects the influence of interfaces and treats every extensive quantity of a heterogeneous system y^{het} and the related total differential dy^{het} as a sum of the corresponding values in the two homogeneous phases:

$$y^{het} = y^{\alpha} + y^{\beta} ; \quad dy^{het} = dy^{\alpha} + dy^{\beta} . \tag{1}$$

This assumption of simple additivity neglects the contribution of the interface and causes an error y^{e}. called excess, which is a measure for the influence of interfacial processes. It can be shown, that in experiments only excess values are resulting quantities /1/. That's why a correct description of the homogeneous system paying attention to the interface is given by

$$y^{het} = y^{\alpha} + y^{\beta} + y^{e} ; \quad dy^{het} = dy^{\alpha} + dy^{\beta} + dy^{e} . \tag{2}$$

Contrary eq. (1) could be considered as a reference system of just hypothetical nature. Eq. (2) is the definition of the excess quantities.

There exists a fundamental equation containing the information of the first and second law of thermodynamics for any of the extensive quantities in eq. (2). We find in case of internal energy $y \equiv u$ for t components in the system and k generalized thermodynamic forces

$$du^{het} = T^{het} ds^{het} + \sum_{j=1}^{k} X_j^{het} dx_j^{het} + \sum_{i=1}^{t} \mu_i^{het} dn_i^{het} \tag{3}$$

$$du^{r} = T^{r} ds^{r} + \sum_{j=1}^{k^r} X_j^{r} dx_j^{r} + \sum_{i=1}^{t^r} \mu_i^{r} dn_i^{r} \; ; \; r = \alpha, \beta . \tag{4}$$

Because of the validity of Euler's theorem for the homogeneous phases α and β the extensive quantities y^{α} and y^{β} can expressed by partial molar quantities

$$y^r = \sum_{i=1}^{t^r} n_i^r Y_i^r \; ; \; r = \alpha, \beta \; . \qquad (5)$$

t^α and t^β are the corresponding numbers of components in phases α and β respectively. It is <u>not necessary</u> that $t^\alpha = t^\beta$. With (5) we get from (2) the equation

$$y^e = y^{het} - \sum_{i=1}^{t^\alpha} n_i^\alpha Y_i^\alpha - \sum_{i=1}^{t^\beta} n_i^\beta Y_i^\beta \; . \qquad (6)$$

In this representation of excess quantities y^e the amounts of substances n_i^α and n_i^β in both phases α and β of the reference system are undetermined coefficients of a linear combination. They must be determined in dependence on the actual interfacial problem and on the appropriate experimental method. Finally we get Gibbs-Duhem equations for the homogeneous phases α and β

$$s^r dT^r - v^r dp^r + \sum_{i=1}^{t^r} n_i^r d\mu_i^r = 0 \; ; \quad r = \alpha, \beta \; . \qquad (7)$$

Every homogeneous part is fixed by t^r+1 intensive variables. The corresponding variables in the phases α and β respectively <u>must not be equal</u> in any case, because these phases could be considered as independent ones. This is in contrast to Gibbs, who formulated equilibrium conditions. Fixing intensive parameters in eq. (6) determines the partial molar quantities but not the coefficients of this linear combination. For it two extensive parameters are necessary (e.g. the volumes of both phases α and β). In general it can be done by specifying either one parameter for every homogeneous phase or one for the whole heterogeneous system and the other for one of the phases α and β respectively. If the unknown coefficients in eq. (6) are determined, than the reference system and the excess quantities are simultaneously completely fixed.

3. Rules for Determination the Reference System and the Excess Quantities /3,4/

Comprimising the results of our paper /1/ we give four rules for determination of the reference system. The actual choose of the quantities depends on the real experimental situation. The following quantities must be fixed:

i) the components in both phases of the reference system (numbers t^{α} and t^{β})

ii) the force acting on the system (numbers k^{α}, k^{β}). Usually it is $k^{\alpha} = k^{\beta} = 1$ and $X^{r} = -p^{r}$; $x^{r} = v^{r}$; $r = \alpha, \beta$

iii) the intensive parameters, their equality or nonequality in the phases α, β and in the real heterogeneous system

iv) two extensive parameters; either one for every phase α, β or one for the whole system and one for one of the phases α or β.

With these rules it is possible to calculate in an uniform way the thermodynamic functions of any surface system which has been investigated before by any experimental method of adsorption.

4. Peculiarities of Adsorption on Solids /3,4/

In this section we want to give a short list of problems concerning adsorption on solids. This should be kept in mind for the next sections, where we will give two examples for the application of the general excess formalism.

The properties of a solid and hence of its surface depend on the previous treatment. A reproducible preparation is very difficult. The phase boundary of highly dispersed powders is not observable and for adsorbents with narrow pores without sense.

The surface tension for powders is not measurable. The primary experimental quantity is the adsorption amount.

The specific surface O_{sp} can be determined only inaccurately and becomes senseless in micropores. Therefore it is better to choose the mass of adsorbent m_A as independent variable characterizing the solid adsorbent.

A lot of information concerning adsorbents (e.g. structure

and chemical properties of the surface region, character of porosity, extent of heterogeneity etc.), which should be known before establishing a theory, results only from adsorption investigations.

5. Reference System and Excess Values for Gas Adsorption of One Component on a Solid Surface

This is a first example for application the rules given in section 3. The procedure is shown in Fig. 1. Phase β is a solid, which is considered as one component. We use index A to characterize the solid adsorbent. Phase α is a pure gas (adsorptiv), which is characterized by index g.

Rule i:

It is easy to see, that $t^{\beta}= 1$ and $t^{\alpha}= 1$. Hence the whole system consists of two components. We exclude absorption from consideration, i.e. $n_1^{\beta} \equiv n_g^{\beta}=0$. Further we postulate that the vapour pressure of the adsorbent is negligible, i.e. $n_1^{\alpha} \sim m_A=0$. Then eq. (6) gives

$$y^e = y^{het} - n_g^{\alpha} y_g^{\alpha} - m_A^{\alpha} y_{A,sp}^{\alpha} \quad . \tag{8}$$

$y_{A,sp}^{\beta}$ is a specific quantity related to the adsorbent mass m_A.

Rule ii:

Only mechanical work must be considered, i.e.

$$k^{\alpha} = k^{\beta} = 1; \; X^{\alpha} = -p^{\alpha}; \; x^{\alpha} = v^{\alpha}; \; X^{\beta} = -p^{\beta} \; ; \; x^{\beta} = v^{\beta} \; . \tag{9}$$

Rule iii:

The temperatures in the reference and in the heterogeneous system are equal, i.e.

$$T^{\alpha} = T^{\beta} = T^{het} \equiv T \tag{10}$$

and the pressures are equal on a plane surfaces, i.e.

$$p^{\alpha} = p^{\beta} = p^{het} \equiv p \; . \tag{11}$$

For curved surfaces it is generally $p^{\alpha} \neq p^{\beta}$.

The chemical potential of the gas has the same value in the reference system and in the heterogeneous system, i.e.

$$\mu_g^{\alpha} = \mu_g^{het} \equiv \mu \; . \tag{12}$$

In comparison the chemical potential of the adsorbent in the heterogeneous system $\mu^{het}_{A,sp} \equiv \mu_{A,sp_o}$ is different from that of the reference system $\mu^{\beta}_{A,sp} \equiv \mu_{A,sp}$. It is

$$\mu_{A,sp} \neq \mu^{o}_{A,sp} \quad , \tag{13}$$

because the solid is disturbed in the heterogeneous system by adsorbate. We introduce the difference of both potentials as a new quantity Φ

$$\Phi \equiv -(\mu_{A,sp} - \mu^{o}_{A,sp}) \quad . \tag{14}$$

Φ is a measure of the disturbance of the adsorbent. For the so called "inert adsorption" it is $\Phi = 0$.

Rule iv:

The choose of the extensive parameters for the reference system depends on the kind of adsorption and on the used experimental method. We consider here the volumetric method as an example.

Before the direct measurement can be started the volume of the whole system v^{het} must be known. Then the free volume v_{He} for the gas is determined with a He-expansion method using the assumption that He is not adsorbed. The adsorbent volume is found by $v^{o}_{A} = v^{het} - v_{He}$. The volumes v^{het}, v_{He} and v^{o}_{A} are considered as fixed during the experiment. With $v^{\alpha} = v_{He}$, $v^{\beta} = v^{o}_{A}$ it follows from eq. (3) ($y \equiv v$):

$$v^{e} = v^{het} - v_{He} - v^{o}_{A} = 0 \quad . \tag{15}$$

The first coefficient of the linear combination (8) is fixed by $v^{\alpha} = v_{He}$, i.e. $n^{\alpha}_{g} = v_{He}/v^{\alpha}_{g}$. v^{α}_{g} is the molar volume of the gas under the present conditions of the adsorption experiment.

Now we consider the balance of the adsorbent mass in the system. The adsorbent mass m_A has to be known. Because of $m^{\alpha}_{A} = 0$ it is in (2)

$$m^{e}_{A} = m^{het} - m^{\beta}_{A} \quad . \tag{16}$$

For physical adsorption, where we exclude any formation of chemical species between gas and surface atoms and therefore any possible appearance of adsorbent in the gas phase, it is

$$m^{het}_{A} = m^{\beta}_{A} \equiv m_{A} \; ; \quad m^{e}_{A} = 0 \quad . \tag{17}$$

The reamining second coefficient of eq. (8) $m_A^\beta \equiv m_A$ is fixed and all excess quantities are determined in an uniform way. With the expressions (15) and (17) the phase boundary is fixed on the adsorbent surface. For the adsorption excess it follows with $n_1^\beta = n_g^\beta = 0$ and $y \equiv n$ from (2)

$$n^e = n^{het} - n_g^\alpha = n^{het} - v_{He}/v_g^\alpha \,. \qquad (18)$$

In case of isothermic conditions n^{het} has to be determined for any equilibrium pressure. v_{He}/v_g^α is under this condition a constant quantity provided that the pressure dependence of the molar volume is negligible.

In case of adsorption gravimetry the coefficients of the linear combination (6) are determined in a similar way /1/.

6. The Derivation of Thermodynamic Formalism in Case of Gas Adsorption on Solid Surfaces

With the rules in section 5 we get from eq. (2)-(4) in case of a plane surface the equations

$$du^e = du^{het} - du_g - du_A^o \qquad (19)$$

$$du^{het} = Tds^{het} - pdv^{het} + \mu dn^{het} + \mu_{A,sp} dm_A \qquad (20)$$

$$du_g = Tds_g - pdv_g + \mu dn_g \qquad (21)$$

$$du_A^o = Tds_A^o - pdv_A^o + \mu_{A,sp}^o dm_A \qquad (22)$$

and consequently

$$du^e = Tds^e - \mu dn^e - \Phi dm_A;\; u^e = Ts^e + \mu n^e - \Phi m_A \qquad (23)$$

with Φ from eq. (14). If the adsorbent surface is a measurable quantity and the linear expression

$$o = O_{sp} m_A \qquad (24)$$

is valid, where o is the absolute surface area and O_{sp} the specific surface, it is possible to eliminate the mass in eq. (23). Simultaneously the surface pressure π can be introduced instead of Φ. It exists the relation

$$-\Phi dm_A = -(\Phi/O_{sp})do = -\pi do;\quad \pi = -(dg^e/do)_{T,n^e} \,. \qquad (25)$$

By Legendre transformations we get the other thermodynamic potentials, i.e.

$$dg^e = -s^e dT + \mu dn^e - \Phi dm_A \; ; \; g^e = \mu n^e - \Phi m_A \qquad (26)$$

and finally the Gibbs-Duhem equation

$$-s^e dT - n^e d\mu + m_A d\Phi = 0 \; . \qquad (27)$$

From eqs.(26) and (27) it can be seen, that there exists the following two representations of the chemical potential:

$$\mu = \mu(T, n^e, m_A) \equiv \mu(T, \Gamma) \; ; \; \Gamma = n^e/m_A ; \; \mu = \mu(T, \Phi) \; . \qquad (28)$$

In particular it is

$$d\mu = -S^e_{diff} dT + (\partial\mu/\partial\Gamma)_T d\Gamma \; ; \; d\mu = -S^e_{int} dT + (1/\Gamma) d\Phi \qquad (29)$$

with the integral and differential molar excess entropies

$$S^e_{int} \equiv s^e/n^e ; \; S^e_{diff} = (\partial s^e/\partial n^e)_{T, m_A} \; . \qquad (30)$$

For the chemical potential of the gas phase the following equation can be written

$$d\mu_g = - S_g dT + V_g dp \; , \qquad (31)$$

where V_g and S_g are molar quantities. From the equilibrium condition $d\mu = d\mu_g$ and from eqs. (29) and (31) result three equations:

$$-(S^e_{int} - S_g) dT - V_g dp + (1/\Gamma) d\Phi = 0 \qquad (32a)$$

$$-(S^e_{diff} - S_g) dT - V_g dp - (\partial\mu/\partial\Gamma)_T d\Gamma = 0 \qquad (32b)$$

$$-(S^e_{int} - S^e_{diff}) dT - (\partial\mu/\partial\Gamma)_T d\Gamma - (1/\Gamma) d\Phi = 0 \; . \qquad (32c)$$

By fixing one variable it is possible to derive partial differential coefficients from eq. (32), which could be instructions for experimental measurements in order to determine thermodynamic adsorption quantities. We illustrate this with three examples. From eq. (32a) we get a relation allowing to calculate under isothermic conditions Φ or π from adsorption isotherms:

$$\Phi = RT \int_0^p \Gamma z \; d\ln p \; ; \quad \pi = RT \int_0^p \frac{n^e}{o} z \; d\ln p ; \; T = const., \qquad (33)$$

where

$$z = p \, V_g/RT = 1 + (\partial \ln f/\partial \ln p)_T \qquad (34)$$

is a correction term for the real gas, which could be measured

by the pressure dependence of the fugacity coefficient. Usually it is z=1, which means that a perfect state for nonadsorbed gas is supposed. For Γ -const. in eq. (32b) a relation for calculating the isosteric heat of adsorption Q_{st} from adsorption isosteres $\ln p = f(1/T)_\Gamma$ follows. It is

$$Q_{st} \equiv -(H^e_{diff} - H_g) = R\, z \left[\partial \ln p / \partial (1/T)\right]_\Gamma \quad . \tag{35}$$

Eq. (32c) yields finally a connection between differential and integral quantities of adsorption, e.g.

$$H^e_{int} - H_g = H^e_{diff} - H_g - \left[\partial (\Phi/T)/\partial (1/T)\right]_\Gamma / \Gamma \quad . \tag{36}$$

7. Reference System and Excess Quantities for Adsorption of Binary Liquid Mixtures of Nonelectrolytes on Solids

Fig. 2 shows a principal diagram for the real adsorption system and the reference system in the case of adsorption from binary liquid mixtures on solids. We apply again the rules of section 3 to fix excess quantities corresponding to the special adsorption system and to the special experimental method of measurement.

Rule i: We have a two-component liquid mixture ($t^\alpha = t = 2$) in the α-phase and exclude by $m^\alpha_A = 0$ any dissolution of the solid in the liquid phase. The solid is considered as one component ($t^\beta = 1$). As in case of gas adsorption we exclude again any absorption of the liquid component into the solid, i.e. $n^\beta_1 = 0$ and $n^\beta_e = 0$.

Rule ii: The same assumptions are valid as for gas adsorption.

Rule iii: We take over the assumptions of section 5 with one exception. Because of two liquid components it is now

$$\mu^{het}_i = \mu^\alpha_i \equiv \mu_1 ; \quad i = 1,2 \quad . \tag{37}$$

Instead of eq. (6) it is now

$$Y^e = Y^{het} - n^\alpha_1 Y^\alpha_1 - n^\alpha_2 Y^\alpha_2 - m^\beta_A Y^\beta_{A,sp} \quad . \tag{38}$$

Rule iv: We have to determine the unknown coefficients n^α_1, n^α_2 and m^β_A in the linear combination (38) by fixing two extensive parameters for both phases of the reference system. We start with the mass balance. The mass of adsorbent m_A is equal

in the adsorption system and in the reference system and eq. (17) is valid. In order to fix the second extensive parameter we need information about the special extension of the adsorption experiment. Here we discuss the following possibility: In the initial solution with total number of moles $n^o = n_1^o + n_2^o$ and molar fraction $x_2^o = n_2^o/n^o$ (T,p=const) the solid adsorbent is diped in. Due to different interactions of both components with the surface of the solid a new molar fraction x_2 in bulk phase is adjusted, which is usually different from x_2^o. We obtain the excess adsorption Γ_2^e, i.e. the excess amount of component 2 per mass of adsorbent. It is

$$\Gamma_2^e = n_2^e/m_A = n^o(x_2^o - x_2)/m_A \ , \qquad (39)$$

where on the r.h.s. only measurable quantities appear. The function $\Gamma_2^e = f(x_2)_T$ is called excess adsorption isotherm. If this is measured for different temperatures, a calculation of the thermodynamic quantities from the obtained set of isotherms is possible. A second approach to thermodynamic quantities uses the measurement of heat effects during wetting or changes of adsorption in a calorimeter /1/. At present we can return to eq. (38). With $n_i^{het} = n_i^o$ and the fact, that the molar fraction of the bulk phase of the real adsorption system should be equal to the same of the α-phase ($x_i \equiv x_i^o$), it follows

$$n_i^\alpha = n^o \, x_i \ ; \ i=1,2 \ . \qquad (40)$$

For the excess amount we get again the result of eq. (39). It is easy to see, that

$$n_1^e + n_2^e = 0 \ ; \ \Gamma_1^e + \Gamma_2^e = 0 \ . \qquad (41)$$

With eq. (40) all remaining coefficients n_1^α and n_2^α of the linear combination (38) are fixed experimentally and the excess quantities are definitely adjusted to the experiment.

8. The Derivation of Thermodynamic Formalism in Case of Adsorption of Binary Liquid Mixtures of Nonelectrolytes on Solids

The thermodynamic formalism is treated in the same way as in case of gas adsorption, provided that the excess quantities

are fixed by equations (36), (17) and (18). The difference related to the existence of two components is removed formally by $dn_1^e = - dn_2^e$ (eq. (41)) and hence one quantity can be eliminated. In this way we get instead of (26) and (27) the equations

$$dg^e = -s^e dT + v^e dp + \mu_{21} dn_2^e - \Phi dm_A ; \quad g^e = \mu_{21} n_2^e - \Phi m_A \qquad (42)$$

$$s^e dT - v^e dp + n_2^e d\mu_{21} - m_A d\Phi = 0 ; \quad \mu_{21} \equiv \mu_2 - \mu_1 \cdot \qquad (43)$$

It can be ssen from these equations, that the following representations of the difference of chemical potentials μ_{21} is possible:

$$\mu_{21} = \mu_{21}(T, p, n_2^e, m_A) = \mu_{21}(T, p, \Gamma_2^e) ; \quad \mu_{21} = \mu_{21}(T, p, \Phi) . \qquad (44)$$

It is in particular

$$d\mu_{21} = -S^e_{diff2} dT + V^e_{diff2} dp + (\partial \mu_{21} / \partial \Gamma_2^e)_{T,p} d\Gamma_2^e \qquad (45a)$$

$$d\mu_{21} = -S^e_{int2} dT + V^e_{int2} dp + (1/\Gamma_2^e) d\Phi \qquad (45b)$$

with $\Gamma_2^e = n_2^e / m_A$ and with the integral and differential molar quantities

$$Y^e_{int2} \equiv y^e / n_2^e \; ; \quad Y^e_{diff2} \equiv (\partial y^e / \partial n_2^e)_{T,p,m_A} \cdot \qquad (46)$$

We can obtain a third equation for $d\mu_{21}$ from the properties of the liquid mixture (α-phase of reference system) /1/

$$d\mu_{21} = -S_{21} dT + V_{21} dp + L_{21} dx_2 \qquad (47)$$

with the differences of partial molar quantities

$$Y_{21} \equiv Y_2 - Y_1 \; ; \quad Y \equiv S, V \qquad (48)$$

and

$$L_{21} = \frac{RT}{1-x_2} \left[\frac{1}{x_2} + (\partial \ln f_2 / \partial x_2)_{T,p} \right] \cdot \qquad (49)$$

f_2 is the activity coefficient of component 2 in the mixture. The equality of l.h.s. of (45a), (45b) and (47) leads in comparison to eq. (32) to three a little bit more complicated equations:

$$-S^a_{int}dT+V^a_{int}dp+(1/\Gamma^e_2)d\Phi-L_{21}dx_2 = 0 \qquad (50a)$$

$$-S^a_{diff}dT+V^a_{diff}dp+(\partial\mu_{21}/\partial\Gamma^e_2)_{T,p}d\Gamma^e_2-L_{21}dx_2 = 0 \qquad (50b)$$

$$-(S^a_{int}-S^a_{diff})dT+(V^a_{int}-V^a_{diff})dp+(1/\Gamma^e_2)d\Phi-(\partial\mu_{21}/\partial\Gamma^e_2)_{T,p}d\Gamma^e_2=0 \qquad (50c)$$

We have used the abbreviations $Y^a_{int} \equiv Y^e_{int2}-Y_{21}$ and $Y^a_{diff} = Y^e_{diff2}-Y_{21}$. In analogy to gas adsorption we obtain from (50a) with T,p=const. by integration the relation

$$\Phi(x_2)-\Phi_{1*} = RT\int_0^{x_2}\frac{\Gamma^e_2}{1-x_2}\left[\frac{1}{x_2}+(\partial\ln f_2/\partial x_2)_{T,p}\right]dx_2 \qquad (51)$$

$\Phi(x_2)-\Phi_{1*}$ can be calculated from an adsorption excess isotherm $\Gamma^e_2 = f(x_2)_T$, if the dependence on the activity coefficients f_2 of pure mixture from molar fraction is known. If the specific surface O_{sp} is also known, than it is possible to introduce by

$$\pi-\pi_{1*} = -(\Phi-\Phi_{1*})/O_{sp} \qquad (52)$$

the surface pressure π. Φ as well as π can be fixed only except a constant, e.g. the surface tension of pure component 1 π_{1*}. But π_{1*} could be calculated from gas adsorption (eq. (33)), if the integration is extendend to the saturated vapour pressure p_{1*}. In analogy to (35)

$$H^a_{diff} \equiv H^e_{diff2}-H_{21} = \frac{RT^2}{1-x_2}\left[\frac{1}{x_2}+(\partial\ln f_2/\partial x_2)_{T,p}\right](\partial x_2/\partial T)_{p,\Gamma^e_2} \qquad (53)$$

is an estimation of the differential change of enthalpy from excess adsorption isosteres $x_2=f(T)_{\Gamma^e_2}$, if a change in molar fraction from x_2 to x_2+dx_2 occurs.

At least we want to point out without derivation, that between $\Phi-\Phi_{1*}$ calculated from an adsorption excess isotherm (eq. (51)) and heats of wetting measured with a calorimeter the following relation exists /1/:

$$(\Delta_W h-\Delta_W h_{1*})/m_A = -\left[\partial[(\Phi-\Phi_{1*})/T]/\partial(1/T)\right]_{p,x_2,m_A} \qquad (54)$$

where $\Delta_w h$ and $\Delta_w h_{1*}$ are enthalpies of wetting of the liquid mixture and the pure liquid 1 respectively. These and other equations allow thermodynamic consistency tests between completely different thermic and calorimetric measurements.

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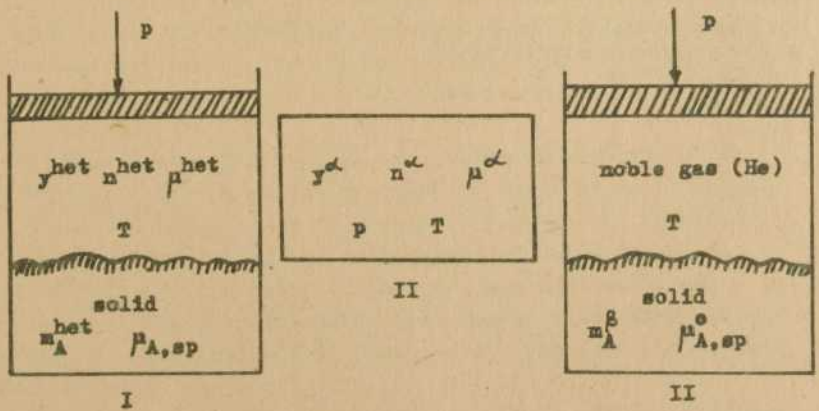

Fig. 1: Simple diagram for determination of excess quantities for gas adsorption on solids
I Real adsorption system
II Reference system

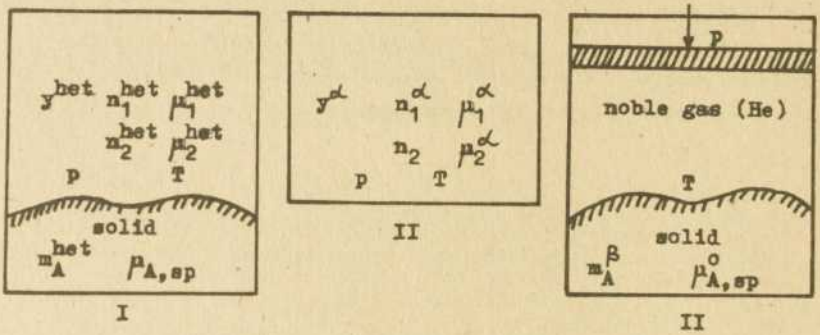

Fig. 2: Simple diagram for adsorption of binary liquid mixtures on a solid surface
I Real adsorption system
II Reference system

Author:

Doz. Dr. P. Bräuer, Dipl.-Chem. M. Heuchel
Karl-Marx-Universität Leipzig
Sektion Chemie
Leipzig
DDR - 7010

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Wolfram Vogelsberger

Considerations on the correct interpretation of the derivative $[\partial\gamma/\partial r]$ in the theory of interface of liquids

The thermodynamic description of systems with two or more phases and interfaces needs a definition of the dividing surface between the adjacent phases. The reason is that the transition zone has a finite thickness and the density varies contineously between the phases. We restrict our considerations on a system containing two phases α and β and only one component. The most important dividing surface in such system is the equimolecular dividing surface. It is given by the relation

$$N = N^{\alpha} + N^{\beta} \tag{1}$$

This special position of the dividing surface is well defined if the total number of molecules in the system N, the total volume V and the densities of the two phases are fixed. (N^{α} and N^{β} are the numbers of the molecules in the two phases α and β .) An other definition of a dividing surface is the surface of tension originally introduced by Gibbs /1/. Kondo et al. gave an interpretation of the surface of tension /2,3/ which is erroneous.

To show this we first summarize the model of Kondo et al. /3/. They consider a system at constant temperature T, composed of two phases α and β separated by a spherical interface as shown in Fig. 1. The system consists of the part of the cone between the two radii R^{α} and R^{β} where $R^{\alpha} < R^{\beta}$ and ω is the solid angle. The two phases are separated by the dividing surface, r. The total volume V is now divided into two volumes V^{α} and V^{β} given by

$$V^{\alpha} = \frac{1}{3}\,\omega\,[r^3 - (R^{\alpha})^3] \tag{2}$$

$$V^{\beta} = \frac{1}{3}\,\omega\,[(R^{\beta})^3 - r^3] \tag{3}$$

The area of the dividing surface A, is

$$A = \omega r^2 \tag{4}$$

The pressures p^α and p^β inside the two phases α and β are related to the densities by the constitutional equations of state.

$$p^\alpha = K^\alpha \frac{N^\alpha}{V^\alpha} \tag{5}$$

$$p^\beta = K^\beta \frac{N^\beta}{V^\beta}$$

(For simplicity we used a linear dependency in both cases.) The two constants K^α and K^β are functions of temperature. The work done by the system if the solid angle is increased from zero to the value ω, keeping all other variables constant is given by

$$\Omega = - p^\alpha V^\alpha - p^\beta V^\beta + \gamma A \tag{7}$$

It is equal to the grand potential, Ω, and γ means the surface tension. By use of eqs. (2) to (4) and differentiation of eq. (7) with respect to r keeping Ω, ω, p^α and p^β constant Kondo et al. /3/ obtain the following relation

$$\gamma + \frac{1}{2} r \frac{\partial \gamma}{\partial r} = \frac{1}{2} r (p^\alpha - p^\beta) . \tag{8}$$

The derivative $\partial\gamma/\partial r$ in eq. (8) is ascribed by Kondo to a pure mathematical displacement of the dividing surface "keeping all the physical quantities inside the system and the external conditions unaltered". This interpretation is erroneous. It is convenient to keep Ω constant during the derivation of eq. (7) because the work should not be affected by an arbitrary displacement of the dividing surface. Kondos derivation of eq. (7), however, contains the change of the volumes V^α and V^β during the displacement of the dividing surface. If the volumes V^α and V^β are altered then the pressures p^α and p^β can only be kept constant by an additional change of a physical quantity in the system. From eqs. (5) and (6) we see that this additional change can be a change of the number of molecules. Thus the derivative $\partial\gamma/\partial r$ is not as stated by Kondo et al. /2,3/ the change of the surface tension by an arbitrary pure mathematical displecement of the dividing surface "keeping all the physical quantities inside the system and the external

conditions unaltered". It rather gives the change in surface tension by the displacement when e.g. the number of particles of the system is changed in such a manner that its pressure is kept constant. A pure mathematical displacement of the dividing surface must keep the volumes V^α and V^β constant. From the mathematical point of view we have the following situation. In the system considered we are concerned with the quantities: T, V, V^α, V^β, p^α, p^β, N, N^α, N^β, γ, r, A, ω, R^α, R^β and Ω. The following ones of these quantities are fixed to be constant by definition: T, p^α, p^β, ω, R^α, R^β, Ω and $N = N_o$ as well as the total volume of the system, V, for we have $V = V(\omega, R^\alpha, R^\beta)$. The remaining variables are: V^α, V^β, r, A, N^α, N^β and γ.

Among these seven variables we have seven relations, eqs. (1) to (7). These seven equations are independent on each other since the functional determinant |D| is not zero.

$$|D| = \omega r^2 A \frac{K^\alpha K^\beta}{V^\alpha V^\beta} \left[\frac{N^\alpha}{V^\alpha} - \frac{N^\beta}{V^\beta} \right] \neq 0 . \qquad (9)$$

Therefore all the seven variables are determined by these equations. The equations (1) to (6) define the equimolecular dividing surface (indicated by the index e) since N_o molecules in the system considered can only form one determined amount of phase α, N_e^α, with pressure p^α. The radius of this equimolecular dividing surface is $r = r_e$ and the corresponding surface tension $\gamma = \gamma_e$ is given by eq. (7). Eq. (8) introduces a new quantity $\partial\gamma/\partial r$. Combination of eq. (8) with eqs. (1) to (7) gives the value of $\partial\gamma/\partial r$ at the equimolecular dividing surface.

Thus all the quantities $V^\alpha = V_e^\alpha$, $V^\beta = V_e^\beta$, $r = r_e$, $A = A_e$, $N^\alpha = N_e^\alpha$, $N^\beta = N_e^\beta$, $\gamma = \gamma_e$ and $\partial\gamma/\partial r = [\partial\gamma/\partial r]_e$ are fixed by the eqs. (1) to (8). There is not possibility to change one of them arbitrarily.

The surface of tension is defined by the condition /3/

$$\partial\gamma/\partial r = 0 . \qquad (10)$$

Introducing this definition into eq. (8) gives

$$\gamma = \tfrac{1}{2} r (p^\alpha - p^\beta) . \qquad (11)$$

Now we would have eight independent relations among seven variables. Of course such situation is mathematically impossible. This clearly shows that if eq. (11) is applied to the definition of a special position of the dividing surface the validity of one of the seven other relations, eqs. (1) to (7) can no longer be maintained, or one of the quantities fixed by definition must become variable. In principle it is possible to drop the constancy of each of the quantities, T, N, p^{α}, p^{β}, Ω and V. In view of the aim of the model of Kondo et al. /3/ we discuss a change in the total number of molecules in the system, N, and its physical consequences. Introducing the excess amount of molecules, N^s, by the definition /3/

$$N_0 = N + N^s = N^{\alpha} + N^{\beta} + N^s \tag{12}$$

and combining the two forms of eq. (7) for the equimolecular dividing surface and for an arbitrary dividing surface we obtain

$$\gamma = \gamma_e \frac{A_e}{A} + \frac{p^{\alpha} - p^{\beta}}{\frac{N^{\beta}}{N^{\alpha}} - \frac{N^{\alpha}}{V^{\alpha}}} \frac{N^s}{A} \tag{13}$$

eq. (13) shows that the change of the surface tension accompanying the arbitrary displacement of the dividing surface in the model of Kondo et al. /3/ is composed of two parts. One part, the first term of the right-hand side of eq. (13), represents the change of the surface tension if it is referred to an arbitrary dividing surface A and not to the equimolecular dividing surface (pure mathematical displacement). The second part, second term on the right-hand side of eq. (13), represents the change of the number of molecules in the system accompanying the arbitrary displacement of the dividing surface necessary to guarantee the constancy of the pressures p^{α} and p^{β}.

Use of eqs. (1) - (4) gives eq. (7) in the form

$$\Omega = \frac{1}{3}\omega\left[(R^{\alpha})^3 p^{\alpha} - (R^{\beta})^3 p^{\beta}\right] - \frac{1}{3}\omega r^3 (p^{\alpha} - p^{\beta}) + \omega r^2 \gamma \tag{14}$$

As we have already shown a change of r in eq. (14) is only possible if the number of molecules is changed in the system.

Since the other quantities are fixed by definition the change of r causes a change of Ω (r, γ = constant) or a change of γ (r, Ω = constant) or a simultaneous change of both these quantities, Ω and γ . Derivation of eq. (14) results in

$$d\Omega = [2\omega\gamma r - \omega r^2(p^\alpha - p^\beta)] + \omega r^2 d\gamma \qquad (15)$$

The two conditions

$$d\Omega = 0 \quad \text{and} \quad d\gamma = 0 \qquad (16)$$

lead to eq. (11). This equation, eq. (11), is therefore valid if one of the quantities Ω and γ is a constant and the other has an extremum or if both of them have an extremum. The mathematical analysis shows the extremum of Ω (r, γ = constant) to be a maximum and that of γ (r, Ω = constant) to be a minimum. This situation is illustrated in Fig. 2. As we can see the line E, M connectes all the maxima of Ω determined by eq. (11). Furthermore eq. (11) selects all those functions γ (r, Ω = constant) having their minimum also at line E, M.

Setting the first term of eq. (14) equal to zero and $\omega = 4\pi$, i.e. the investigation of one droplet, yields the following expression for the extrema of the grand potential, Ω^* .

$$\Omega^* = \frac{1}{3}\gamma A \qquad (17)$$

This is the work to form a critical nucleus in classical nucleation theory.

The model of Kondo et al. /3/ therefore considers the effect of changing the number of molecules in the system on surface tension. It shows that critical clusters have minimal surface tension.

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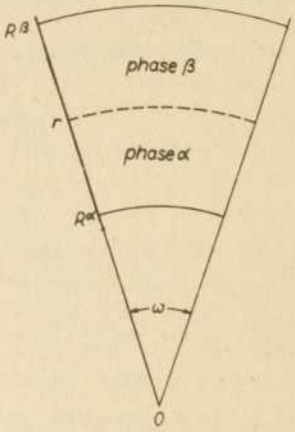

Fig.1: Schematic representation of a system with spherical geometry and composed of two phases α and β separated by an interface layer.

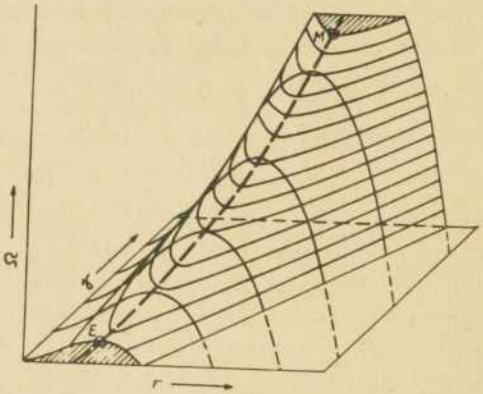

Fig. 2: Graphical representation of the relation between grand potential, Ω , surface tension, γ , and radius of curvature of the interface, r.

Author:

Dr. sc. W. Vogelsberger
Friedrich-Schiller-Universität Jena
Sektion Chemie
Lessingstraße 10
Jena
DDR - 6900

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Jürn Schmelzer

Curvature Dependence of Surface Tension of Drops and Bubbles in Multicomponent Systems

1. Introduction

Equations, describing the curvature dependence of surface tension were proposed by different authors (see, e.g. /1-9/) for one-component systems mainly. Since the investigation of nucleation in multicomponent systems is a field of active current research a formula describing the effect of the curvature on the surface tension in multicomponent systems is believed to be of interest.

For an exact calculation of this dependence the chemical potential and the surface tension as functions of the composition and pressure have to be known. Since such a complete knowledge is, in general, not available an approximative equation is derived here, which is of a relatively general nature and allows in addition to take into account specific properties of the system of interest.

2. General Thermodynamic Relations

The general thermodynamic relations the derivation is based on are the Gibbs adsorption equation (1)

$$d\sigma = -\sum_{i=1}^{k} \Gamma_{i0}\, d\mu_{i0} \qquad \Gamma_{i0} = n_{i0}/A \tag{1}$$

the Gibbs-Duhem equations (2)

$$dp_\alpha = \sum_{i=1}^{k} \rho_{i\alpha}\, d\mu_{i\alpha} \qquad dp_\beta = \sum_{i=1}^{k} \rho_{i\beta}\, d\mu_{i\beta} \tag{2}$$

and the necessary conditions for a thermodynamic equilibrium (3)

$$\mu_{i\alpha} = \mu_{i\beta} = \mu_{i0} \qquad p_\alpha - p_\beta = 2\sigma/R_s \tag{3}$$

n_{io} is the superficial mole number of the different components (i=1,2,...,k), ϱ is the molar density, μ the chemical potential, p the pressure, A the surface area of the cluster (drop or bubble), R_s its radius (both taken with respect to Gibbs' surface of tension). The subscript α specifies the thermodynamic parameters of the cluster, β the parameters of the medium surrounding the cluster.

3. Approximations and Results

If we consider first the case of formation of drops we obtain from the general relations (1) - (3) eq. (4):

$$\sum_{i=1}^{k} \{ \varrho_{i\alpha} - \varrho_{i\beta} \} \, d\mu_{i\beta} = d\left\{ \frac{2\sigma}{R_s} \right\} \tag{4}$$

Assuming the gas can be considered as a perfect one, the change of the chemical potential of the different components is given by

$$d\mu_{i\beta} = RT \, d(\ln \frac{p_\beta}{p'} + \ln x_{i\beta}) \qquad x_i = \frac{n_{i\beta}}{\sum n_{i\beta}} \tag{5}$$

p' being the value of the pressure of gas and liquid in stable equilibrium at a planar interface.

If it is assumed further, that the composition of the gas does not depend significantly on the size of the drop, eq. (5) yields

$$d\mu_{i\beta} = \frac{RT}{p_\beta} dp_\beta \tag{6}$$

and finally we get

$$\frac{d\sigma}{\sigma} = - \frac{2\,\delta_m}{1 + \frac{2\,\delta_m}{R_s}} \, d\left(\frac{1}{R_s} \right) \qquad \delta_m = \frac{\sum \Gamma_{io}}{\sum (\varrho_{i\alpha} - \varrho_{i\beta})} \tag{7}$$

The general solution (8) of the differential equation (7) has the same form as obtained earlier for the one-component case /8,9/

$$\sigma(R_s) = \frac{\sigma_\infty}{1 + \frac{2\delta_m}{R_s}} \exp\left\{ 2 \int_\infty^{R_s} \frac{\frac{1}{r}\frac{\partial \delta_m}{\partial r}}{1 + \frac{2\delta_m}{r}} dr \right\} \qquad (8)$$

Again, eq. (8) can be solved only if the curvature dependence of the generalized Tolman parameter δ_m as a function of R_s is known. In a first approximation $\delta_m = \delta_{mo} = \text{const.}$, we get a Tolman-like formula (9):

$$\sigma(R_s) = \frac{\sigma_\infty}{1 + \frac{2\delta_{mo}}{R_s}} \qquad (9)$$

Moreover, the same proposals (10) and (11)

$$\delta_m(R_s) = \delta_{mo} \frac{R_s}{a(T) + R_s} \qquad (10)$$

$$\delta_m(R_s) = \delta_{mo} \frac{R_s + b(T)}{R_s + a(T)} \qquad (11)$$

as for one-component systems can also be used to find other classes of equations for the curvature dependence of surface tension in multicomponent systems (see /8,9/).

The eqs. (10) and (11) were proposed based on two arguments; first, δ_m has to become equal to the constant value δ_{mo} for sufficiently large clusters, and, second, as the result of integration physically reasonable (non-divergent) expressions for σ have to be obtained. In addition, specific properties of the system of interest have to be reflected (here expressed by the parameters a and b).

For a derivation of the equations for the curvature dependence of bubbles instead of eq. (4) we have to apply eq. (12):

$$\sum_i \{ \varrho_{i\alpha} - \varrho_{i\beta} \} d\mu_{i\alpha} = d\left\{ \frac{2\sigma}{R_s} \right\} \qquad (12)$$

Since the subscript α specifies the gas phase, now, eq. (6) can be used to replace $d\mu_{i\alpha}$ in eq. (12), which results in eq.

(7), again. But note, that δ_m for a given value of the sum $\sum \Gamma_{io}$ has different signs in dependence, whether the formation of drops or bubbles, respectively, is considered.

If δ_{mo} is greater than zero eq. (10) is to be applied which results for different values of the parameters in curves for the curvature dependence of surface tension as presented qualitatively in Fig. 1. Eq. (11) has to be used in the case $\delta_{mo} < 0$ leading to a behaviour shown in Fig. 2.

4. Discussion

The final results of our analysis, in particular, eqs. (7) are based upon two approximations, the assumption of a perfect gas law for the description of the gas (which is believed not to be a serious limitation) and the assumption of a constant molar fraction of both phases independent of the size of the cluster. This second approximation will not lead to significant deviations, if the surface tension does not depend strongly on composition. It means, that the second term in eq. (13)

$$d\sigma = -RT \sum_{i=1}^{k} \Gamma_{io}\, d\left\{ \ln \frac{p_{gas}}{p'} + \ln x_{i\,gas} \right\} \qquad (13)$$

has to be small compared with the first. Whether this condition is fulfilled, depends, of course, on the special system considered.

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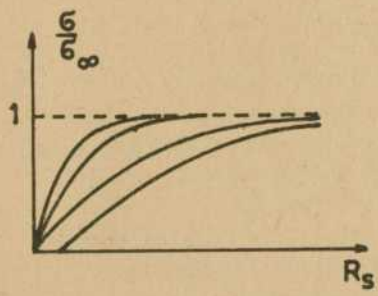

Fig. 1: Curvature dependence of the surface tension of droplets in the gas phase

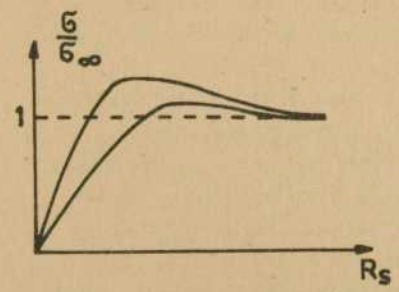

Fig. 2: Curvature dependence of the surface tension of bubbles in the liquid phase

Author:

Dr. sc. Jürn Schmelzer
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock
DDR - 2500

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Frank Schweitzer, Jürn Schmelzer

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 supersaturated 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 formulaes 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 χ 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).

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:

$$y_o(N,V,T) = \frac{N k_B T}{p_\infty V} = \frac{p}{p_\infty(T)} \qquad (1)$$

Here we assume an initial state with N free particles. Further in this paper only isothermal processes are supposed (T = const.). In general cooling rates change the supersaturation rapidely. 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

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

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_o):

$$F_{het} = F_\alpha + F_\beta + F_o \qquad (3)$$

The droplet phase is spatially distributed, that means

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

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 (l).

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

discussed, where F_{hom} means the free energy of the initial homogeneous system: $F_{hom} = -pV + \mu N$ 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/:

$$\Delta F = (p - p_\beta) V + (\mu_\beta - \mu) N$$

$$+ \sum_{l=1}^{s} \left\{ (p_\beta - p_\alpha^{(l)}) V_\alpha^{(l)} + (\mu_\alpha^{(l)} - \mu_\beta) N_\alpha^{(l)} + \sigma O_\alpha^{(l)} \right\} \qquad (5)$$

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:

$$f_1 = \mu_\alpha(N_\alpha, V_\alpha) - \mu_\beta(N_\beta, V_\beta) = 0$$

$$f_2 = p_\alpha(N_\alpha, V_\alpha) - p_\beta(N_\beta, V_\beta) - \frac{2\sigma}{r_\alpha} = 0 \qquad (6)$$

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

f_1 and f_2 define implecitely 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/:

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

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/

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

p_β is the vapor pressure

$$p_\beta = \frac{N_\beta k_B T}{V} = \frac{(N - N_\alpha) k_B T}{V}$$

and the ratio p_β/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:
(i) The work of formation of equilibrium droplets is obtained

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

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

The first term on r.h.s. is denoted as W_{Gibbs}, because Gibbs has found $W = \frac{1}{3}\sigma O$ 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/

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

y_c has to reach <u>at least</u> 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 hight 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/

$$\frac{dN_\alpha}{dt} = -\frac{c_\beta D}{k_B T}\,\frac{1}{l}\,4\pi r_\alpha^2 \left|\frac{\partial_\Delta \Phi}{\partial N_\alpha}\right| \qquad (11)$$

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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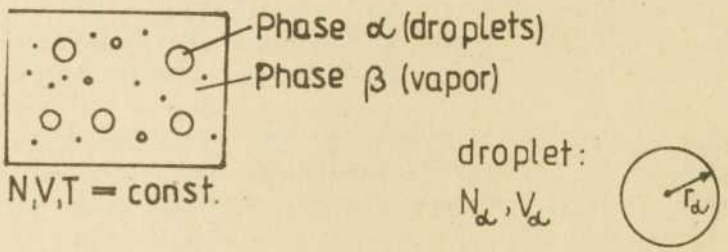

Fig. 1: The finite heterogeneous system for the condensation process in a supersaturated vapor.

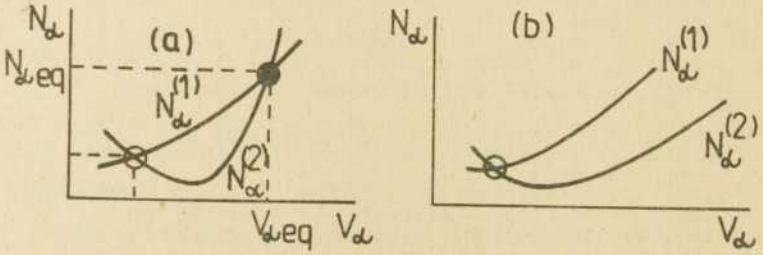

Fig. 2: Sketch of the functions $N_\alpha^{(1)}(V_\alpha)$ and $N_\alpha^{(2)}(V_\alpha)$ representing the equilibrium conditions (6). The points of intersections give the equilibrium states ($N_{\alpha eq}$, $V_{\alpha eq}$).
(a) N,V,T = const., (b) N,P,T = const. /10/

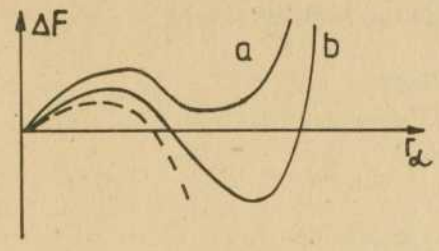

Fig. 3: Schematic plot of the free energy vs. droplet radius r_α . The initial supersaturation of plot (b) is larger than this of plot (a). The dashed line gives the free energy for the droplet formation in an infinite system.

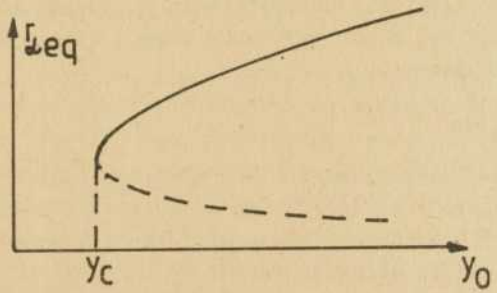

Fig. 4: Equilibrium droplet size ($r_{\alpha\, eq}$) vs. initial supersaturation y_0. The solid line gives the stable droplet radius, the dashed line the critical radius. An overcritical droplet is found only for initial supersaturations larger than y_c (eq. (10) /12/).

Authors:

Dr. F. Schweitzer
Dr. sc. J. Schmelzer
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock 1
DDR - 2500

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Nikolai F. Patsegon, Ivan Ye. Tarapov

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/ assigment 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:

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

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/:

$$\frac{d}{dt}\int_{\tau}\rho\, d\tau = 0\,, \quad \frac{d}{dt}\int_{\tau}\rho\, v_i d\tau = \int_{\Sigma} p_{ik}N_k d\Sigma \qquad (2.1)$$

$$\frac{d}{dt}\int_{\tau}\rho\,(k_i + \mathcal{E}_{ijk}x_j v_k)d\tau = \int_{\Sigma} Q_{ik}N_k d\Sigma + \int_{\Sigma}\mathcal{E}_{ijk}x_j p_{ks}N_s d\Sigma$$

$$\frac{d}{dt}\int_{\tau}\rho\,(V + \frac{v^2}{2})d\tau = -\int_{\Sigma}\mathcal{J}_k N_k d$$

Here: τ is an individual volume of medium, bounded by the surface Σ with normal $\vec{N}$, $\vec{v}$ - velocity of the medium, $\{\mathcal{E}_{ijk}\}$ - antisymmetric unite tensor, p_{ik} and Q_{ik} - components of stress tensor and momentum stress tensor (tensor of intrinsic moment of momentum diffusion) respectively, $\vec{\mathcal{J}}$ - energy flux density vector, $\vec{x}$ - radius-vector of elementary volume $d\tau$ in the reference frame.

Eqs. (2.1) should be completed by the equation of quasistationary electrodynamics in integral form.

Besides mass, momentum, moment of momentum and energy there is a volume magnetic momentum as an additive function of medium volume /3/. As volume density of a magnetic momentum is magnetization $\vec{M}$ of medium, we postulate the equation of changing medium individual volume magnetic momentum in the following balance equation form

$$\frac{d}{dt}\int_{\tau} M_i d\tau = \int_{\Sigma} m_{ik}N_k d\Sigma + \int_{\tau} r_i d\tau \qquad (2.2)$$

where $\{m_{ik}\}$ - tensor of magnetization diffusion, $\vec{r}$ - the volume source of magnetization. The presence of the source in this equation is due to the fact, that magnetization $\vec{M}$ only describes the medium, which is a part of the closed system "medium, electromagnetic field". The addend in the surface integral form in eq. (2.2) represents changing individual volume magnetic momentum of the medium with time under the influence of the adjacent volumes field of magnetization. Such interaction is of magnetodipole nature; in the ferrofluid it is, in general, of short distances action and is transfered through the surface, as its potential with the distance d decreases as d^{-3} /3/ and damps at the distances of the order of dispersed ferromagnetic particles sizes ($d \gtrsim 10^{-6}$ m). Its intensity can be described

by vectors $\vec{m}_n$ of generalized force pairs acting on unite surface with normal $\vec{n}$. Then $\vec{m}_n = \vec{m}_k n_k$, where $\vec{m}_k$ are the pairs on the three perpendicular surfaces. For gyromagnetic media ($\rho \propto \vec{k} = \vec{M}$, $\propto$ - gyromagnetic ratio) the eq. (2.2) must coincide with the equation of changing of intrinsic moment of momentum in the system (2.1), so that the componente of tensors $\{m_{ik}\}$ and $\{Q_{ik}\}$ will be proportional ($\propto Q_{ik} = m_{ik}$) . Hence, tensor $\{m_{ik}\}$ is refered to as "tensor of magnetic momentum tensions". In general, tensors of momentum and magnetic momentum tensions are defined independently in ferrofluids.

From eqs. (2.1), (2.2) and equations of electrodynamics in integral form the following conditions on the steady discontinuity surfaces are obtained

$$\langle \rho v_n \rangle = 0 \; ; \quad \langle p_{ik} n_k - \rho v_i v_n \rangle = R_i \qquad (2.3)$$

$$\langle Q_{ik} n_k - \rho v_n k_i \rangle = K_i - \varepsilon_{ijs} x_j R_s ; \; \langle \mathcal{U}_n + \rho v_n (V + \frac{v^2}{2}) \rangle = - W$$

$$\langle B_n \rangle = 0 ; \quad \langle \vec{H}_\tau \rangle = \frac{4}{c} \vec{i} \times \vec{n}$$

$$\langle m_{ik} n_k - M_i v_n \rangle = \mathcal{M}_i$$

Here: $\vec{n}, \vec{\tau}$ - unite vectors of normal and tangent to discontinuity surface, v_n - normal constituent of vector $\vec{v}$ relative discontinuity surface, $\vec{i}$ - surface current density, $\vec{B} = \vec{H} + 4\pi \vec{M}$ - magnetic induction; $\vec{R}$, $\vec{K}$, $\vec{\mathcal{M}}$, W - the surface densities of external force, momentum of force, magnetic momentum and energy respectively. $\langle \ldots \rangle$ denote the jump of quantity contained in them on the discontinuity surface.

For tangential discontinuities ($v_n = 0$) in the absence of surface phenomena ($\vec{R}$, $\vec{K}$, $\vec{\mathcal{M}}$, W all equal to zero) from eqs.(2.3) the continuity of tensions, momentum tensions, normal componente of flux energy vector and magnetic momentum tension follow. Note that without using eq. (2.2) in integral form the absence of the last condition (2.3) occurs, so that the number of jump conditions becomes less than the member of constitutive parameters and corresponding differential equations.

3. Complete System of Differential Equations

In regions of continuity of constitutive parameters with their derivations to the second order including the fluid flows are described by the following system of differential equations

$$\frac{d\rho}{dt} + \rho v_{k,k} = 0 \; ; \quad \rho \frac{dv_i}{dt} = p_{ik,k} \tag{3.1}$$

$$\rho \frac{dk_i}{dt} = Q_{ik,k} + \varepsilon_{ijk} p_{kj} ; \quad \frac{d}{dt} \frac{M_i}{\rho} = m_{ik,k} + r_i$$

$$\rho \frac{d}{dt} \left(V + \frac{v^2}{2}\right) = - \mathcal{W}_{k,k}$$

$$\operatorname{div} \vec{B} = 0, \quad \operatorname{rot} \vec{H} = \frac{4\pi}{c} \vec{J} \; , \quad \operatorname{rot} \vec{E} = - \frac{1}{c} \frac{\partial \vec{B}}{\partial t}$$

where $\vec{E}$ - electric field strength, $\vec{J}$ - volume current density, comma before the index denotes the covariant derivative.

From the expression (1.1) for internal energy, assuming isotropy of medium, Gibb's identity is written in the following form /1,4/:

$$dV = Td\mathcal{S} - pd\left(\frac{1}{\rho}\right) + \vec{\Omega}^e d\vec{k} + \vec{H}^e d \frac{\vec{M}}{\rho} + \frac{\vec{H}}{4\pi} d \frac{\vec{H}}{\rho} \tag{3.2}$$

where: T - temperature, p - pressure, $\vec{\Omega}^e$ - effective angular velocity of ferroparticles, $\vec{H}^e$ - effective magnetic field

$$\vec{\Omega}^e = \frac{\vec{k}}{I} + \alpha \frac{M}{\rho} \; ; \quad \vec{H}^e = \frac{\vec{M}}{\chi} + \alpha \vec{k} \tag{3.3}$$

Effective phenomenological parameters: I - average inertial momentum of ferroparticles in unit mass, χ - equilibrium magnetic susceptibility, α - gyromagnetic ratio - are introduced in the following way

$$I^{-1} = 2 \frac{\partial V}{\partial k^2} \; , \quad \rho \chi^{-1} = 2 \frac{\partial V}{\partial \frac{M^2}{\rho^2}} \; , \quad \alpha = \frac{\partial V}{\partial \frac{\vec{k}\vec{M}}{\rho}} \tag{3.4}$$

In the case, when I, χ, α depends only on ρ and T, using (3.2) we obtain

$$p = p_0(\rho, T) + \frac{H^2}{8\pi} + \frac{M^2}{2}\left(\frac{\rho}{\chi}\right)_{,\rho} + \rho \alpha_{,\rho} (\vec{k}\vec{M}) - \frac{k^2 \rho^2}{2I^2} \; I_{,\rho} \tag{3.5}$$

$$s = s_0(\rho, T) + \frac{M^2}{2\rho\chi^2} \chi_{,T} - \frac{\vec{k}\vec{M}}{\rho} \alpha_{,T} + \frac{k^2}{2I^2} I_{,T}$$

where $a_{,u}$ denotes the partial derivative of a with respect to u p_o, s_o - pressure and entropy in the absence of the field and internal moment of momentum. Using the methods of nonequilibrium thermodynamics /5/ and eqs. (3.1)-(3.5) we get the following expressions for the vector of flux energy density $\vec{\mathcal{J}}$, stress tensor $\{p_{ik}\}$ and entropy production θ :

$$\mathcal{J}_k = (p - \frac{\vec{B}\vec{H}}{4\pi})\, v_k + \frac{c}{4\pi}[\vec{E}\times\vec{H}]_k + q_k - v_i \Pi_{ik} - \Omega^e_i Q_{ik} - h_i m_{ik} \tag{3.6}$$

$$p_{ik} = -p\,\delta_{ik} + \frac{H_i B_k}{4\pi} + \Pi_{ik}$$

$$\theta = -\frac{q_k}{T} T_{,k} + \Pi_{ik} v_{ik} + Q_{ik}\Omega^e_{i,k} + m_{ik} h_{i,k} - \varepsilon_{isk}\Omega^e_i \Pi_{ks} +$$

$$+ \vec{J}\vec{E}' - h_i(r_i + \lambda_1 \varepsilon_{isk} M_s \Omega^e_k + \lambda_2 \frac{\chi}{I} H_s k_k + \frac{\lambda_3}{\alpha I}\varepsilon_{isk} M_s H_k)$$

Here: $\vec{q}$ - vector of heat flux density, $\vec{h} = \vec{H}^e - \vec{H}$, $\vec{E}' = \vec{E} + \frac{\vec{v}\times\vec{B}}{c}$; $\lambda_1, \lambda_2, \lambda_3$ - random functions of constitutive parameters, satisfying the condition

$$\lambda_1 + \lambda_2 + \lambda_3 = 1$$

Hence, assuming the symmetry of phenomenological coefficients in linear approximation we get the following material equations, closing eqs. (3.1):

$$p_{ik} = -p\,\delta_{ik} + \frac{H_i B_k}{4\pi} + 2\eta v_{ik} + (\beta - \frac{2}{3}\eta)\,\mathrm{div}\,\vec{v}\,\delta_{ik} + \tag{3.7}$$

$$+ \frac{\rho l}{2\tau_s}\varepsilon_{iks}(\Omega^e_s - \Omega_s) - \frac{\varepsilon_{iks}}{2\tau_m} h_s ;$$

$$Q_{ik} = \delta_1 \Omega^e_{i,k} + (\delta_2 - \delta_3)\,\mathrm{div}\,\vec{\Omega}^e\,\delta_{ik} + \delta_3 \Omega^e_{k,i} + \sigma_1 h_{i,k} +$$

$$+ (\sigma_2 - \sigma_3)\mathrm{div}\,\vec{h}\,\delta_{ik} + \sigma_3 h_{k,i} + \varepsilon_1 \varepsilon_{iks} E'_s - \omega_2 \varepsilon_{iks} T_{,s} ;$$

$$m_{ik} = m_1 h_{i,k} + (m_2 - m_3)\mathrm{div}\,\vec{h}\,\delta_{ik} + m_3 h_{k,i} + \sigma_1 \Omega^e_{i,k} +$$

$$+ (\sigma_2 - \sigma_3)\mathrm{div}\,\vec{\Omega}^e\,\delta_{ik} + \sigma_3 \Omega^e_{k,i} - \omega_1 \varepsilon_{iks} T_{,s} + \varepsilon_2 \varepsilon_{iks} E'_s ;$$

$$\vec{r} = \frac{1}{\tau_m}(\vec{\Omega}^e - \vec{\Omega}) - \frac{\vec{h}}{\tau} - \lambda_1 \vec{M}\times\vec{\Omega}^e - \frac{\lambda_2 \chi}{I}\vec{H}\times\vec{k} - \frac{\lambda_3}{\alpha I}\vec{M}\times\vec{H} ;$$

$$\vec{J} = \sigma\vec{E}' - \frac{\varepsilon_3}{T}\nabla T - \varepsilon_1 \operatorname{rot}\vec{\Omega}^e - \varepsilon_2 \operatorname{rot}\vec{h};$$

$$\vec{q} = -\lambda\nabla T + \varepsilon_3\vec{E}' - \omega_2 T \operatorname{rot}\vec{\Omega}^e - \omega_1 T \operatorname{rot}\vec{h};$$

$$\vec{\Omega} = \frac{1}{2}\operatorname{rot}\vec{v},$$

where $\{v_{ik}\}$ is rate deformation tensor.
According to the second law of thermodynamics, dissipative coefficients satisfy the following inequalities:

$$\lambda \geq 0,\ \zeta \geq 0,\ \eta \geq 0,\ \sigma \geq 0,\ \rho I/\tau_\zeta \geq 0,\ 1/\tau \geq 0 \qquad (3.8)$$

$$m_1 - m_3 \geq 0,\ m_1 + m_3 \geq 0,\ \delta_1 - \delta_3 \geq 0,\ \delta_1 + \delta_3 \geq 0$$

$$3\delta_2 - 2\delta_3 + \delta_1 \geq 0,\ 3m_2 - 2m_3 + m_1 \geq 0$$

$$(\sigma_1 - \sigma_3)^2 \leq (m_1 - m_3)(\delta_1 - \delta_3),\ (\sigma_1 + \sigma_2)^2 \leq (\delta_1 + \delta_3)(m_1 + m_3)$$

$$1/\tau_m^2 \leq \rho I/\tau\tau_\zeta,\ 2\omega_1^2 T \leq \lambda(m_1 - m_3),\ 2\omega_2^2 T \leq \lambda(\delta_1 - \delta_3)$$

$$2\varepsilon_1^2 \leq \sigma(\delta_1 - \delta_3),\ 2\varepsilon_2^2 \leq \sigma(m_1 - m_3),\ \varepsilon_3^2 \leq \lambda\sigma T$$

Equality to zero of the following dissipated coefficients: $\sigma_1, \sigma_2, \sigma_3, \varepsilon_1, \varepsilon_2, \varepsilon_3, \omega_1, \omega_2, \tau_m^{-1}$ - corresponds to considering only direct effects in eqs. (3.1)-(3.7). Setting in this case α, λ_2, λ_3, $\lambda_3\alpha^{-1}$, m_1, m_2, m_3 equal to zero we get the equations of the work /1/. With additional assumptions $\delta_1 = \delta_2 = \delta_3 = 0$ equations of the work /6/ are obtained. Note, that inequalities (3.8) lay the restrictions on the character of tending to zero of dissipated coefficients.

4. Results

The general system of equations describing diffusion of intrinsic moment of momentum and magnetization both is obtained. The complete system of jump conditions on discontinuity surfaces in micropolar ferrohydrodynamics is analyzed.

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Authors:

Ass.-Prof. N.F. Patsegon, Prof. I.Ye. Tarapov
The State University of Kharkov
Kharkov 310077
USSR

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A. Richter, W. Pompe, J. Bartels

Transient Nucleation Effects

Abstract

Transient nucleation is investigated under isothermal and non-isothermal conditions with a quench rate as well as for depletion effects. These processes are characterized by deviations from the steady state nucleation, so that time regimes play an important role. Time dependent cluster populations, time lag and nucleation frequencies are calculated by a numerical simulation which models directly the reactions by which clusters are produced during time and temperature changes. A simple estimation is presented for determining when transient effects are important.

1. Introduction

Many phase transformations occur as a complex process of nucleation and growth. The transient period in a nucleation process will be refered to as the time during which the nuclei production rate is increasing to its steady value. In selected systems this period can be long, so that experimental observation is possible. In these cases it is important to take account of transient nucleation behaviour in interpretation of phase transformation kinetics.

Transient effects are important under different conditions. At constant temperature, time dependent cluster populations exist characterized by an effective time lag, since it will take some time for the steady state nucleation rate to be established. If the system has a low steady state nucleation rate, the depletion of the number of atoms in the initial state does not affect the process and can be ignored. Time dependent monomer and/or preexisting cluster distributions of the initial state including also depletion result in an additional time dependence of the nonstationary nucleation rate beyond

conventional time lags. Transient effects are especially important, if supersaturation varys rapidly by changes of temperature, pressure and/or chemical compositions. An example may be found in the formation of an amorphous structure, which occurs if crystallization is bypassed because the transient periods are relatively long. This can be established by high cooling rates.

The aim of the present paper is to investigate deviations from the steady state solutions in the context of classical nucleation theory. A numerical technique was developed to investigate the time dependent cluster populations in the isothermal and non-isothermal case. Results are applied to obtain conditions under which transient effects dominate. The influence of transient nucleation kinetics on experimental methods is discussed.

2. Basic Rate Equations

Classical nucleation theory /1/ describes the nucleation of a phase by the occurrence of clusters. The free energy of formation of a cluster of n atoms ΔG_n is given by

$$\Delta G_n = n\delta g + \sigma A_n \,, \qquad (1)$$

where δg is the Gibbs free energy per atom of the new phase, σ is the interfacial free energy per unit area and A_n is the surface area of a cluster of n atoms. In the classical theory δg and σ are taken to have macroscopic values independent of n. There may be additional contributions to ΔG_n resulting from phonons and elastic deformations in solids /2/ not explicitely given in (1). In this paper spherical clusters with $A_n \sim n^{2/3}$ are considered, but extensions to other cluster shapes can be obtained, too. The driving force for the reaction in non-isothermal processes is proportional to the undercooling

$$\delta g = \Delta S(T_o - T) \,. \qquad (2)$$

In this paper we only consider this case mainly relevant for transformations from a liquid to a solid. However, in deposition from the vapour, the supersaturation depends strongly on

the pressure and the deposition rate and modified, but similar temperature treatments have to be used /3/.

The free energy of a cluster goes through a maximum as the cluster size is increased and defines a critical cluster n_c. Smaller clusters tend to shrink, large clusters tend to grow. Assuming that growth and decay of these clusters occur only through attachment and detachment of single atoms, we can write the following equations

$$\frac{dZ_n(t)}{dt} = D^+_{n-1}(t)Z_{n-1}(t)+D^-_{n+1}(t)Z_{n+1}(t)-D^+_n(t)Z_n(t)-D^-_nZ_n(t)$$

$$= I_{n-1}(t)-I_n(t) \ . \qquad (3)$$

Here $D^+_n(t)$ and $D^-_n(t)$ are the frequencies of a single atom attachment to and detachment from a cluster of n atoms. $Z_n(t)$ denotes the time dependent population of a cluster with size n. $I_n(t)$ is the net nucleation rate, in general a function of time and cluster size. Expressions for the frequency $D^+_n(t)$ suppose a time independent constant proportional to the number of single atoms on the surface of a cluster with size n and to the jump rate γ which is related to the adatom diffusion coefficient $D^+_n \sim \gamma n^{2/3}$. The atomic jump frequency was calculated from the diffusion coefficient which was assumed to be

$$D = D_o \exp\left(-\frac{E}{T-T_u}\right) \ . \qquad (4)$$

Contrary to the usual Arrhenius temperature dependence, a Vogel-Fulcher expression is used indicating a slowing down of the atomic motion, if the temperature reaches a lower limit T_u. The detachment frequency is related to D^+_n by means of the equilibrium distribution

$$Z^e_n(t) = N(t) \exp\left(-\Delta G_n/kT\right) \qquad (5)$$

for clusters of size n

$$D^-_n(t) = D^+_n(t)\,\frac{Z^e_n(t)}{Z^e_{n+1}(t)} \ . \qquad (6)$$

N(t) is the time dependent number of single atoms when the system is in quasi-equilibrium. Depletion of monomers is taken

into account by the boundary condition

$$Z_1(t) = N(t_o) - \sum_{n>2}^{\infty} n\, Z_n(t) \quad . \qquad (7)$$

Solution of equation (3) is performed by numerical simulation of the reactions involved in cluster formation. The essence of the approach is to devide time into small intervals δt. If the number of clusters is $Z_n(t)$ at the start of the intervall, then at the end of the interval we have

$$Z_n(t+\delta t) = Z_n(t) + \delta t\, I_{n-1}(t) - I_n(t) \quad . \qquad (8)$$

The expression does not take into account the alteration in the cluster population during the intervall and is true only in the limit $\delta t \rightarrow 0$. The value of δt depends on the molecular jump rate γ and on the minimum and maximum cluster size n considered in the model calculations. The extension of this method to the non-isothermal case is more sophisticated, since the time interval cannot be chosen constant. Moreover, at high temperatures critical nuclei are very large, so that simulation can be started only at an appropriate temperature determined by the range of cluster size. Starting values for the nucleation rate at that temperature are steady state frequencies. Actual temperatures are defined by quench rates T and time intervals. The calculation of nucleation rates at that temperature continues using the cluster distribution inherited from the previous temperature.

3. Deviations From Steady State Solutions

In the transient regime, unlike the steady state, the nucleation rate at any instant is a function of cluster size in the isothermal case (Fig. 1). Although all the rates converge to the steady state nucleation rate, there is an overshoot for $n < n_c$. Similar results are presented by Kelton et al. /4/. The cluster population $Z_n(t)$ (Fig. 2) increases monotonically to the steady state distribution, which obviously depends on the cluster size. Large clusters need more time to reach the level of constant population than smaller ones. Therefore, time lag and related particle size control phase transforma-

tion kinetics in the isothermal case. An effective time lag was estimated from the relation between cluster population of size n and time /5/. At different temperatures under isothermal conditions, the effective time lag varys over a large time scale (Fig. 3). Small temperatures correspond to large time lags and vice versa. However, an Arrhenius dependence with a modified activation energy due to transient effects as discussed in /4/ could not be obtained. Deviations mainly occur because of a different temperature behaviour of the diffusion.

Depletion of atoms in the initial state as described by (7) is demonstrated in Fig. 4. In the beginning of the nucleation process no deviations from the known behaviour with reference to transient stages are observed. The effect of a vanishing monomer density manifests itself in the halt of the nucleation process after a characteristic time /6/. This result in a modification of the behaviour shown in Figs. 1 and 2. The transient nucleation rate reaches only a portion of the stationary value (e.g. 30%), which strongly depends on the value of the steady state nucleation frequency. Large clusters are not produced, and the population of smaller clusters does not reach the steady state value.

Non-isothermal nucleation shows qualitatively new features. Since the temperature changes during the whole process, the steady state nucleation frequency is a function of temperature. Its value corresponds to the steady state frequency at the actual temperature calculated in the isothermal limit. The temperature dependence of the stationary nucleation rate is governed by the interplay of the nucleation driving force and atomic mobility described by diffusion. Therefore, a maximum nucleation rate exists at a temperature characteristic for the set of parameters considered. Quench rates result in nucleation frequencies below the steady state value (Fig. 5). At high temperatures all curves approach the stationary rate. Deviations from the steady state with decreasing temperature reflecte decreasing atomic mobility. Increasing quench rates lower drastically the transient nucleation frequency and displace the maximum nucleation rate to higher temperatures. The larger de-

viations from the steady state, the more increases the probability that crystallization is bypassed and an amorphous structure is formed. Since transient effects can gradually lower the nucleation rate at a given temperature, the crystalline volume fraction may be very small, even with high growth velocities. Therefore, transient nucleation kinetics lowers the limiting cooling rates required to obtain an amorphous structure in comparison with estimations obtained with steady state frequencies.

The importance of transient effects on crystallization is connected with a criterion for the transformed volume fraction q during the effective time lag Θ_{eff}:

$$q = \sum_{n>2} n\, q_n \quad \text{with} \quad q_n = \int_{t=0}^{\Theta_{eff}} dt\; I_n(t) \,. \tag{9}$$

If a sufficient volume fraction during that period is crystallized, time stages play a dominant role in phase transformation kinetics. Since q has to be chosen arbitrarily, a range of values is given in Fig. 6. The tendency to distinguish between thermodynamically and kinetically controlled nucleation is obvious. The size of the critical nucleus and the activation energy barrier can be changed by several experimental techniques. Low ΔG_c values as well as small critical nuclei favour transient behaviour of nucleation.

Laser plasma deposition of thin films /7/ reveals as an experimental method to control crystallization by time stages. With the use of laser pulses it is possible to define time intervals experimentally. High heating and cooling rates are also involved in that deposition process, which can be varied by the power density of the laser beam and the time of flight of the plasma. Substrate heating can gradually decrease the time lag. Moreover, high deposition rates indicate a low activation energy ΔG_c for crystallization. In this respect we could demonstrate that transient effects are important in interpretation of experimental results and in controlling the crystallization process. A simple analysis could be presented to evaluate these effects.

Acknowledgement

One of the authors A.R. gratefully acknowledges helpful and stimulating discussions with Prof. I. Gutzow and Dr. D. Kashchiev during a kind hospitality in Sofia.

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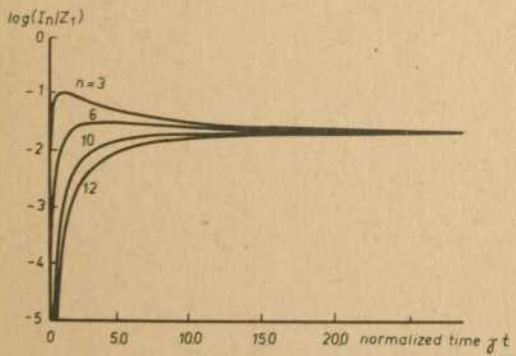

Fig. 1: Nucleation rate $I_n(t)$ in dependence on normalized time steps τt for different cluster sizes n (n_c = 10)

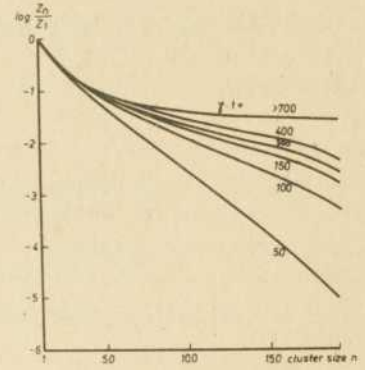

Fig. 2: Cluster population $Z_n(t)$ versus cluster size n at different time stages

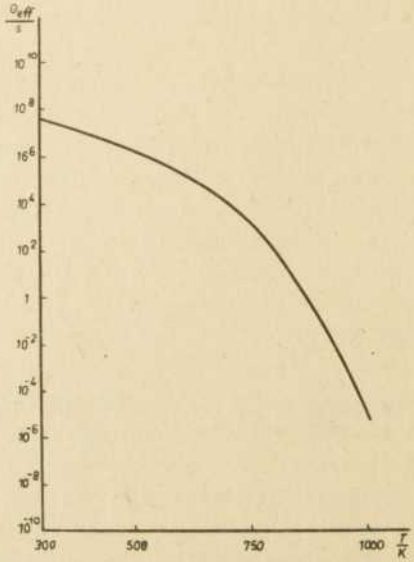

Fig. 3: Effective time lag versus temperature

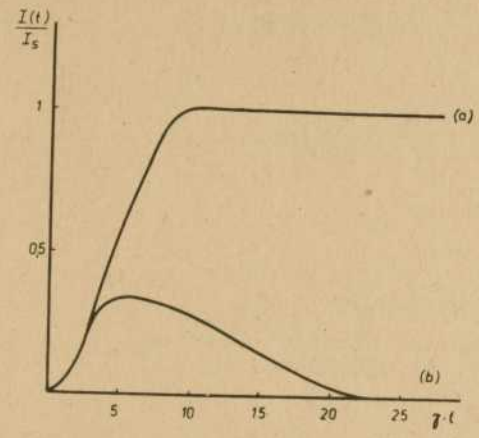

Fig. 4: Time dependence of the nonstationary nucleation rate for a system with a constant number of monomers (a) and depletion of the number of atoms in the initial state (b)

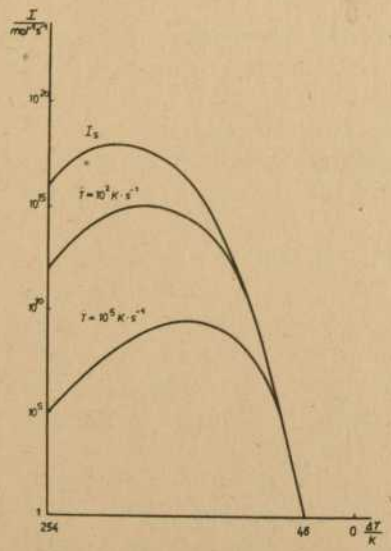

Fig. 5: Nucleation rate as a function of undercooling and quench rate

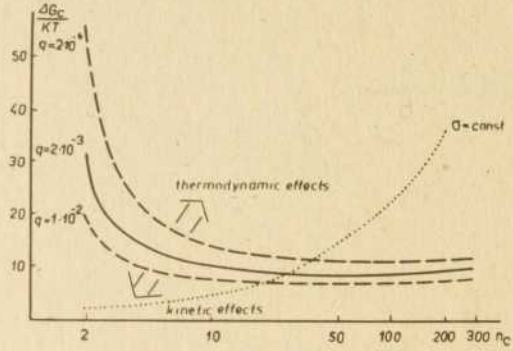

Fig. 6: Schematic representation of nucleation and growth processes distinguishing areas of thermodynamically and kinetically controlled nucleation

Authors:

Dr. A. Richter, Prof. W. Pompe
Zentralinstitut für Festkörperphysik und
Werkstofforschung der AdW der DDR
Helmholtzstraße 20
Dresden
DDR - 8027

stud.phys. J. Bartels
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock
DDR - 2500

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Reinhard Mahnke

On the Kinetics of Ostwald Ripening in Finite Systems

1. Introduction

A complete theory of the dynamics of first-order phase transitions in equilibrium and nonequilibrium systems would give an important impetus to investigate such physical processes like nucleation, spinodal decomposition, growth of clusters and late-stage coarsening in different materials. But until now such theories have to be confined to certain aspects of the total dynamics starting from an initial quench to the establishment of full phase separation. In general such a quenched system evolves from a nonequilibrium situation (metastable or unstable state) to an thermodynamic equilibrium state, which consists of two coexisting phases. Recent reviews concerning the highly nonlinear dynamics of phase transitions can be found in /1/-/3/.

In this work we are dealing with a one-component system after a quench from the one phase region into the metastable region. After an initial nucleation (compare /4/ for the stochastic formation of clusters) where the supersaturation is high enough a growth of all precipitating droplets of the newly formed phase takes place. In the late-stage of phase separation where the supersaturation is small and near to the equilibrium value, we find that larger drops grow at the expense of smaller ones which disappear. This process is called Ostwald ripening or coarsening and it is closely related to the competitive growth of selfreplicative units in selforganizing systems /5/.

The dynamics of Ostwald ripening is investigated by studying the set of kinetic equations recently derived for the intermediate as well as late stage of first-order phase transitions /6/. Besides the standard theory of Lifshitz-Slyozov-Wagner /3/ a number of attempts has been made to include new aspects /7/-/11/.

Starting from the basic equations of the competitive growth problem we derive a set of ordinary nonlinear differential equations governing the constrained growth of a droplet ensemble with s components. Numerical solutions for the evolution of the droplet ensemble are given. We conclude that the average curvature of all droplets is a non-increasing function of time. Finally we present the kinetic equation for the mean curvature and discuss the analogy in modeling phase transitions on the one hand and evolution processes in biophysics on the other /11/.

2. Basic Equations of the Competitive Growth Problem

In the following we consider a model of the quenched system where spherical clusters are located in the otherwise homogeneous surrounding medium. We have to distinguish between free monomers (phase β) and bound states of monomers (clusters or droplets as phase α). A detailed explanation of the model is given elsewhere /6,13/. Our basic quantities describing a closed two-phase system in volume V are:

- for the vapour phase

$c(t) = M_\beta(t)/V$ concentration of free monomers (1)

$y(t) = (c(t)-c_{eq}(\infty))/c_{eq}(\infty)$ supersaturation (1')

- for the liquid phase

$f(n,t) = N(n,t)/V$ cluster density distribution function (2)

We mention that the distribution function (2) is normalized to the total droplet density

$$\int_0^\infty f(n,t)\, dn = N_\alpha/V \tag{3}$$

and for the first moment of (2) we get the total number of bounded monomers M_α per volume

$$\int_0^\infty n\, f(n,t)\, dn = M_\alpha/V \tag{4}$$

The basic equations of the competitive growth problem read as follows (compare e.g. /1,3,5/):

(i) Continuity equation

$$\frac{\partial f(n,t)}{\partial t} + \frac{\partial}{\partial n}\left(v \cdot f(n,t)\right) = 0 \tag{5}$$

(ii) Growth law

$$dn/dt = v(n,y) = D\, l_o^{-1}\, A(n)\, (c(t)-c_{eq}(n)) \qquad (6)$$

with

$$c_{eq}(n) = c_{eq}(\infty)\exp(l_o k(n)) \approx c_{eq}(\infty)(1+l_o k(n)) \qquad (7)$$

where

$$l_o = 2\sigma(c_\alpha k_B T)^{-1} \approx 1 \text{ nm} \quad \text{capillary length} \qquad (8)$$

$$A(n) = 4\pi(c_\alpha 4\pi/3)^{-2/3}\, n^{2/3} \quad \text{surface of a size-n-droplet} \qquad (9)$$

$$k(n) = (c_\alpha 4\pi/3)^{1/3} n^{-1/3} \quad \text{curvature of a size-n-droplet} \qquad (10)$$

(iii) Conservation of monomers (closure condition)

$$c(t) + \int_0^\infty n\, f(n,t)\, dn = M_o/V \qquad (11)$$

These basic equations embody much of the physics of phase transitions. So the well-known droplet kinetics (6), (7) indicates that monomers will flow from regions of high to low curvature. But in the balance equation (5) we neglect the production-decay term (r.h.s. equals zero) which would introduce new droplet of a given size class into the system. In comparison with a Fokker-Planck-Equation we deal with drift contributions only. Processes, which create a second derivative term in (5), arise from statistical correlations among the droplets /10/. Finally we consider the depletion of monomers in a finite system by the conservation law (11).

From the general theory of Fokker-Planck-Equations it is well known, that a kinetic equation like the Liouville or continuity equation (5) describes the deterministic motion of the droplet ensemble in the s-dimensional size space $n_1,\ldots,n_s$. Starting with a cluster distribution in the form

$$f(n,t) = \frac{1}{V} \sum_{i=1}^{s} N_i(t)\, \delta(n-n_i(t)) \qquad (12)$$

where $N_i(t)$ is the number of clusters and $n_i(t)$ the size (number of bounded monomers) of the clusters of class i at time t. After inserting the ansatz (12) into (5) we get for i=1,2,...,s

$$N_i(t) = N_i(0) \; ; \; dn_i/dt = v_i(n_1,\ldots,n_s,y,dy/dt) \qquad (13)$$

Now we calculate (13) explicitely. The details can be found in /12/. The result obtained is the following equation

$$\frac{dn_i}{d\tau} = c_\alpha l_o A(n_i)\left[l_o(\langle k\rangle - k(n_i)) - \frac{c_{eq}(\infty)V}{c_\alpha l_o}\,\frac{1}{A_\alpha}\,\frac{dy}{d\tau}\right] \qquad (14)$$

with

$$\frac{dy}{d\tau} = -\frac{c_\alpha l_o}{c_{eq}(\infty)V}\,A_\alpha(\tau)\left[y_o - \frac{c_\alpha}{c_{eq}(\infty)V}\,V_\alpha(\tau) - l_o\langle k\rangle\right] \qquad (15)$$

where

$$A_\alpha(\tau) = \sum_{i=1}^{s} N_i A(n_i) \qquad \text{total surface of all droplets} \qquad (16)$$

$$V_\alpha(\tau) = \sum_{i=1}^{s} N_i n_i \qquad \text{total volume of all droplets} \qquad (17)$$

$$\langle k\rangle(\tau) = \frac{\sum K(n_i)\,N_i A(n_i)}{\sum N_i A(n_i)} \qquad \text{mean curvature} \qquad (18)$$

Note, that we use for simplicity instead of time t the reduced time $\tau = t/t_o$ with $t_o = c_\alpha l_o^2\,(c_{eq}(\infty)D)^{-1}$. To find trajectories of the time evolution of the droplet ensemble in state space $(n_1, n_2, \ldots, n_s)$ we have to solve the set of coupled nonlinear equations (14,15) numerically. Results will be given in the next chapter, the one-dimensional case (s=1) was already studied in detail /6,13/.

3. Results and Discussion

The basic equations (14,15) describe the rapid growth of the droplet ensemble (second term on r.h.s. of (14)) and the slow selection process between the droplets (first term on r.h.s. of (14)). Numerical solutions, for a droplet distribution with three classes of drops (s=3) are given in Fig. 1a and Fig. 2a. In a short time regime the size of all drops (number of bounded molecules) is increasing and the two phase system will reach a so-called internal equilibrium, a nonstationary situation where the α-phase (liquid) is in a quasi-equilibrium with its surrounding β-phase (vapor). Since the raw material (monomers) is limited at the end of this stage the total volume V_α (or mass) of the new phase is very close but not equal to its equilibrium value (Fig. 1b). In the final long-time regime a competitive ripening process takes place which minimizes the total surface A_α. At the end of the coarsening process the dynamic system

has reached a stable fixed point where only one droplet is present (Fig. 1a, 2a). The other smaller clusters dissolved to give monomers to the winner, the biggest drop. Fig. 2b shows the mean curvature $\langle k \rangle$ (18) as a non-increasing function of time. The step-like behaviour of the mean curvature corresponds to the shrinkage of small droplets, compare Fig. 2a with Fig. 2b.

We have calculated the quantity $\langle k \rangle (\tau)$ for each time step using formulae (18) with the actual values of the sizes n_i comming from the numerical integration of the basic kinetic equations (14,15). An other way is to derive a kinetic equation for the mean curvature. Derivating $\langle k \rangle$ (18) with respect to time and inserting n_i (14) we get

$$\frac{d}{d\tau}\langle k \rangle = - l_o^2(\langle k^3 \rangle - 3\langle k \rangle \langle k^2 \rangle + 2\langle k \rangle^3) - \\ - \frac{c_{eq}(\infty)V}{c_\alpha} \frac{1}{A_\alpha} \frac{dy}{d\tau} (\langle k^2 \rangle - 2\langle k \rangle^2) \qquad (19)$$

Solutions of (19) agree with the curves shown in Fig. 2b.

Finally we focus our attention on the similarities between the theory of Ostwald ripening presented here and the theory of natural selforganization in biophysics. As was pointed out by Eigen and others that Darwinian evolution can be characterized by an extremum principle, which defines the behaviour of self-replicative units. Selection and evolution of selfreproductive biological macromolecules can be describes appropriately by a system of differential equations based on the formalism of deterministic chemical kinetics. In the Fisher-Eigen model of prebiotical evolution /14/

$$\frac{dx_i}{dt} = (E_i - \langle E \rangle) x_i \quad \text{with} \quad \sum_{i=1}^{s} x_i = C \qquad (20)$$

the species with the highest reproduction rate $E_m = \max\{E_1, \ldots, E_s\}$ (selection value) will increase to the finite value C and all others must die out ($x_i \to 0$ for $i \neq m$). Eq. (20) describes explicitely a selection procedure: Under stated selection constraints (constant overall organization in Fisher-Eigen model) the population numbers of all but one species will decay.

It is obvious that our derived basic equations (14) are a realistic physically motivated example for natural selforganization. Note that in both cases (Fisher-Eigen model with popu-

lation average fitness $\langle E \rangle$, Ostwald ripening of precipitates with mean curvature of the droplet ensemble $\langle k \rangle$) the interaction of the different species is modeled by an overall dilution flux only which corresponds to the mean-field concept of many body physics. For the mean productivity $\langle E \rangle = \Sigma E_i x_i / \Sigma x_i$ we obtain

$$\frac{d}{dt} \langle E \rangle = \langle E^2 \rangle - \langle E \rangle^2 \geq 0$$

in comparison to (19).

Figure Captions

Fig. 1a: Growth and competition of a droplet ensemble with three size classes (s=3). The time evolution of the droplet sizes n_1, n_2, n_3 is shown (initial values: $n_1(0)=40$, $n_2(0)=50$, $n_3(0)=75$) in comparison with the critical value n_c.

Fig. 1b: Time dependence of total volume V_α resp. total surface A_α of the newly formed phase α showing the differences between growth and ripening regime.

Fig. 2a: Same situation as in Fig. 1a, but initial values are $n_1(0)=20$, $n_2(0)=30$, $n_3(0)=43$.

Fig. 2b: Time dependence of the mean curvature of the evolving droplet ensemble.

List of parameters used for the calculations of the figures:

c_α = 33.5 particles/nm^3

$c_{eq}(\infty)$ = $3.35 \cdot 10^{-3}$ particles/nm^3

σ = $7.3 \cdot 10^{-20}$ Ws/nm^2

T = 293 K

D = 10^4 nm^2/ns

$l_o = 2\sigma(c_\alpha k_B T)^{-1} = 1.078$nm

$t_o = c_\alpha l_o^2 (c_{eq}(\infty) D)^{-1} = 1.16$ ns

V = 52 453 nm^3

M_o = 10^3 particles

$y_o = (M_o/V - c_{eq}(\infty))/c_{eq}(\infty) = 4.691$

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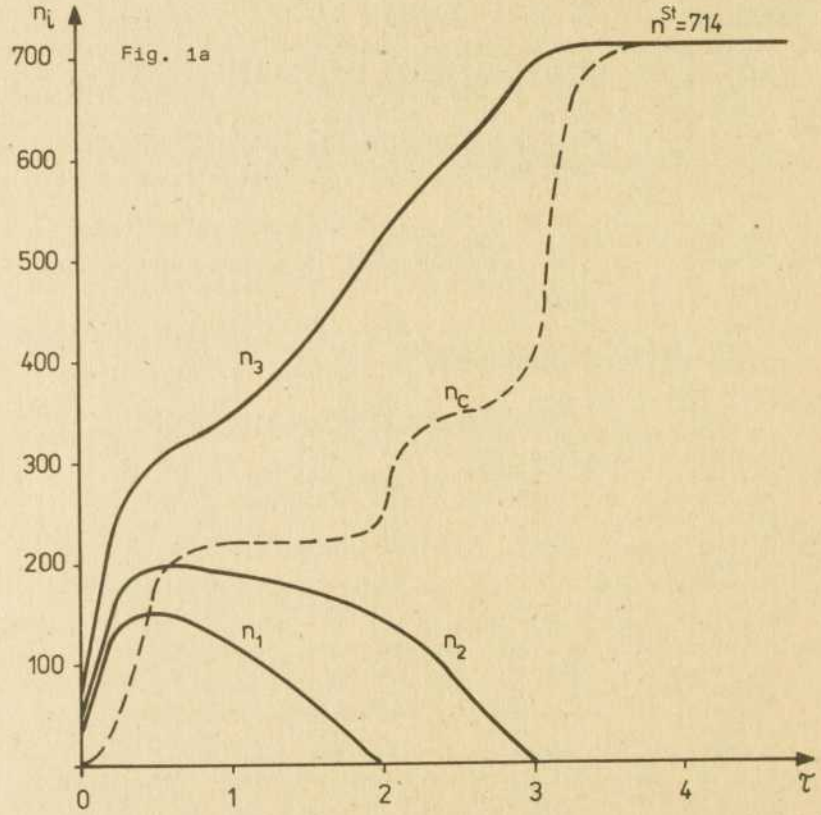
Author: Dr. R. Mahnke
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock
DDR - 2500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500
400
300
200
100
$n^{St}=714$
n_3
n_c
n_1
n_2
0
1
2
3
4
τ

Fig. 1a

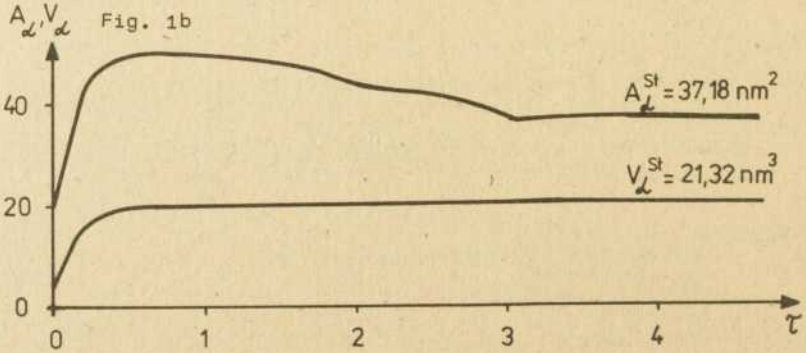
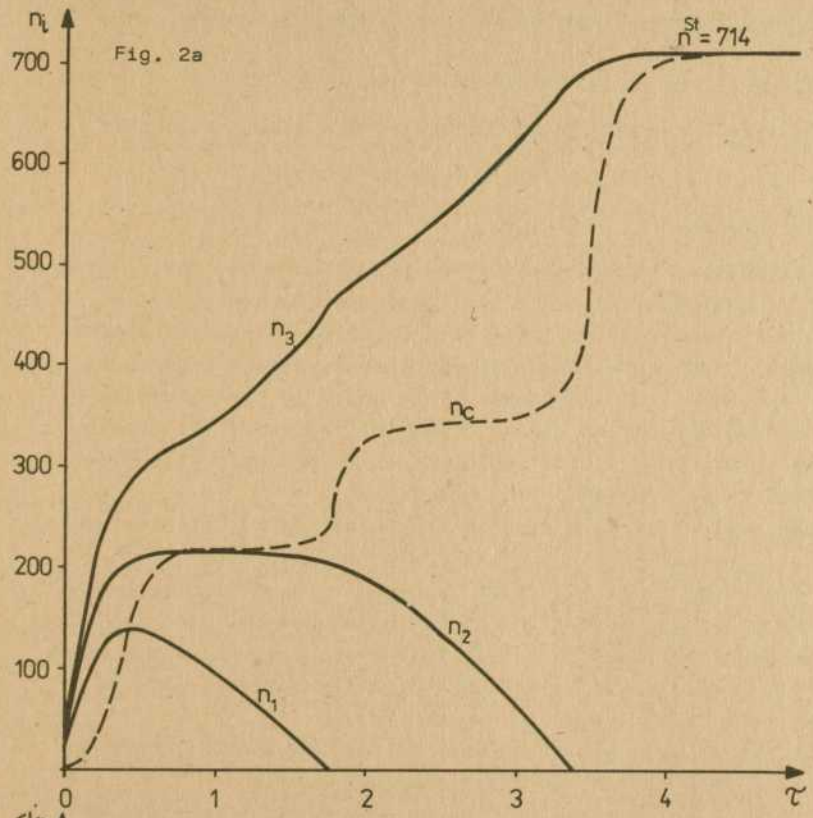
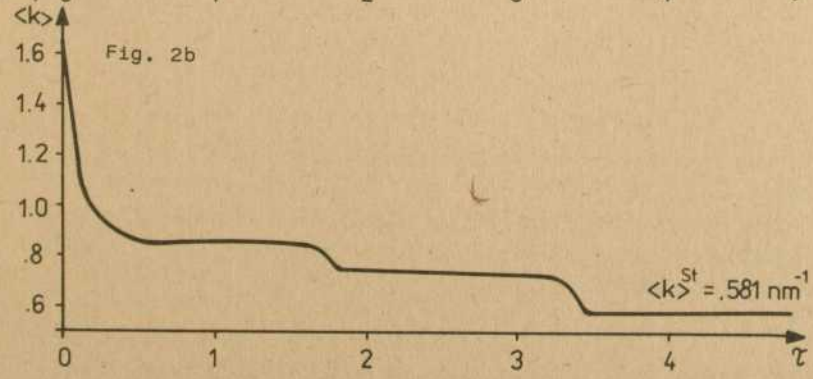

A_α, V_α
40
20
0
$A_\alpha^{St}=37,18\ nm^2$
$V_\alpha^{St}=21,32\ nm^3$
0
1
2
3
4
τ

Fig. 1b


n_i
Fig. 2a
$n^{St} = 714$
700
600
500
400
300
200
100
n_3
n_c
n_2
n_1
0
1
2
3
4
τ


<k>
Fig. 2b
1.6
1.4
1.2
1.0
.8
.6
$\langle k \rangle^{St} = .581\ nm^{-1}$
0
1
2
3
4
τ

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Bernd Lorenz

Grain Size Distribution in Nucleation and Growth Reactions

1. Introduction

The kinetics of first-order phase transitions has been a subject of increasing attention. The time development of the stable phase within the metastable initial phase of a thermodynamic system is frequently described by the Kolmogorov model /1/ for nucleation and growth. This model is characterized by random nucleation and linear growth of nuclei of the stable phase within the untransformed phase. Accordingly, the kinetic process is determined by two quantities,
i) the nucleation rate I(t) is the number of nuclei created in the unit volume of the initial phase per unit time
ii) the growth rate v = dR/dt represents the growth velocity of the growing particle in any linear dimension (for simplicity we consider isotropic conditions where the nuclei are spherically shaped). For interface controlled phase transformations the growth rate v is constant /2/.

If two growing particles impinge they continue to grow at the same rate, except at their common interface.

The nucleation rate I(t) can be an arbitrary function of time t. We will consider the two limit cases,

$I(t) = n_0 \delta(t)$ heterogeneous nucleation

and

$I(t) = I_0 = \text{constant}$ homogeneous nucleation.

n_0 is the density of nuclei per unit volume and $\delta(t)$ is the Dirac δ-function.

Only few exact results of the Kolmogorov model are known. The volume fraction of the transformed phase is given by the Johnson-Mehr-Avrami equation /1/

$$x(t) = 1 - \exp\left\{ - \frac{4}{3} \pi v^3 \int_0^t I(t')(t-t')^3 dt' \right\} \qquad (1)$$

and the total number of nuclei at time t follows from (1),

$$z(t) = \int_0^t I(t')(1-x(t'))\,dt' \,. \qquad (2)$$

Furthermore, the kinetics of the one-dimensional model has been treated rigorously /3/.

During their growth neighbouring particles impinge and form larger aggregates which we denote as grains. Grains consisting of a given number of nuclei differ in their shape and volume. The time dependent grain size distribution is a characteristic function which strongly depends on the nucleation process. In this paper a general formalism for the calculation of the grain size distribution is given (Section 2) and applied to the cases of heterogeneous and homogeneous nucleation (Section 3).

2. Grain Size Distribution

We calculate the grain size distribution function $W(R) = \sum_l W_l(R)$ by the suczessive calculation of the partial distribution functions $W_l(R)$ ($l=1,2,3\ldots$) for grains consisting of l nuclei. To characterize the size of a grain we introduce an effective radius R by $\frac{4}{3}\pi R^3 = V_g$, where V_g denotes the volume of the grain. By this definition $W(R)dR$ is the number of grains per unit volume with effective radii between R and R+dR.

The problem results in the calculation of the volume distribution at time t in an ensemble of grains built up by nuclei of radius $r_i = v(t-t_i')$. t_i' is the creation time of thei-th nucleus. We assume that the nuclei grow spherically with constant velocity. Depending on the nucleation process there results a distribution of radii of the growing nuclei $n(r,t)$ which is the basic function for the calculation of $W(R)$. In order to treat nuclei of different radii as statistically independent we allow for the creation and growth of phantom nuclei in the already transformed phase. This procedure corresponds to the extended volume concept applied to the derivation of (1) /2/. In the calculation of the grain size distribution the phantom nuclei have to be excluded.

The distribution $n(r,t)$ is then given by

$$n(r,t) = \frac{1}{v} I(t - \frac{r}{v}) \, \Theta \, (t - \frac{r}{v}) \quad , \tag{3}$$

where $\Theta(x)$ is the step function. In what follows we consider a fixed time t and suppress the time argument in $n(r,t)$.

2.1. Isolated nuclei, l=1

The distribution of nuclei which show no impingement with other ones is written as

$$W_1(R)dR = n(R) \, W^0(R)dR \; . \tag{4}$$

$W^0(R)$ is the probability that a growing nucleus with radius R does not impinge with any other nucleus and is calculated by simple statistical considerations for an infinitely large system,

$$W^0(R) = \exp\left\{ - \frac{4}{3}\pi \int_0^R [(r+r)^3-(R-r)^3]n(r)dr - \frac{4}{3}\pi \int_R^\infty (R+r)^3 n(r)dr \right\} . \tag{5}$$

Let us note that the volume fraction of the untransformed phase is given by

$$1 - x = W^0(R=0) = \exp\left\{ - \frac{4}{3}\pi \int_0^\infty r^3 n(r)dr \right\} .$$

Substituting $r = v(t-t')$ equation (1) is derived.

2.2. Two connected nuclei, l=2

The probability distribution of l=2 cluster is given by

$$W_2(R_1,R_2,\Delta)dR_1dR_2d\Delta = \widetilde{W}_2(R_1,R_2,\Delta)W_2^0(R_1,R_2,\Delta)dR_1dR_2d\Delta \; . \tag{6}$$

R_1, R_2 and Δ are the radii of the two nuclei and their overlap distance, respectively. The distance between the centres of the two nuclei is $R_1+R_2-\Delta$. The probability W_2^0 that the cluster has no contact to other nuclei is calculated analogous to the former case l=1. $\widetilde{W}_2(R_1,R_2,\Delta)$ denotes the density of pairs of nuclei with radii R_1, R_2 and overlap Δ ,

$$\widetilde{W}_2(R_1,R_2,\Delta) = n(R_1)n(R_2)2\pi(R_1+R_2-\Delta)^2 \quad . \tag{7}$$

The volume of that cluster is calculated as

$$V_2(R_1,R_2,\Delta) = \frac{4}{3}\pi\left\{R_1^3 + R_2^3 - \left(\frac{\Delta}{4}\right)^2\left[\alpha_2^2(3R_1 - \alpha_2\frac{\Delta}{2}) + \alpha_1^2(3R_2 - \alpha_1\frac{\Delta}{2})\right]\right\} , \tag{8}$$

$$\alpha = (2R_i - \Delta)/(R_1 + R_2 - \Delta) .$$

The three-parameter distribution (6) is reduced to a one-parameter probability distribution by summation over all cluster with equal volume. Introducing the effective radius R defined above we get

$$W_2(R)dR = \int W_2(R_1,R_2,\Delta)\ \delta(R - \left[\frac{3}{4\pi}V_2(R_1,R_2,\Delta)\right]^{1/3})dR_1 dR_2 d\Delta\, dR . \tag{9}$$

2.3. Larger aggregates, $l > 2$

The partial distribution functions W_1 for $l=1,2$ are given rigorously by (4), (9). However, for $l > 2$ approximations have to be introduced. For the calculation of W_3 we substitute the $l=2$ cluster by a spherically shaped nucleus with effective radius R and density $n_2(R)$ which is defined by

$$W_2(R)dR = n_2(R)W^0(R)dR . \tag{10}$$

The distribution of the $l=2$ cluster is thus approximated by that of spherical nuclei with the renormalized density $n_2(R)$ and the algorithm described above can now be applied to the calculation of W_3. Repeating this procedure we get a recursion relation of W_1

$$W_l(R)dR = \int n_{l-1}(R_1)n(R_2)2\pi(R_1+R_2-\Delta)^2\ W_2^0(R_1,R_2,\Delta)\cdot$$
$$\cdot\ \delta(R - \left[\frac{3}{4\pi}V_2(R_1,R_2,\Delta)\right]^{1/3})dR_1 dR_2 d\Delta\, dR , \tag{11}$$

$$W_{l-1}(R) = n_{l-1}(R)\ W^0(R)\ dR .$$

3. Results and discussion

With the partial grain size distribution functions (11) some characteristic quantities can be calculated. The total number of grains per unit volume consisting of l nuclei and the net volume fraction of these grains are given by

$$z_l = \int W_l(R)dR \quad , \quad x_l = \int \frac{4}{3}\pi R^3 W_l(R)\ dR . \tag{12}$$

In the following we consider the two cases of heterogeneous and homogeneous nucleation as defined in Section 1 and give some explicit results for l=1.

3.1. Heterogeneous nucleation

In this case all nuclei are created at the beginning of the kinetic process and have the same radius R_o=vt during their growth. The density distribution is given by

$$n(R) = n_o \, \delta (R-R_o) \quad . \tag{13}$$

With (13) we get

$$W_1(R) = n_o \, \delta(R-R_o) \exp\left\{ - \frac{32}{3} \pi n_o R_o^3 \right\} ,$$

$$z_1 = n_o \exp\left\{ - \frac{32}{3} \pi n_o R_o^3 \right\}, \quad x_1 = \frac{4}{3} \pi R_o^3 \, z_1 \, . \tag{14}$$

The result (14) has also been obtained in /4/. z_1, x_1 ($l > 1$) are calculated from (11), (12) with (13).

3.2. Homogeneous nucleation

In the absence of preferred nucleation sites nuclei are created by thermal fluctuations in the metastable initial phase at constant nucleation rate I_o. The density distribution is obtained as

$$n(R) = \frac{1}{v} I_o \, \Theta \, (R_o-R) \, . \tag{15}$$

R_o = vt represents the largest possible radius of the nuclei at time t. For l=1 we get

$$z_1 = \frac{1}{v} I_o \int_o^{R_o} W^o(R) dR \, , \quad x_1 = \frac{4}{3} \frac{\pi}{v} I_o \int_0^{R_o} R^3 W^o(R) dR \, , \tag{16}$$

$$W_1(R) = \frac{1}{v} I_o \, W^o(R) \, \Theta \, (R_o-R) \, ,$$

with $W^o(R) = \exp\left\{ - \frac{\pi}{3v} I_o \left[(R+R_o)^4 - 2R^4 \right] \right\}$.

Inserting (15) into (11) the corresponding quantities for $l > 1$ are calculated.

3.3. Grain size distributions

In Fig. 1 the grain size distributions $W(R) = \sum_l W_1(R)$ for he-

terogeneous and homogeneous nucleation are shown at a reaction time corresponding to a transformed volume fraction of x=0.1. Obviously, both distribution functions show considerable differences.

In the case of heterogeneous nucleation (Fig. 1a) at least three sharp peaks are resolved. The first one resulting from $W_1(R)$ is a δ-function singularity at $R=R_0$. The second peak is mainly due to $W_2(R)$ and shows a divergence at $R=R_0\sqrt[3]{2}$. The partial distributions for larger cluster ($l>2$) give rise to some further peaks with decreasing height and increasing width.

On the other hand, the grain size distribution for homogeneous nucleation is a continuous function except of a remarkable step at $R=R_0$, the largest radius for the nuclei (Fig. 1b). For $R>R_0$ no isolated nuclei contribute to W(R) and it decreases discontinuously.

The experimental determination of the dominant nucleation mechanism in a nucleation and growth reaction is a complicated task. Usually, the time exponent in the exponential of the Johnson-Mehl-Avrami equation (1) is determined by very careful measurements of the transformed volume fraction x(t) in order to select the physical nucleation mechanism /2,5/. As demonstrated above the grain size distribution function is very sensitive to the underlying nucleation scheme and yields important information on the physics of nucleation and growth processes.

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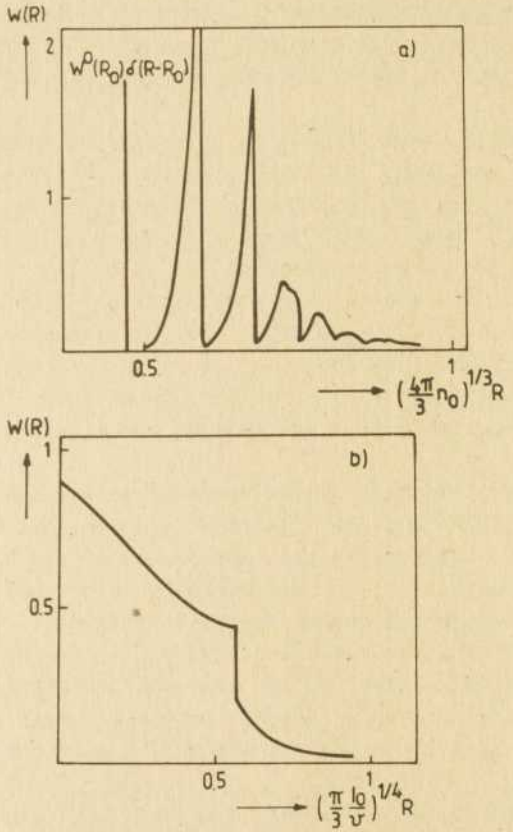

Fig. 1: Grain size distribution functions for a transformed volume fraction of 10 percent
a) heterogeneous nucleation
b) homogeneous nucleation

Author:

Dr. Bernd Lorenz
Zentralinstitut für Physik der Erde
Telegrafenberg
Potsdam
DDR - 1500

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Gerd Röpke

Quantum Statistical Approach to Cluster Formation and Phase Transition in Dense Systems

1. The kinetic properties of systems in the vincinity of a first order phase transition, especially the kinetics of nucleation, are described as usually within a mesoscopic picture. Nucleation is simulated by a master equation which describes a stochastic process. Specific properties as, e.g., mobility and diffusion, attachment probability, free energy of clusters and surface energy are introduced in a phenomenological way.

In contrast, a rigorous microscopic approach to the behaviour of systems near the phase transition region should start from the Hamiltonian of the system. Using the concept of statistical mechanics of equilibrium and non-equilibrium, the macroscopic processes should be derived, in principle, from the elementary interaction between the constituents. However, at present such a concept cannot be realized because of the mathematical effort. Furthermore, the phenomenological treatment provides us with intuitive heuristic approximations which are not immediately evident from a throughout microscopic approach. Parameters which enter the mesoscopic description can be motivated by a microscopic approach.

A special problem to be considered here refers to the connection between density fluctuation, cluster formation, and nucleation. Given the elementary interaction potential between the constituents, clusters or bound states are obtained by solving the Schrödinger equation, and therefore a quantum statistical approach is necessary to describe cluster formation and nucleation near the phase transition region. An interesting, generally accepted hypothesis is that with increasing particle number a cluster, i.e. a bound state in the sense of quantum mechanics, behaves like a droplet of the new, dense phase. Usually, the properties of clusters with arbi-

trary size are described by interpolation between a droplet model including the concept of a surface and a few-particle cluster.

Such interpolation formulae are known along time before in nuclear physics as, e.g., the Bethe-Weizsäcker formula for the binding energy of nuclei /1/, and are used in the last time to describe cluster formation in metallic vapors /2/.

2. We shortly outline the quantum statistical approach to cluster formation in dense systems. Using a formalism given in /3/ for the inclusion of two-particle states, in /4/ a general approach for arbitrary cluster size was formulated and applied to nuclear matter. This formalism which starts from the normalization condition of the single particle Green function was further applied to plasma physics, see /5/ and references given therein.

The starting point is the relation between the density ϱ as function of the chemical potential μ and the temperature T, and the single particle Green function G(p,z), where p denotes momentum (spin and species are not considered explicitely) and z a complex frequency variable:

$$\varrho(\mu,T) = \frac{1}{Vol} \sum_p \int \frac{d\omega}{\pi} f(\omega)\, Im\, G(p,\omega+i0), \tag{1}$$

$f(\omega) = (\exp\beta(\omega-\mu)+1)^{-1}$ is the Fermi distribution function in the case of a system of Fermions. The Green function $G(p,z) = (z - E(p) - \Sigma(p,z))^{-1}$ is determined by the self-energy $\Sigma(p,z)$ which can be treated by a cluster decomposition /2,3/ given in short by a diagram notation

$\Sigma(p,z) =$  (2)

where T_n^L are the n-particle ladder t-matrices. As a result we find

$$\varrho(\mu,T) = \sum_{A=1}^{\infty} \varrho_A(\mu,T) \qquad + (\text{scattering contributions}) \quad (3)$$

where

$$\varrho_A(\mu,T) = \sum_{\alpha} \int \frac{d^3p}{(2\pi)^3} \left[e^{\beta(E_{A\alpha P} - \mu_A)} - (-1)^A \right]^{-1} \quad (4)$$

is the partial density of A-particle bound state clusters, α denotes the internal quantum state, $\mu_A = A\mu$. The bound state energy

$$E_{A\alpha P} = E^{o}_{A\alpha} + \frac{1}{2M_A} P^2 + \Delta E_{A\alpha P} \quad (5)$$

contains the binding energy $E^{o}_{A\alpha}$ of the isolated A-particle cluster in the quantum state α, the kinetic energy $P^2/2M_A$ and the energy shift $\Delta E_{A\alpha P}$ of the A-particle cluster due to the interaction with the surrounding medium. The binding energy of the isolated A-particle cluster follows from the A-particle Schrödinger equation

$$H_A \Psi_{A\alpha P}(1 \ldots A) = E^{o}_{A\alpha P} \Psi_{A\alpha P}(1 \ldots A). \quad (6)$$

The energy shift $\Delta E_{A\alpha P}$ can be obtained from an effective medium Hamiltonian (optical potential) which needs a more detailed treatment of the influence of the surroundings on the A-particle cluster as given, e.g., in /4,5/. A typical contribution is the Hartree-Fock shift of the single particle energy

$$\Delta E(p) = \sum_{p'} \left[V(pp',pp') - V(pp',p'p) \right] F(E_{p'}) \, . \quad (7)$$

This mean field contribution can account for a first order phase transition, see /4/.

In a simple approximation, the energy shift $\Delta E_{A\alpha P}$ in (5), the scattering contributions in (3) and the effects of quantum degeneration in (4) can be neglected, and we end up with the equation of state

$$\varrho(\mu,T) = \sum_{A=1}^{\infty} \Lambda_A^{-3} \left(\sum_{\alpha} e^{-\beta E^{o}_{A\alpha}} \right) e^{A\beta\mu} \qquad (8)$$

where $\sigma_A(T) = \sum_{\alpha} \exp(-\beta E^{o}_{A\alpha})$ is the internal partition function of the A-particle cluster, and $\Lambda_A^2 = 2\pi\hbar^2/M_A k_B T$ is the thermal wave length of the A-particle cluster. Eq. (8) is the equation of state of an ideal mixture of non-interacting clusters with possible chemical reactions so that a law of mass action for the concentration of different clusters holds.

From the equation of state $\varrho = \varrho(\mu,T)$ the free energy $f(\varrho,T)$ is obtained by resolving $\mu = \mu(\varrho,T)$ and integration

$$f(\varrho,T) = \frac{1}{\varrho} \left\{ \int_{\varrho_o}^{\varrho} \mu(\varrho',T)\, d\varrho' + \varrho_o f(\varrho_o,T) \right\}, \qquad (9)$$

so that all thermodynamic properties can be derived if this thermodynamical potential (9) is known in an appropriate approximation.

3. The determination of the energy eigenvalues $E^{o}_{A\alpha}$ and the internal partition function $\sigma_A(T)$ within the frame of quantum mechanics is possible for special models. For instance, within the jellium model a metallic A-particle cluster is described by a positive homogeneous background charge with density ϱ_o. The electrons are considered as a inhomogeneous gas of interacting Fermions moving in the potential of this positively charged background. For the formalism to evaluate the ground state energy and electron density see refs. /6-8/. For instance, the surface energy of metals is well reproduced /8/, the surface energy of finite droplets can be evaluated, and, as a special example where excellent values for cluster binding energies are known, the Bethe-Weizsäcker formula /1/ provides us with a remarkable good interpolation formula up to few-nucleon clusters.

The internal partition function can immediately evaluated for the simple model of a Fermi gas included in a volume corresponding to the A-particle cluster. Expressions for the density of states $D_A(E)$ may be found, e.g., in /1/, so that

$$\sigma_A(T) = \int dE\, D_A(E)\, e^{-E/k_BT} . \qquad (10)$$

4. To obtain transport coefficients and reaction rates, quantum statistical approaches are possible as, e.g., the method of Zubarev or the technique of non-equilibrium Green functions. For the application to a system of charged particles see /5,9/. With the help of these quantum statistical methods a first principle approach to attachment and diffusion is possible, but at present the application to complex systems is not in reach.

In conclusion, a quantum statistical approach to cluster formation should be taken into account if nucleation is modeled, but explicite results are available at present only for simple systems as metallic droplets or nuclei.

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Author:

Doz.Dr.sc.nat. G. Röpke
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock 1
DDR - 2500

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Torsten Boseniuk

Stochastic Nucleation in a Discrete Reaction-Diffusion System

Abstract
For a special bistable reaction-diffusion system nucleation is described by a new simulation algorithm. The model is especially suited for systems with small particle numbers. Stochastic effects play an important role.

1. Introduction

The description by reaction-diffusion systems is well established in physics, chemistry, biology and ecology. Among the phenomena occuring in RD-systems nucleation processes play an important role. There exist a whole range of works dealing with nucleation /e.g. 2,3,4,6,8,10,11/.

Many types of equations have been developed to describe RD-systems. The simplest type is the deterministic equation:

$$d_t n(\underline{r},t) = f(n(\underline{r},t) + D\Delta n(\underline{r},t) \qquad (1)$$

which consist of two parts describing reaction processes and diffusion. $n(\underline{r},t)$ is the concentration of particles which depends on coordinates $\underline{r}$ and time t. Another way describing reacting systems is the Master equation formalism. It especially takes the discretness of particles into account. Thus it is well suited for systems with a small number of particles. It automaticly includes the stochasticity of the reaction process. Diffusion can be involved by dividing the volume into small boxes /5,13/. Then the exchange of particles from one to another box can be described like a reaction. But this is not a good reflection of homogeneous systems. Feistel proposed another way for describing diffusion /1,3/.

2. Functional Master Equation

This formalism is detailed described in 1. Here we give only a short outline of the basic ideas which is necessary to understand the simulation algorithm. The FME describes the probability $P(N,\underline{r}_1 \cdots \underline{r}_N, t)$ to find N particles at the positions $\underline{r}_1 \cdots \underline{r}_N$ at the moment t:

$$d_t P = W_{ch}(P) + W_{diff}(P) \qquad (2)$$

The right-hand side of (2) again consist of two parts. The first describes reactions. Now the reaction probability depends on the distance between the particles. So the probability for a two particle reaction can be expressed by $c_2(\underline{r}_I, \underline{r}_J)$ which is only a function of the distance $r=|\underline{r}_I-\underline{r}_J|$. In our simulation we used the ansatz $c_2(r) = n_o \cdot \theta(r_o - |r|)$. The reaction function is normalized to 1. The diffusion part is similar to (1) but the Laplacian acts on all particle-coordinates. The FME can be used for analytical calculations. But for describing nucleation phenomena Monte-Carlo-Simulation is more suited. Before explaining the simulation algorithms we give a short introduction of the used model.

3. The Schlögl Model

The simplest reaction-model showing bistability was introduced by Schlögl /6,3,12/. It contains only one reacting substance X. We will use the following notation:

$$0 \underset{B}{\overset{A}{\rightleftharpoons}} X \qquad 2X \underset{C}{\overset{E}{\rightleftharpoons}} 3X \qquad (3)$$

That yields the deterministic equation:

$$d_t n(t) = f(n) = A - B \cdot n + E \cdot n^2 - C \cdot n^3 \qquad (4)$$

Fig. 1 shows f(n) for the parameters A = 2.0; B = 23.0; E = 4.0; C = 0.05. In this case (4) has the 3 stationary solutions $n_1 = 0.1$, $n_2 = 6.0$, $n_3 = 74.0$. Two of them n_1 and n_3 are stable. But it is obvious that the stability of n_3 is greater then this of n_1. If we add an diffusion part to (4) this equation con describe nucleation. If we start with the metastable

concentration n_1 in the whole system and only a small nucleus of n_3 the last will push away the other if it is sufficiently large. There exist a lot of works calculating critical radius and other values for the Schlögl system /2,3,11/. The obtain $r_{cr} = (2 \cdot D/c)^{1/2}/[n_1+n_3-2 \cdot n_2]$ for the two dimensional case. It is also possible to calculate r_{cr} by numerical integration of (1). Here we want determine the critical radius by Monte-Carlo-Simulation. Following we give a description of the used algorithm.

4. Simulation Algorithm

There are a lot of Monte-Carlo techniques for solving Master equations often based on waiting time distributions /2,5,7/. For spatial distributed systems however it can be useful to work with discrete time steps of length Δt. Each step again consist of a reaction and a diffusion step.

In the reaction step we compute which particles decay and where new particles arise. Therefore we have to calculate distances between two or three particles. Since $r_0 \ll 1$ (1 - length of the reaction volume) it is not necessary to compare all pairs of particles. So we divided the volume into small boxes and compared only particles from one box and their neighbour particles. But this is only a technical trick to reduce computation expense and does not result into an inhomogeneous space. The size of this boxes depends on r_0 and also on the particle concentration which can be expected.

After putting all particles lying in one box and their neighbourhood into a new array we compute at first where new particles arise. The probability p_R for each reaction can be determined easy:
The probability that one particle arises in the volume V_{box} due to reaction A is $p_A = A \cdot V_{box} \cdot \Delta t$.
The probability that one particle decays due to reaction B is $p_B = B \cdot \Delta t$.
The probability that one particle arises near $\underline{r}$, due to reaction E is $p_{EI} = E \cdot \sum_J c_2(\underline{r}_I, \underline{r}_J) \cdot \Delta t$. (Don't forget the oposite probability p_{EJ}!)

The probability that particle i decays due to C is $p_{CI} = C \sum_{J,k} c_2(\underline{r}_I, \underline{r}_J)\ c_2(\underline{r}_I, \underline{r}_K)\ \Delta t$.

t must be choosed in such a way that all $p_R \ll 1$. After determing p_R for one particle it must be deceided whether the reaction occurs or not. This is done by the help of a random number between 0 and 1. If the random number is lower than p_R then the reaction occurs in the opposite case not. Because most of the p_R are very low we did not calculate a random number for each reaction but calculated when the next random number p_R will occur. This can be done similar to calculation of waiting times /2/. That reduces computing time again by a factor of 10.

After determing the numbers of decaying particles and the birthplaces of new particles for all boxes we can change our particle array and the reaction step is finished.

In the diffusion step all particles get new coordinates due to diffusion in the intervall Δt. This was done in the kind of random walk with an average $\Delta \underline{r}$ of $\langle \Delta \underline{r}^2 \rangle = 2\ D\ \Delta t$ for the two dimensionacacase. We made all nucleation simulations for a two dimensional square with an area V. For determing probability-distributions we also made one dimensional simulations /4/.

But the algorithm can easily be transfered to three dimensional problems.

5. Results

The parameters used in the simulation were A=2.0; B=23.0; E=4.0; C=0.05; r_0=0.2 and V=50.0. The diffusion constant D was varied from 10 to 200. The stable concentrations were n_1=0.1 and n_3=74.0 and the corresponding particle numbers for the whole system about 5 and 3500. So we startet with a nucleus of N particles in the centre of the volume (N: 2...100) to avoid boundary effects. These N particles were distributed with the concentration n_3. The concentration in the outer space was 0 (n_1). The resulting development then depends on the size of the initial nucleus (see Figs. 2,3). If the nucleus is overcritical it grows otherwise it decays. After a certain time (c in 2 and 3) this is obvious; then we stopped simulation.

To determine critical radius we started with nuclei of different size N_o and performed 50 simulation stepts with $\Delta t = 0.001$.

Fig. 4 shows the dependence of the particle number after 50 Monte-Carlo steps from initial nucleus size for different values of diffusion constant D. At first we see that the probability for nucleation increases with the initial size of nucleus. This agrees with the existence of a critical radius which can be obtained by analytical and numerical calculations. But in the deterministic case all nuclei with a size greater than r_{cr} grow. Our simulation shows the stochastic character of nucleation. This represents the natural behaviour of nuclei with a small number of primary particles or under conditions with high noise. The size of critical radius strongly depends on the value of the diffusion constant. With growing D the size of r_{cr} increases. This corresponds to the analytical results ($r_{cr} \sim D^{1/2}$). The stochastic simulation very good shows the reason for this dependence. At first nearly all nuclei start to grow. But due to diffusion the size of the nucleus grows faster than the number of particles in the nucleus. As a result the concentration in the nucleus decreases. If the concentration is lower than n_2 the nucleus decays. But as can be seen from 4 the diffusion also can accelerate nucleation. For D=50 the number of particles after 50 Monte-Carlo steps is always lower than 400; but for D=100 numbers up to 500 can be reached. This is a result of higher front velocity. Analytical calculations don't show an growing velocity but the were made for high r and our simulation is limited to small nuclei.

At least Fig. 5 shows the dependence of critical particle number from D. We used a critical particle number and not a critical radius because it is more suited for numerical simulation. However $N_{cr}(N)$ shows the same qualitative behaviour like $r_{cr}(D)$. Here must be said that the determination of a average critical particle number was not easy because of the high variance for small numbers.

6. Conclusions

A stochastic description of the Schlögl model was given. It shows the effects of small particle numbers. Nucleation for different values of the diffusion constant was investigated.

I would thank R. Feistel for fruitful discussion.

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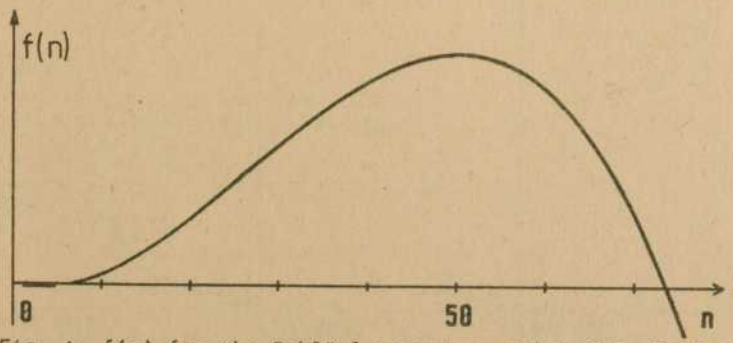

Fig. 1: f(n) for the Schlögl reaction with A=2.0; B=23.0; E=4.0; C=0.05

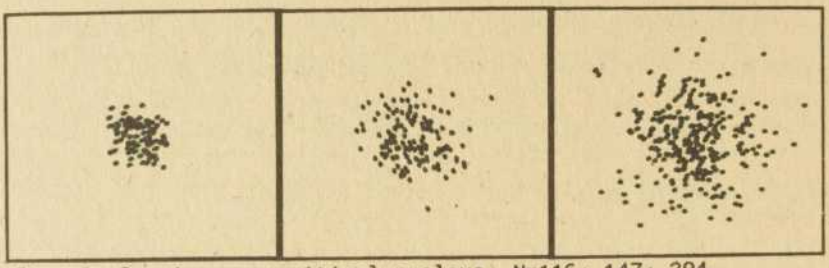

Fig. 2: Growing overcritical nucleus; N=116; 147; 294

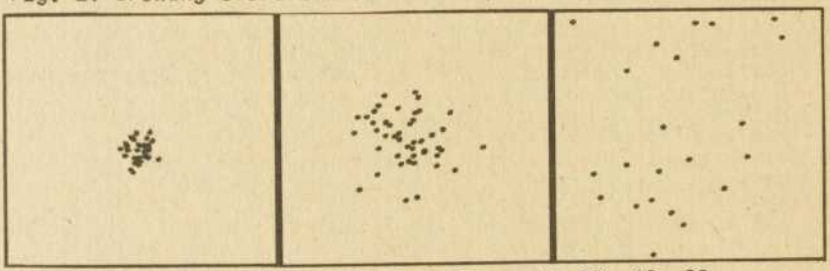

Fig. 3: Decaying undercritical nucleus; N= 38; 46; 22

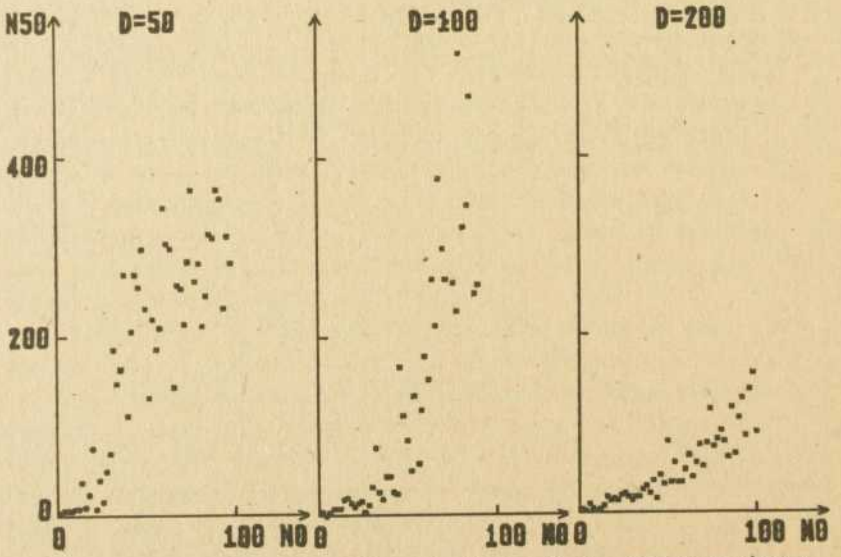

Fig. 4: Particle number after 50 Monte-Carlo steps in dependence of the initial nucleus size - for various D

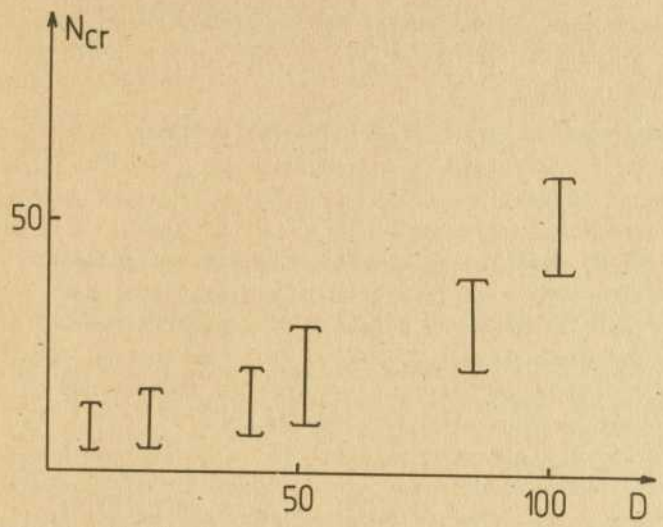

Fig. 5: Critical particle number N_{cr} for various D

Author:

Dipl.-Phys. Torsten Boseniuk
Humboldt-Universität zu Berlin
Sektion Physik
Invalidenstraße 42
Berlin
DDR - 1040

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Frank Schweitzer

A Stochastic Approach to Nucleation in Finite Systems

1. The considered model

The theory of first-order phase transitions, e.g. of condensation processes, include a variety of deterministic theories which describe sufficiently the dynamics of a given number of nuclei of the new phase (see e.g. /1-3/). But the initial formation of the nuclei is an intrinsic stochastic process and can't be explained in a deterministic sense.

Here we present a stochastic approach for a nucleation process in a finite system consisting of the formation of clusters by free particles /4,5/. Apart from other theories we fix the overall particle number N, the system volume V and the temperature T of the system:

$$N,\ V,\ T = \text{const.} \tag{1}$$

Due to interactions between the particles the N particles will bound in clusters. Thus we have a particle configuration

$$\underline{N} = \{N_1\ N_2\ \dots\ N_l\ N_{l+1}\ \dots\ N_N\} \tag{2}$$

where N_1 is the number of free particles and N_l $(l=2,\dots,N)$ the number of clusters with l bound particles. $\underline{N}$ describes the cluster distribution in the finite system. Because of (1) it helds

$$N = \sum_{l=1}^{N} l\ N_l\ ;\ 0 \leq N_l \leq \frac{N}{l}\ (l=1,\dots,N) \tag{3}$$

In the following we are interested in the probability $P(\underline{N},t)$ to find a given cluster distribution $\underline{N}$ at the time t.

The time evolution of $P(\underline{N},t)$ can be described by a Master equation /4,5/:

$$\frac{\partial}{\partial t} P(\underline{N},t) = \sum_{\underline{N}'} w(\underline{N}|\underline{N}')P(\underline{N}',t) - w(\underline{N}'|\underline{N})P(\underline{N},t) \tag{4}$$

$\underline{N}'$ specifies those distributions which are attainable from the assumed distribution $\underline{N}$ with the transition probabilities per unit time $w(\underline{N}'|\underline{N})$.

2. The equilibrium probability distribution

The equilibrium state is characterized by the condition of detailed balance:

$$w(\underline{N}'|\underline{N})P^{o}(\underline{N}) = w(\underline{N}|\underline{N}')P^{o}(\underline{N}') \qquad (5)$$

where $P^{o}(\underline{N})$ is the equilibrium probability of the distribution $\underline{N}$. The maxima of $P^{o}(\underline{N})$ denote the equilibrium cluster distribution in agreement with the deterministic theory.

$P^{o}(\underline{N})$ is given by the following relation /4/:

$$P^{o}(\underline{N}) = \frac{1}{Z(T,V,N)} \exp\left\{-\frac{1}{k_B T} F(T,V,\underline{N})\right\} \qquad (6)$$

Here $Z(T,V,N)$ is the canonic partition function of the interacting N particle system. It is a constant and stands for the normalization. $F(T,V,\underline{N})$ is the free energy of the considered cluster distribution $\underline{N}$ assuming the clusters and free particles as an ideal mixture /4,5/:

$$F(T,V,\underline{N}) = \sum_{l=1}^{N} N_l \left\{ f_l + k_B T\left(\ln \frac{N_l}{V}\lambda_l^3 - 1\right)\right\} \qquad (7)$$

$F(T,V,\underline{N})$ considers the partial pressure of the clusters and free particles and the mixing entropy (see also /6/). λ_l is the de-Broglie wave length. f_l is a potential term which includes the binding energy of the cluster and the surface energy. For large clusters we choose /4/:

$$f_l = -Al + Bl^{2/3} \qquad (8)$$

while for small clusters

$$f_l = -\frac{A}{2}\,l\,(l-1) \qquad (9)$$

is hold /5/. A and B are temperature depending constants /7/:

$$A = -k_B T \ln \frac{p_\infty}{k_B T}\lambda_1^3 \;; \quad B = 4\pi\left(\frac{4\pi}{3}c_\alpha\right)^{-2/3}\sigma \qquad (10)$$

with σ being the surface tension of the cluster, c_α the particle density in the cluster, p_∞ the saturation pressure over a macroscopic flat liquid surface.

3. Kinetic assumptions

To determine the transition probabilities per unit time $w(\underline{N}'|N)$ we choose the following kinetic ansatz

$$A_1 + A \underset{w^-}{\overset{w^+}{\rightleftharpoons}} A_{1+1} \tag{11}$$

It means that the growth or shrinkage of a cluster of size 1 occurs only by the attachment or evaporation of a free particle, w^+ and w^- are the probabilities of the given reactions.

We assume further that the probability of an attachment of a free particle to a cluster of the size 1 increases with the surface of the cluster, with the number of clusters of size 1 and with the density of particles /4/:

$$w^+(N_1 N_1) = \alpha\, 1^{2/3} N_1 \frac{N_1}{V}, \quad N_1 = N - \sum_{l=2}^{N} l N_l \tag{12}$$

α is a constant what depends from the specific properties of the cluster. It determines the time scale.

With the condition of detailed balance (5) and (7),(10) we find the transition probability of the opposite process (evaporation) /4,5/:

$$w^-(N_1) = \alpha\, 1^{2/3} N_1 \frac{p_\infty}{k_B T} \exp\left\{\frac{2}{3}\frac{B}{k_B T}\, 1^{-1/3}\right\} \tag{13}$$

The transition probabilities characterize the mean life time $\vartheta_{\underline{N}}$ of a given cluster distribution $\underline{N}$ /5/:

$$\vartheta_{\underline{N}} = \left\{\sum_{\underline{N}'} w(\underline{N}'|\underline{N})\right\}^{-1} \tag{14}$$

The real life time of the cluster distribution is determined by a random process and can be investigated by means of computer simulations. We use the stochastic dynamic technique /5/.

4. Discussion of the stochastic evolution

(i) First we discuss the time evolution of a single cluster in the system /3/. In this case the transition probabilities are a function only of the cluster size 1 and the thermodynamic constraints. We obtain them from (12), (13):

$$w_1^+ = \alpha\, 1^{2/3} \frac{(N-1)\, k_B T}{p_\infty V}$$
$$w_1^- = \alpha\, 1^{2/3} \exp\left\{\frac{2}{3}\frac{B}{k_B T}\, 1^{-1/3}\right\} \tag{15}$$

$w^+(l)$ and $w^-(l)$ are presented in Fig. 1. The points of intersection are hold for the equilibrium states of the cluster /7/. The first point of intersection gives the critical cluster size (instable equilibrium state), the second point gives the stable cluster size. It is determined by the thermodynamic constraints and represents a coexistence of the cluster and the free particles. In Fig. 2 the stochastic droplet evolution is shown /5/. The time to reach the stable cluster state depends strongly from the initial supersaturation $y_o = Nk_BT/p_\infty V$ which includes the thermodynamic constraints. For lower initial supersaturations the cluster has only a short time to stay in the thermodynamically determined stable state.
(ii) The evolution of the cluster distribution is discussed in terms of the probability distribution p(l,t) /5/. It gives the probability to find clusters with size l at a given time t and has to be found by averaging over a large number of simulations. (In Fig. 3 there is presented only a single simulation.) For the evolution of the probability distribution we distinguish two characteristic time scales. First in a quasistationary scale the initial state of the N free particles relaxes into a state with free particles and small clusters. That's the metastable state, characterized by a poisson-like probability distribution near the initial state (Fig. 3a). This state is left in a stationary time scale if fluctuations allow to form some overcritical clusters (Fig. 3b). When the stable state of the system is reached a poisson-like distribution near this state is built up (Fig. 3c). Thus the nucleation process is characterized by a stochastic tunnel process through unprobable states to reach the final equilibrium state which exists for finite systems.

Acknowledgements: The author is indebted to Prof. Dr. W. Ebeling and Dr. sc. L. Schimansky-Geier, Berlin, for many suggestions and valuable discussions.

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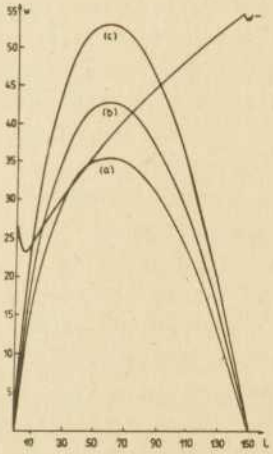

Fig. 1: Transition probabilities w_1^+ and w_1^- (15) vs. cluster size l
(a) $y_o = 3.86$ (b) $y_o = 4.63$ (c) $y_o = 5.79$

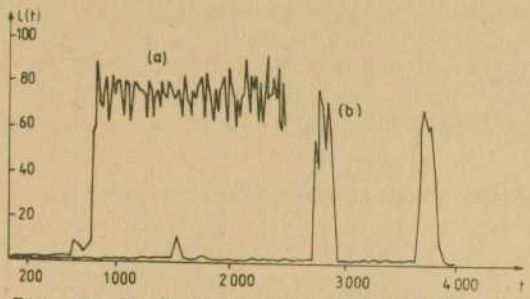

Fig. 2: Stochastic evolution of the cluster size l vs. time t (in time units)
(a) $y_o = 4.36$ (b) $y_o = 4.21$

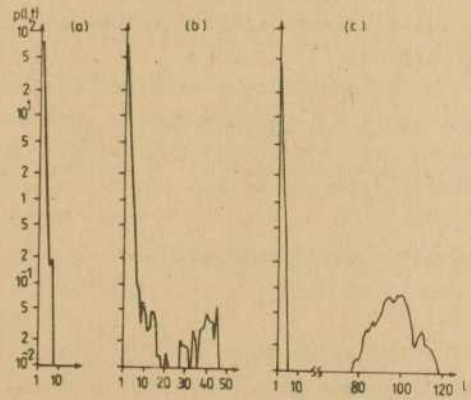

Fig. 3: Distribution of clusters of size l during a given time t (in time units)
R - number of elementary reactions (11), $y_o = 7.5$
(a) $R = 5 \cdot 10^2$; t = 0.452
(b) $R = 5 \cdot 10^3$; t = 4.946
(c) $R = 5 \cdot 10^4$; t = 143.551

Author:
Dr. Frank Schweitzer
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock 1
DDR - 2500

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Axel Budde, Reinhard Mahnke

Isoenergetic Nucleation in Finite Systems

In this paper we consider the kinetics of nucleation under different thermodynamic boundary conditions. This contribution is based on investigations concerning the condensation of liquid drops from a supersaturated vapour under isothermic-isochoric boundary conditions /1/. We use here the same droplet model as for the isothermic case, which is described in detail elsewhere /1-3/. The dynamics of isothermic nucleation (condensation of water droplets with fixed temperature and volume of the system) is summarized in Fig. 1.

In the following we consider an ensemble of clusters with the distribution $\underline{N} = (N_1, N_2, \ldots, N_n, \ldots, N_n)$ in a finite system $M_0 = \sum_1 n\, N_n = \text{const}$. The theory starts with the following free energy as state function comming from statistics ($F=-kT \ln Z$, ideal gas)

$$F(T,V,\underline{N}) = -\frac{3}{2} kTN_0 \ln T/T_0 - kTN_0 \ln V/V_0 + kT\sum_1 N_n \ln N_n - kTN_0 \qquad (1)$$

$$- \frac{3}{2} kT\sum_1 N_n \ln n + \sum_2 N_n f_n(T)$$

with the reference values $T_0 = 293$ K, $V_0 = (h/\sqrt{2\pi mkT_0})^3 \approx 1.4 \cdot 10^{-5} nm^3$ and $N_0 = \sum_1 N_n$ as overall number of particles. The function $f_n(T)$ gives the potential contributions of a size-n-cluster. Taking into account bulk ($\mu_\infty(T) \cdot n$) and surface ($\sigma A(n)$) terms we use (compare /2,3/)

$$f_n(T) = \mu_\infty(T) \cdot n + \sigma A(n) \qquad (2)$$

with $$\mu_\infty(T) = -\frac{3}{2} kT \ln T/T_0 + kT \ln(c_{eq}(T) V_0) \qquad (2a)$$

and $$c_{eq}(T) = c_0 (T/T_0)^{-1} \exp\{\varepsilon\,(1/T_0 - 1/T)\} \quad (\varepsilon = 5000 \text{ K}) \qquad (2b)$$

Inserting (2) in (1) we get

$$F(T,V,\underline{N}) = -kT(\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha)\ln T/T_0 - kTN_0 \ln V/V_0 + kT\sum_1 N_n \ln N_n \qquad (3)$$

$$-kTN_0 - \tfrac{3}{2}kT\sum_1 N_n \ln n + \sigma A_\alpha + kTM_0 \ln c_0 V_0 + k\varepsilon M_\alpha T/T_0 - k\varepsilon M_\alpha$$

with $M_\alpha = \sum_2 n N_n$, $A_\alpha = \sum_2 n A(n)$

This state function (3) is the basic quantity to understand the nucleation in closed systems. But it may be that the exchange of heat takes longer time than the nucleation itself. Therefore we calculate from (3) the inner energy

$$U(T,V,\underline{N}) = kT(\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha) + \sigma A_\alpha - k\varepsilon M_\alpha \qquad (4)$$

which is decreasing for growing nuclei.

Now we replace the condition T=const by the energy conservation U=const. The corresponding state function is the entropy $S=S(U,V,\underline{N})$, which we calculate from (3) by $S(T,V,\underline{N}) = -\partial F/\partial T$ and replacing the temperature $T=T(U,V,\underline{N})$ using (4). The result is

$$S(U,V,\underline{N}) = k\left(\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha\right) \ln \frac{U - \sigma A_\alpha + k\varepsilon M_\alpha}{kT_0\left(\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha\right)} + k N_0 \ln V/V_0$$

$$- k\sum_1 N_n \ln N_n + \tfrac{5}{2} k N_0 + \tfrac{3}{2} k \sum N_n \ln n + k\left(\tfrac{5}{2} - \frac{\varepsilon}{T_0} - \ln c_\alpha V_0\right) M_\alpha \qquad (5)$$

The temperature in the whole system is given by

$$T(U,V,\underline{N}) = (U - \sigma A_\alpha + k\varepsilon M_\alpha) / \left[k\left(\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha\right)\right] \qquad (6)$$

Fig. 2 shows the properties of entropy S (5) and the changing of temperature (6) in the case of one cluster in the surrounding gas.

The kinetics of nucleation in isolated systems is very similar to that with fixed temperature. From the isothermic transition probabilities per unit time /1,3/, which read exactly /2/

$$W_n^+(N_n) = (D/l(T))\, A(n) N_n N_1 / V$$
$$W_1^+(N_1) = (D/l(T))\, A(1) N_1 (N_1 - 1)/V \qquad (7)$$

where D - diffusion coefficient, $l(T) = 2\sigma/(c_\alpha kT)$ capillarity length, we get in the isoenergetic case the following rates of attachment

$$W_n^+(N_n) = \frac{D c_\alpha}{2\sigma} \frac{U - \sigma A_\alpha + k\varepsilon M_\alpha}{\tfrac{3}{2}N_0 + \tfrac{5}{2}M_\alpha} A(n) N_n N_1 / V \qquad (8)$$

and for the reverse process (evaporation rates)

$$W_n^-(N_n) = W_{n-1}^+(N_{n-1}+1) \exp\left\{\frac{1}{k}\left[S(U,V,\underline{N}^*) - S(U,V,\underline{N})\right]\right\} . \qquad (9)$$

Acknowledgement: The authors thank Prof. W. Ebeling and Dr. L. Schimansky-Geier (Berlin) for fruitful discussions and advises.

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F. Schweitzer; L. Schimansky-Geier: J.Coll.Interface Sci. (in press)

Figure Captions

Fig. 1: Nucleation under isothermic-isochoric boundary conditions. Evolution of the droplet ensemble by solving the master equation numerically. Snapshoots of the distribution function for different times.
Parameters: $T=293$ K; $V=26000\ nm^3$, $M_0=300$
$c_4 = 33{,}5\ nm^{-3}$; $c_0 = 5.78 \cdot 10^{-4}\ nm^{-3}$;
$D = 10^4 nm^2/ns$; $\sigma^0 = 0.073\ kg/s^2$

a) 0 collisions (initial situation): t = 0 ns ; $N_1=300$; y = 19
b) 100 collisions: $t = 7.5 \cdot 10^{-3}$ ns; y = 10.4
c) 2000 collisions: t = 0.177 ns; y = 8.85
d) 13000 collisions: t = 1.21 ns; y = 8.25
e) 52000 collisions: t = 4.85 ns; y = 7.0
f) 55000 collisions: t = 5.31 ns; y = 5.85
g) 56000 collisions: t = 5.59 ns; y = 3.33
h) 57000 collisions: t = 6.04 ns; y = 2.93
i) 58000 collisions: t = 6.87 ns; y = 1.66

Fig. 2a: State function entropy S = S(U,V,n) showing the critical (n_{cr}) and stable (n_{st}) size

Fig. 2b: For fixed energy U = const the temperature is increasing for growing clusters.

Authors:

Dipl.-Phys. A. Budde
Dr. R. Mahnke
Wilhelm-Pieck-Universität Rostock
Sektion Physik
Universitätsplatz 3
Rostock 1
DDR - 2500

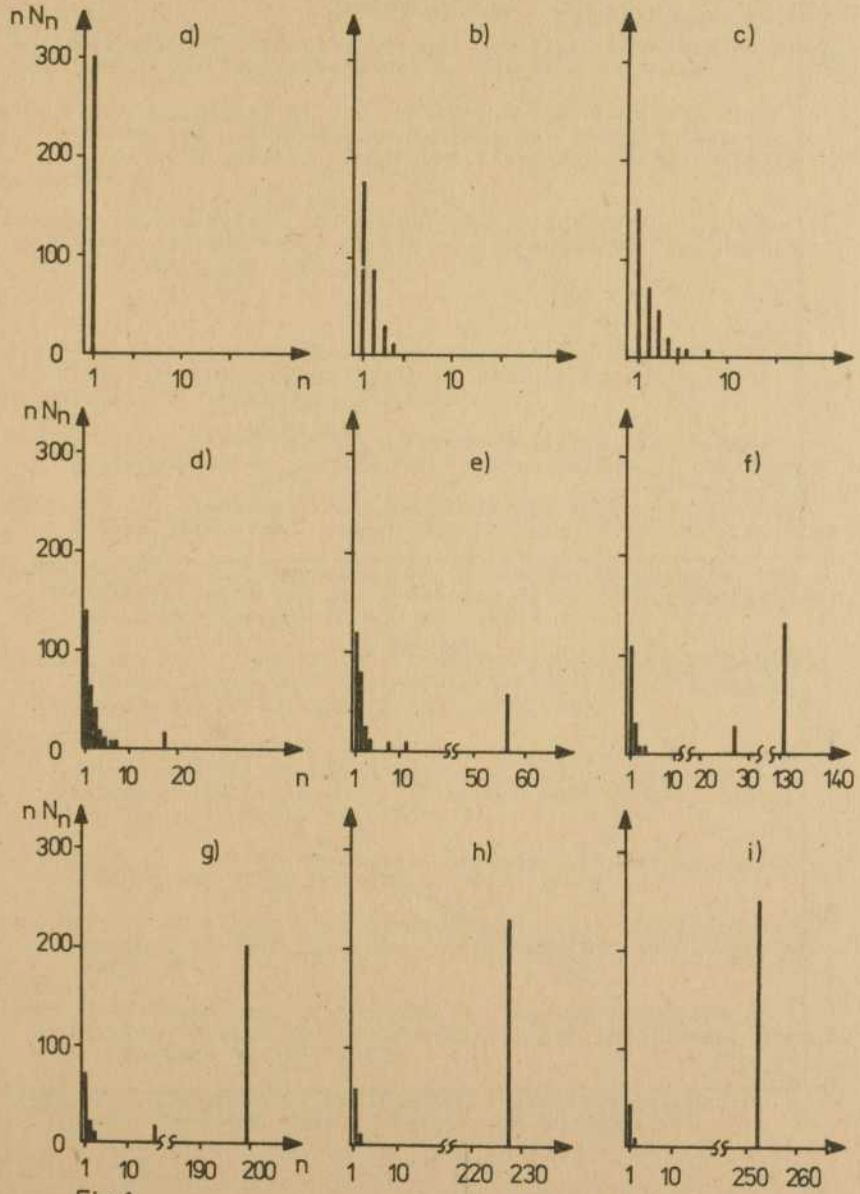

n N_n
a)
b)
c)
d)
e)
f)
g)
h)
i)
300
200
100
0
1
10
20
50
60
190
200
220
230
250
260
130
140
n
Fig.1

Fig. 2a

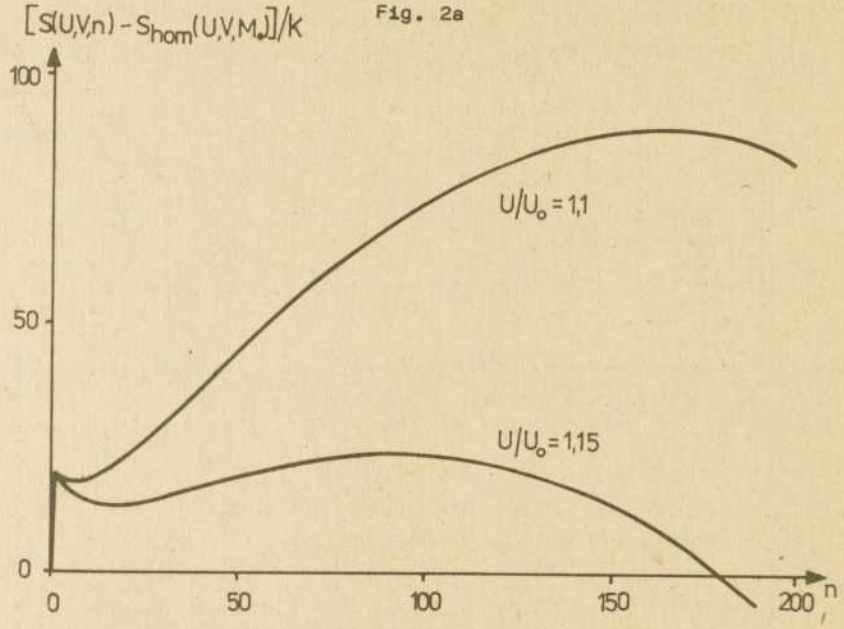
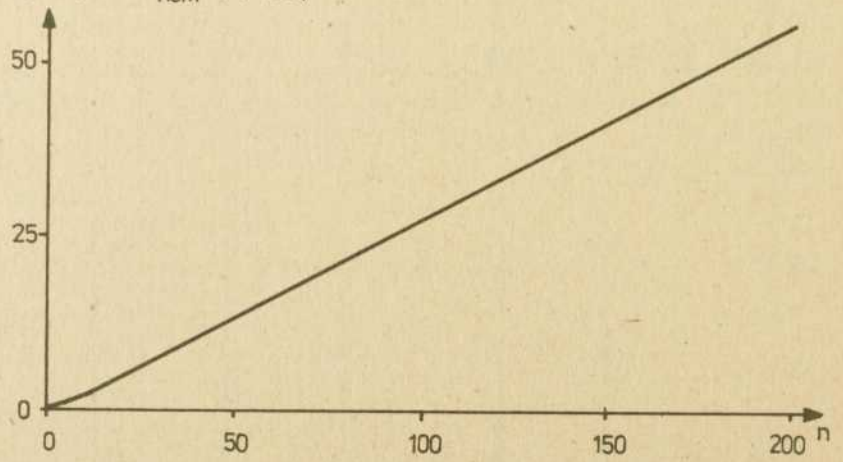

[S(U,V,n) - S_hom(U,V,M_o)]/K
100
50
0
U/U_o = 1,1
U/U_o = 1,15
0
50
100
150
200
n

Fig. 2b


[T(U,V,n) - T_hom(U,V,M_o)]/K
50
25
0
0
50
100
150
200
n

H i n w e i s

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ew

$$\nu(n,y) = D\, l_o^{-1}\, A(n)\, (c(t)-c_{eq}(n)) \qquad (6)$$

$$c_{eq}(\infty)\exp(l_o k(n)) \approx c_{eq}(\infty)(1+l_o k(n)) \qquad (7)$$

$(c_\alpha k_B T)^{-1} \approx 1$ nm — capillary length (8)

$\pi (c_\alpha 4\pi/3)^{-2/3}\, n^{2/3}$ — surface of a size-n-droplet (9)

$c_\alpha 4\pi/3)^{1/3} n^{-1/3}$ — curvature of a size-n-droplet (10)

ation of monomers (closure condition)

$$\int_0^\infty n\, f(n,t)\, dn = M_o/V \qquad (11)$$

quations embody much of the physics of phase tran-
he well-known droplet kinetics (6), (7) indicates
will flow from regions of high to low curvature.
Lance equation (5) we neglect the production-decay
equals zero) which would introduce new droplet of
class into the system. In comparison with a Fokker-
n we deal with drift contributions only. Proces-
ate a second derivative term in (5), arise from
rrelations among the droplets /10/. Finally we
depletion of monomers in a finite system by the
aw (11).

neral theory of Fokker-Planck-Equations it is well
kinetic equation like the Liouville or continuity
describes the deterministic motion of the droplet
he s-dimensional size space $n_1,\ldots,n_s$. Starting
distribution in the form

$$\frac{1}{V} \sum_{i=1}^{s} N_i(t)\, \delta(n-n_i(t)) \qquad (12)$$

the number of clusters and $n_i(t)$ the size (number
omers) of the clusters of class i at time t. After
ansatz (12) into (5) we get for i=1,2,...,s

$$N_i(0) \; ; \; dn_i/dt = v_i(n_1,\ldots,n_s,y,dy/dt) \qquad (13)$$

te (13) explicitely. The details can be found in
lt obtained is the following equation