

Heinz Ulbricht Reinhard Mahnke

Nonlinear irreversible processes and phase transitions : selected lectures of the third international conference on "Irreversible Processes and Dissipative Structures", Kühlungsborn, 18. - 22. 3. 1985

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Preface

In Spring 1977 on the occasion of the second "Days of Sciences and Culture" at the Wilhelm-Pieck-Universität Rostock an international meeting on "Nonlinear Irreversible Processes and Self-organization" was held. This first conference, organized by the Sektion Physik of the Wilhelm-Pieck-Universität and mainly by Prof. W. Ebeling and his group, was focused on the stochastic theory of irreversible processes in physical and non-physical systems. Some selected main lectures have been published in "Rostocker Physikalische Manuskripte", Vol. 2, 1977 (Ed: W. Ebeling) under the title "Stochastische Theorie der nicht-linearen irreversiblen Prozesse". The second conference on "Irreversible Processes and Dissipative Structures" (2. IPDS) took place in February 1982 at the Humboldt-Universität Berlin.

In March 18-22, 1985 the third international conference on "Irreversible Processes and Dissipative Structures" (3. IPDS) was held in Kühlungsborn, a resort place at the Baltic Sea near Rostock, organized by the Physical Society of the GDR in cooperation with the Wilhelm-Pieck-Universität Rostock (chairman of the scientific committee: Prof. Werner Ebeling, Berlin, and Prof. Heinz Ulbricht, Rostock). The conference was an interesting forum for scientists working actively in this new field. The following subjects were emphasized

- statistical and stochastic theory of irreversible processes
- dissipative structures, hydrodynamic problems, reaction-diffusion problems, nucleation in theory and experiment
- selforganization and evolution processes.

Over 150 participants took part in the work of the conference to exchange ideas and to present results dealing with nonlinear phenomena to understand chaos and order in nature.

This new edition of the series "Rostocker Physikalische Manuskripte" is devoted to nonlinear irreversible processes and phase transitions and collects some of the lectures and posters presented at the 3. IPDS. The relations between the theory of selforganization and the theory of nucleation are discussed.

It is, for instance, shown that the kinetics of an ensemble of coarsening particles of different sizes is a competition process, which is quite similar to the selection in biological or ecological systems. For further information concerning the theory of selforganization or synergetics, which has been developed fastly in the last 15 years, we recommend

- W. Ebeling, R. Feistel: "Physik der Selbstorganisation und Evolution", 1982, 2nd ed. in preparation (in German)
- W. Ebeling, Y.L. Klimontovich: "Selforganization and Turbulence in Liquids", Teubner Texte zur Physik, Vol. 2, 1984
- W. Ebeling, H. Ulbricht (Ed.): "Selforganization by Non-linear Irreversible Processes", Springer-Series in Synergetics, in preparation for 1986.

Last not least we want to take the opportunity to thank all those who have collaborated in the organization and running of the 3. IPDS.

Dr. R. Mahnke

Prof. H. Ulbricht
Co-chairman

Rostock, September 1985

Thermodynamic Parameters and Structural Criteria for Phase Transformations in Amorphous Covalent Bound Materials

W. POMPE and A. RICHTER

1. Introduction

Crystallization studies are of interest not only for examining the fundamentals of the involved nucleation and growth processes in some detail, but also for learning to produce novel microstructures by controlled crystallization. Experimental and theoretical investigations of crystallization of amorphous solids show that the formation of metastable crystals occurs as transient or final stages /1,2,3/. This phenomenon is known as Ostwald's rule of stages according to which the less stable phase is always formed first. Therefore, the general question analysed is, how structural peculiarities determine the kinetics of formation of critical nuclei and their growth rates during partial crystallization of different phases. Special emphasis is put on the role of stored elastic energy and the influence of interfacial energy on steady-state and transient nucleation within the context of classical nucleation theory /4/ applied to small crystalline particles embedded in a solid matrix.

Considering different mechanisms of structural transformations, two possible ways are discussed:

(i) The first one may be called "thermodynamically controlled nucleation" that contains crystallization under elastic constraints to such an extent that the metastable phase is the phase with the minimum of free energy

$$F_{\text{met}}(Z_n(t \rightarrow \infty); \phi) < F_{\text{stab}}(Z_n(t \rightarrow \infty); \phi). \quad (1)$$

$Z_n(t \rightarrow \infty)$ is the probability of the existence of a critical nucleus with size n at time $t \rightarrow \infty$ and ϕ is a set of constraints explained later.

(11) The second one will be termed "kinetically controlled nucleation" that means crystallization under conditions where the probability $Z_n^{\text{met}}(t)$ for the existence of a metastable nucleus of size n is larger than the corresponding probability of the stable phase $Z_n^{\text{stab}}(t)$ though condition (1) is not fulfilled

$$Z_n^{\text{met}}(t) > Z_n^{\text{stab}}(t). \quad (2)$$

Thus, the crystallization process is characterized by different time stages, so that metastable crystals are preferably formed before the steady-state nucleation rate for the thermodynamically stable phase is the dominant nucleation process. However, the metastable phase formed by kinetically controlled nucleation is only useful, if the structure built during a defined time regime can be frozen-in.

These general theoretical considerations originate from experimental investigations of amorphous carbon films. With a laser plasma, carbon films are deposited on different substrate materials /5/. Depending on deposition conditions, but also in the result of a defined thermal treatment of these layers, diamond and various carbines are obtained as crystalline particles within the amorphous matrix. Therefore, it seems possible to produce metastable carbon phases by the unconventional way of irradiation of graphite with high energy laser beams during short time pulses. A similar behaviour can be observed for other carbon films deposited by high energy beam techniques, for instance ion beam sputtering /6/.

2. Theoretical Model

Applying the well-known Becker-Döring theory to solid-solid transformations, calculations of changes in the free energy between different phases have to be performed:

$$\Delta F = \Delta F_{\text{ph}} + \Delta F_{\text{el}} + F_{\text{Y}}. \quad (3)$$

ΔF_{ph} describes the volume free energy change to form from a phase β the quantity β without internal mechanical stresses. Additional contributions ΔF_{el} to the volume part of the free

energy arise from elastic deformations within the amorphous matrix itself, but also due to elastic interactions between the crystalline nucleus and the amorphous matrix. F_γ represents the internal boundary energy corresponding to the surface term in nucleation theory. Liquid phases as intermediate states during structural changes are excluded from the present considerations.

2.1. Amorphous Matrix

The atomic structure of non-crystalline carbon contains not only topological disorder of atoms, but variation in bond character, too, that is a mixture of both sp^2 and sp^3 hybridized atoms [7]. The bond structure also characterizes crystalline phases as carbines (sp), graphite (sp^2) and diamond (sp^3). Therefore, the introduction of an effective structural parameter would offer a good approximation to estimate the free energy contribution ΔF_{ph} . Taking into account phonons as a sensitive measure for local atomic bond characteristics and assuming this contribution to be the dominante one, the Einstein temperature θ_d determines the free energy of the phase d as a structural parameter in a first approach

$$F(\theta_d) = 3NkT \left[\frac{1}{2} \frac{\theta_d}{T} + \ln(1 - \exp(-\theta_d/T)) \right]. \quad (4)$$

The Einstein temperature for structures with covalent bonding can be estimated with the binding energy U_b and the nearest neighbour distance r_0 with

$$\theta' = \frac{k}{\hbar} \left[\frac{27}{r_0^2} U_b z \langle d \rangle \right]^{1/2}, \quad (5)$$

where k is Boltzmann's constant and \hbar Planck's constant. z is the average coordination number and the factor $\langle d \rangle$ describes the spatial distribution of lattice vibrations. Amorphous carbon contains the fraction x sp^3 bonds and the fraction $(1-x)$ sp^2 bonds. Different amorphous carbon structures correspond to Einstein temperatures in the range of $\theta_{a1} = 1862$ K and $\theta_{a2} = 1558$ K. Using formula (5) for the limiting case of crystalline phases, too, calculated Einstein temperatures agree well with

experimentally determined Debye temperatures /8/. The free energy difference of the amorphous phase compared to the crystalline carbon structures, diamond and graphite, is given by

$$F_{ph} = F(\theta_a) - F(\theta_c), \quad (6)$$

where θ_a and θ_c are the Einstein temperatures of the amorphous and crystalline phase, respectively.

An additional contribution to the free energy arises from topological disorder of the amorphous solid described by a defect network /9,10/. Structural elements of amorphous covalent bound materials are identified with defects, mainly disclinations /11,12/. Thus, the ring structure of amorphous carbon can be modelled by a distribution of wedge disclinations with positive and negative sign of rotation angle w . Analysis of experimental investigations of amorphous carbon enables the estimation of the disclination density in the range $\xi = 0.3 \dots 0.6$. Moreover, there exists an asymmetry between five- and sevenfold rings $a = |\xi^- - \xi^+|/\xi = 0.25$, where ξ^\pm are the partial disclination densities for positive and negative rotation angles. Such a defect network contains stored energy from elastic strains. Each structural unit has energy contributions from the self-energy E_1^s and interactions w_{1j} with all other defects j in the surrounding defined by a cut-off radius r_{c1}

$$E_1 = E_1^s + \frac{1}{2} \sum_{j \in U_1} w_{1j} \quad (7)$$

Such a cluster defect structure with internal interfaces built up with screened disclinations in a non-balanced distribution ($a \neq 0$) corresponds to a dipol distribution of simple non-screened disclinations ($a = 0$). The average elastic strain energy E of the defect network has been estimated with 3.3 and 4.5 kJ mol⁻¹ for soft and hard amorphous carbon layers, respectively, using different elastic moduli for the material considered.

Applying cluster analysis to the defect network /10/, structural inhomogeneities are detected characterized by fluctuations of the average stress and energy of the structure. Strongly

strained clusters contain a high amount of elastic strain energy and represent pre-stages of crystalline nuclei. The size of these patterns ranges between 15 to 35 Å in diameter, the relative volume fraction compared to the whole material is about 15%. These highly strained defect clusters with local energies of 22 ... 30 kJ mol⁻¹ can be regarded as "weak spots", which can be transformed with low activation energies in crystalline particles.

The free energy of the amorphous phase compared to the crystalline carbon structures, diamond and graphite, is thus given by

$$F = F(\Theta_a) - F(\Theta_c) + \Delta F_{el}(\xi), \quad (8)$$

where ΔF_{el} results from the elastic strain energy of the frozen-in defect structure. Fig. 1 shows the variation of ΔF versus temperature for different amorphous carbon layers characterized by an effective Einstein temperature Θ_a . Without external pressure the ground state of carbon is graphite. Since all amorphous states lie energetically above graphite, phase transformations into graphite are always possible. Diamond represents the metastable carbon phase under normal conditions. Preferably hard amorphous carbons with high Einstein temperatures can be transformed into diamond by nucleation processes.

2.2. Partially Crystallized Solid

Small solid particles in a solid amorphous matrix cause contributions to the free energy. Due to interfaces between the two phases, a surface free energy F_{γ} has to be taken into account. The interface energy has been estimated within an atomistic model in terms of nearest neighbour bond energies /13/. In case of covalent bound materials, the surface free energy contains an energy contribution of unsaturated bonds $F_{\gamma,f}$ and another one from a misfit between bonds of different phases $F_{\gamma,m}$

$$F = F_{\gamma,f} + F_{\gamma,m} \\ = O \left[(c_a - c_p) \Sigma_{pp} + c_a \left(\Sigma_{ap} - \frac{\Sigma_{aa} + \Sigma_{pp}}{2} \right) \right] \quad \text{for } c_p > c_a \quad (9)$$

σ is the surface of the nucleus, c_1 denotes the number of bonds per surface of the phase 1 and \sum_{ij} is the binding energy per bond between atoms of phase 1 and j. Supposing a non-ideal solid solution, the misfit contribution is approximated by $c_1(\sum_{11} - \sum_{pp})$. The local coordination numbers enter dominantly in the quantities c_1 and characterize the crystalline as well as the amorphous phases. In fig. 2 surface energies for graphite and diamond nuclei in an amorphous carbon matrix in dependence on its average coordination number z_a are shown. The parameter α_p is the ratio between the fraction of sp^3 bonds and that of the sum of sp^2 and dangling bonds. Anisotropy of nuclei growth relevant for graphite and a slight temperature dependence of the surface energy can easily be included within this model /14/.

Growth of crystalline nuclei is connected with an elastic misfit between the crystalline phase and the amorphous matrix, which causes an elastic contribution ΔF_{el} to the free energy. For a given stress-free deformation

$$\epsilon_{ij}^T = e^T \delta_{ij} + e_{ij}^T \quad (10)$$

denoting isotropic dilatation or compression e^T and shear deformation e_{ij}^T , the density of the elastic energy u can be calculated in dependence on the volume fraction of nuclei and effective shear and compression moduli G^* and K^* , respectively. The effective quantities can be estimated within Hashin's approximation /15/ in case of a distribution of elastic isotropic nuclei. The elastic energy density u contains contributions from isotropic deformation, shear deformation and according to forces between the thin deposited layer and the substrate, contributions of a fixed macroscopic external stress /16/

$$u = f(V_n, K_1, G_1) (e^T)^2 + f(G_1, G^*, \nu^*) \left(\frac{1}{2} e_{ij}^T e_{ij}^T \right) + f(K^*, G^*) (\epsilon_0 - \epsilon^*)^2 \quad (11)$$

V_n is the volume fraction of nuclei, K_1 and G_1 are compression shear moduli of the phase 1, respectively, ν^* is the effective Poisson ratio and ϵ_0 and ϵ^* is the deformation according to

an external stress σ_0 and the deformation in the stress-free state of the heterogeneous layer system, respectively. The deformation e^T can be estimated by changes of the mass density between the two phases

$$e^T = \frac{1}{3} \frac{\rho_a - \rho_c}{\rho_c}, \quad (12)$$

where ρ_a and ρ_c are the mass densities of the amorphous and crystalline phase, respectively. The elastic free energy density depends strongly on this material parameter. Moreover, the used elastic constants for the amorphous matrix are dependent on the sp^3 bonding fraction related to the mass density. In order to regard the influence of very high stresses, it has to be assumed that the moduli of graphite increase with pressure /17/. The third term in (11) cannot be neglected, since it gives energy contributions of the strained heterogeneous system in the same range as those of the transformation amorph-crystalline without external stresses. In fig.3 /16/ the change of the elastic energy with the volume fraction of crystalline nuclei is plotted versus the density of the amorphous carbon layer in dependence on the external pressure σ_0 . For high mass densities of the matrix, the necessary elastic energy change for crystal growth of diamond nuclei is smaller than that for graphite and is even lowered for increasing external stress. Applying these results to the calculation of the critical activation energy for a nucleus, two characteristic regions of formation of phases are obtained depending on the density of the layer and the initial stress (fig.4). Thus, diamond will preferably grow in amorphous films with a high mass density.

3. Kinetically Controlled Phase Transitions

According to different stages of nucleation and growth of nuclei, characteristic times can be distinguished /18/:

$$- \quad t_s = I_s^{-1} = \left\{ N R n_c^0 \left[\frac{F_c}{kT} \frac{1}{3\pi n_c^2} \right]^{1/2} \exp(-F_c/kT) \right\}^{-1}, \quad (13)$$

the average steady-state nucleation time

- the time lag of establishing the steady-state distribution of nuclei

$$\tau = \frac{0.32\pi}{R} \frac{n_c^{2-\beta}}{\beta F_c / kT} \quad (14)$$

- the growth time

$$t_g = n_{\max}^{(1-\beta)} \frac{n_c}{\beta R F_c / kT} \quad (15)$$

I_s is the stationary nucleation rate, k is Boltzmann's constant, N is the number of nucleation centres. The size of the critical nucleus is given by

$$n_c = \left(\frac{\beta \gamma}{\int f} \right)^{\frac{1}{1-\beta}} \quad (16)$$

and the critical free energy by

$$F_c = \frac{1-\beta}{\beta} \int f \cdot n_c \quad (17)$$

if $\Delta F = -\int f n + \gamma n^\beta$ contains volume and surface contributions corresponding to formula (3). β can take two values, $\beta = 2/3$ for isotropic nucleus growth and $\beta = 1/2$ for anisotropic two-dimensional growth. R denotes a characteristic frequency of local mass transport $R = \nu_0 \exp(-U/kT)$ where U is the activation energy for the transport of an atom across the interface of a nucleus. The maximum nucleus size can be approximated by /19/

$$n_{\max}^{-1} \simeq I_s \cdot t_g \frac{1-\beta}{2-\beta} \quad (18)$$

The different relations of characteristic times in dependence on supersaturation, critical nucleus size and free energy of the critical nucleus allow estimations on time development of phase formation. For thermodynamically controlled transitions, nucleation is a steady-state process and growth is determined by high values of supersaturation $\int f$ obtained by constraints, e.g. elastic deformations. Therefore, the final phase is the phase with minimum free energy. Kinetically controlled transitions characterize nucleation processes that deviate from stationary nucleation. The growth time is larger than the steady-state nucleation time t_s , since critical activation energies for nucleation are small. This means, if the surface energy of the metastable crystalline phase is smaller than that of the

stable crystalline phase, metastable crystalline nuclei can be formed by kinetically controlled nucleation processes (fig.5). In order to distinguish these two main processes of nucleation, the following characteristic can be given:

| thermodynamically controlled nucleation | kinetically controlled nucleation |
|--|--------------------------------------|
| $t_s/\tau > 1$ | $t_s/\tau < 1$ |
| $t_s/t_g > 1$ | $t_s/t_g < 1$ |

A more detailed evolution of the nucleus size distribution Z_n with time can be calculated from the Master equation

$$\frac{\Delta Z_n}{\Delta t} = I_{n-1} - I_n \quad (19)$$

with

$$I_n = R n^3 N_n \left[\frac{Z_n}{N_n} - \frac{Z_{n+1}}{N_{n+1}} \right] \quad (20)$$

The number of nuclei Z_n of size n for $t \rightarrow \infty$ is given by an equipartition

$$N_n = N \exp(-F_n/kT) \quad (21)$$

In order to discuss the peculiarities of kinetically controlled nucleation, the time evolution of two distributions with $Z_{n=1}(t) = N$ and $Z_{n>1}(0) = 0$ is shown in fig.6. This is an example for a situation where in the result of smaller critical free energy, phase A with a smaller supersaturation δf is formed with a higher probability than the thermodynamically favoured phase B.

In conclusion we state that Ostwald's rule of stages can be interpreted in view of thermodynamically as well as kinetically controlled nucleation processes. The elastic constraints change the free energy to such an extent that the metastable phase becomes the phase of the absolute minimum of free energy within the context of thermodynamically controlled transitions. Low surface energies and small critical activation energies favour the nucleation of metastable phases in the frame of kinetically controlled nucleation processes.

Acknowledgement

We are indepted to our colleagues A. Bahr, W. Kreher and H.-J. Weiß for many helpful discussions and support in performance of part of the calculations.

Figure Captions

- Fig.1 Differences of the free energies between various amorphous carbon structures and graphite (a) and diamond (b) versus temperature
- Fig.2 Surface energy of graphite (a) and diamond (b) nuclei in an amorphous matrix with the average coordination number z_a
- Fig.3 Change of the elastic energy during nucleation in an amorphous carbon layer depending on its mass density and external stresses
- Fig.4 Regions of formation of graphite (G) and diamond (D) in dependence on the mass density of the amorphous carbon layer
- Fig. 5 Schematic representation of nucleation and growth processes; the two straight lines distinguish between areas of thermodynamically (upper line) and kinetically (lower line) controlled nucleation,
 $\gamma_1 = 1.42 \text{ J m}^{-2}$, $\gamma_2 = 1.02 \text{ J m}^{-2}$
- Fig.6 Time evolution of size distribution of nuclei of two phases (kinetically controlled nucleation)

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Prof. W. Pompe and Dr. A. Richter
Zentralinstitut für Festkörperphysik
und Werkstofforschung der Akademie
der Wissenschaften der DDR

DDR - 8027 Dresden

Helmholtzstraße 20

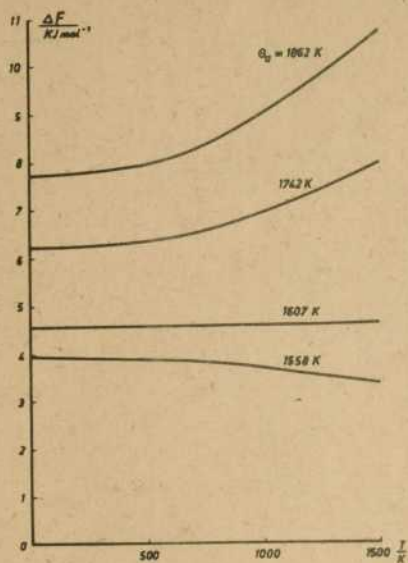


Fig. 1a

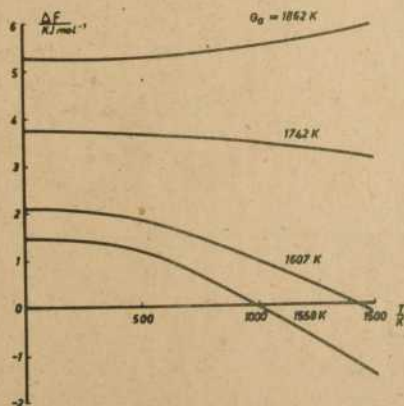


Fig. 1b

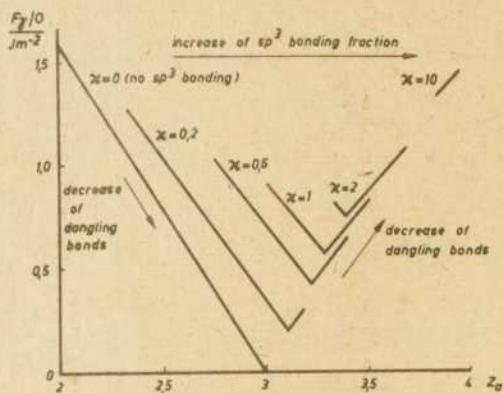


Fig. 2a

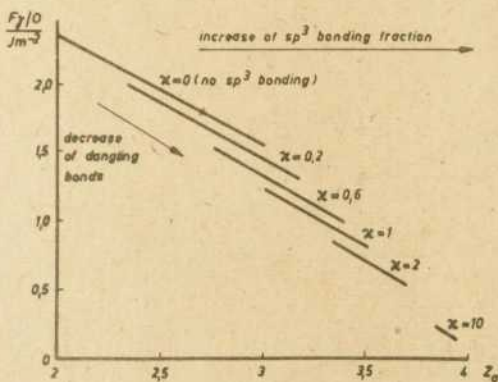


Fig. 2b

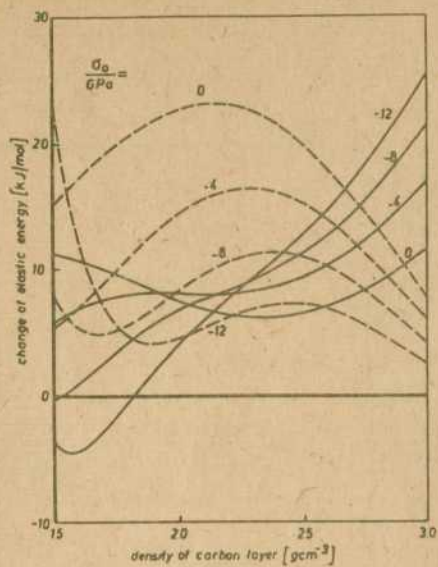


Fig.3

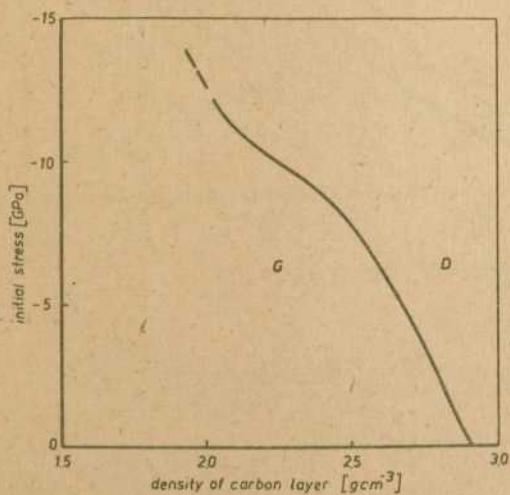
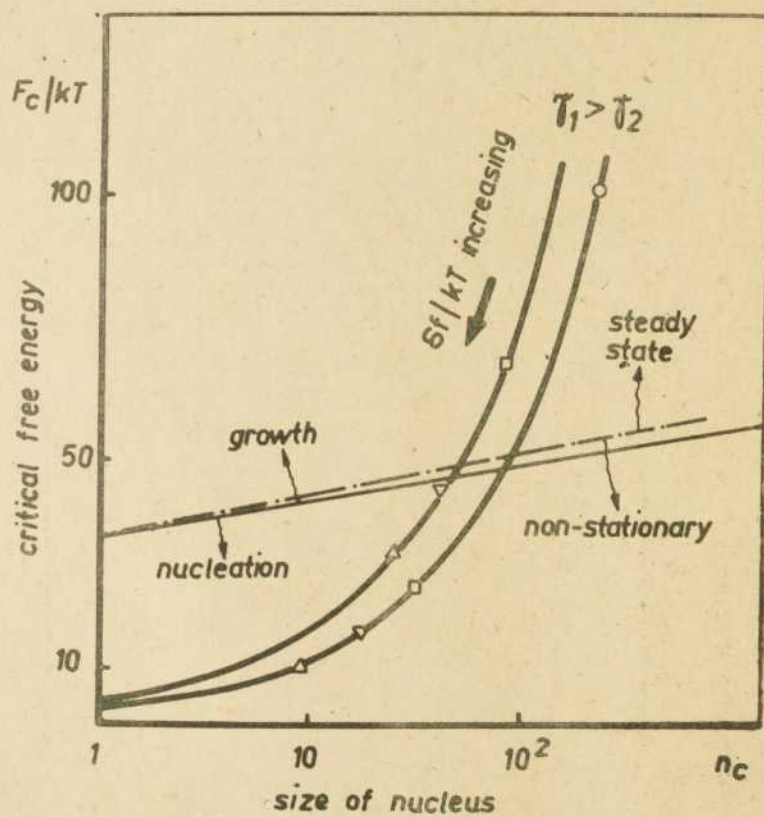


Fig.4



δf [kJ/mol]: 10 - \circ ; 20 - \square ; 25 - ∇ ; 30 - \triangle

Fig. 5

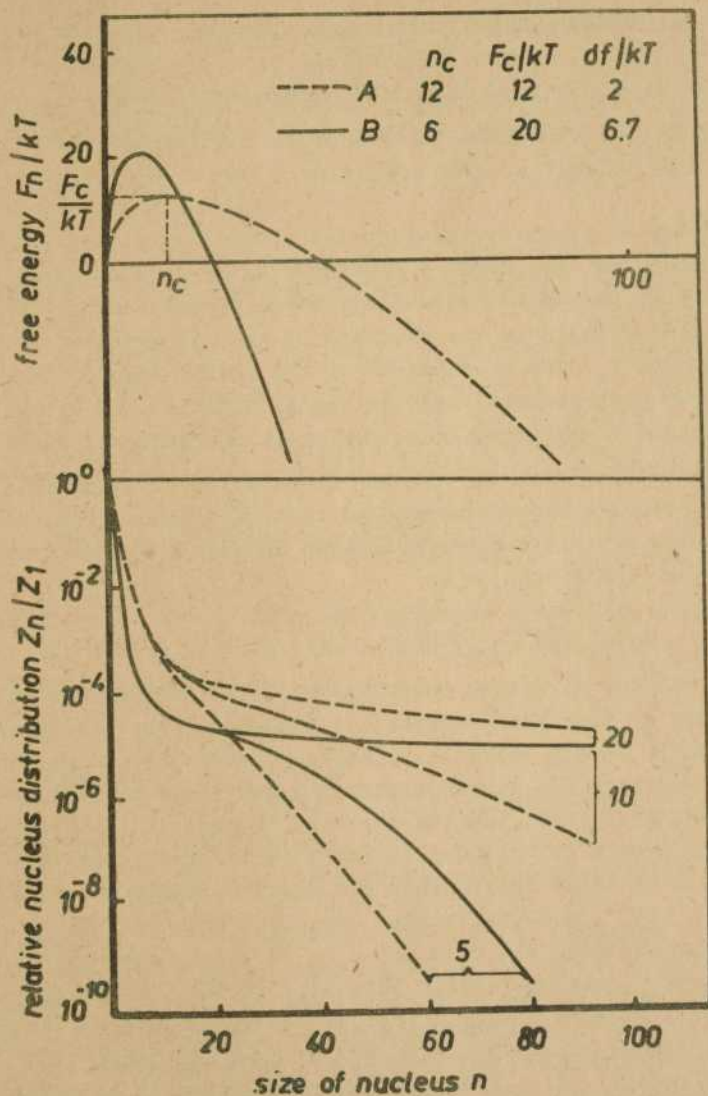


Fig. 6

Nucleation and Crystal Growth in Viscoelastic Media

I. GUTZOW, J. SCHMELZER, R. PASCOVA and B. POPOW

The theory of phase segregation and crystal growth is extended to include the influence of elastic strains developing in elastic solids and in viscoelastic fluids, in particular, in glassforming melts in the vicinity of the temperature of vitrification T_g . The predictions of the theory are in coincidence with experimental results on the kinetics of formation and Ostwald ripening of AgCl in a model photochromic glass.

1. We consider first the growth of a complex of B-molecules, formed within a supersaturated solid A,B-solution. The thermodynamics of irreversible processes defines the flux J of B-molecules to the complex as

$$J = - \frac{D_B C_B}{kT} \cdot \text{grad } \mu \quad (1)$$

Here D_B is the diffusion coefficient of the B-molecules in the solution, C_B is their distance and time-dependent concentration and μ is the chemical potential (referred to a B-molecule) determining the growth process; k and T denote as usual Boltzmann's constant and the absolute temperature. Supposing that the growth of the complex leads to the development of elastic strains μ splits into two additive parts according to $\mu = \mu_c + \mu_e$: a concentration dependent potential μ_c (assuming an ideal solution $\mu_c = \mu_0 + kT \ln x_B$ where $x_B = C_B / (C_A + C_B)$) and an elastic term μ_e . If the profile of the density of elastic energy ξ (per cm^3 of the solution) is known then μ_e can be expressed by $\mu_e \cong \bar{v}_B^0 \xi$, if \bar{v}_B^0 denotes the volume of a B-molecule. Assuming spherical symmetry a generalized Fickian equation /1/ can be obtained from (1) in the form

$$J(r) = - D_B \left[\frac{\partial C(r)}{\partial r} + f(r) \frac{C(r)}{kT} \right] \quad (2)$$

r being the distance from the centre of the B-complex and $f(r) = \bar{v}_B^0 \frac{\partial \mathcal{E}(r)}{\partial r}$ denotes a generalized force, determined by the energy of elastic strains produced by the growth itself. By an application of the theorem of Gauss-Ostrogradskij to eq. (2) (see also /2,3/) the volume growth rate of a nucleus of the radius R can be determined as

$$\frac{dV}{dt} = \frac{4\pi R^2}{C_k} J(r) \Big|_{r=R+0} = \frac{4\pi R^2}{C_k} D_B \frac{\partial C_B(r)}{\partial r} \Big|_{r=R+0} + f(r) \frac{C_B(r)}{kT} \Big|_{r=R+0} \quad (3)$$

Here $C_k \approx 1/\bar{v}_B^0$ is the concentration of B-molecules in the growing B-complex and, consequently, we get:

$$f(r) C_B(r) \Big|_{r=R+0} \approx \frac{C_B(r)}{C_k} \cdot \frac{\partial \mathcal{E}(r)}{\partial r} \Big|_{r=R+0} \quad (4)$$

In the considered case of spherical symmetry the radial distribution of the density of the elastic energy in the nucleus and in the matrix is given by /4,5,6/

$$\mathcal{E}(r) = \begin{cases} \pi_k \delta^2 & \text{for } r \leq R \\ \pi_M \delta^2 (R/r)^6 & \text{for } r > R \end{cases} \quad (5)$$

This type of strains develop when there exists a relative difference $\delta = \frac{\bar{v}_{AB}^0 - \bar{v}_B^0}{\bar{v}_B^0}$ in the density of the matrix building

units (\bar{v}_{AB}) and the B-molecules in the growing complex. It is assumed in the derivation of equ. (5) that the strain energy is generated exclusively by the exchange of the building units of the solute with B-atoms. The constants π_k and π_M are determined in a known way (see /4,5,6/) by the elastic constants of the system nucleus/matrix and the total energy of elastic strains due to the development of a nucleus of the volume $V = 4/3 \pi R^3$ is given by

$$\Phi = \int_0^R 4\pi r^2 \pi_k \delta^2 dr + \int_R^\infty 4\pi \frac{R^6}{r^4} \pi_M \delta^2 dr = (\pi_k + \pi_M) \delta^2 V \quad (6)$$

The crux of the problem in solving eq. (3) and determining the kinetics of growth in an elastic matrix is the knowledge of the value of $\partial \xi(r)/\partial r|_{r=R+0}$. For the discussed case eqs. (4), (5) and (6) lead to

$$f(r)|_{r=R+0} = -\frac{6}{c_k R} \pi_M \delta^2 \approx -\frac{6}{c_k} \cdot \frac{1}{R} \frac{\Phi}{V} \left(\frac{\pi_M}{\pi_k + \pi_M} \right) \quad (7a)$$

and with $\frac{V}{V_0} = n_k$ eq. (7a) reads

$$f(r)|_{r=R+0} = \text{const} \frac{1}{R} \cdot \frac{\Phi}{n_k} \quad (7b)$$

n_k is the number of B-molecules forming the growing complex. Thus in similar situations where the $\xi(r)$ function is not known or can be constructed with great difficulty, an expression of the type

$$f(R) \approx -\text{const} \frac{1}{L} \cdot \frac{\Phi(R)}{V_0} \quad (8a)$$

can be used, L being some specific length ($L \approx R$ for diffusion limited growth and $L \approx d_0$ when the transfer takes place only at intermolecular dimensions) and V being the increase of the volume of the cluster from 0 or from V_0 to V . From eq. (6) it follows that

$$\frac{\Phi}{V} = \frac{d\Phi}{dV} - V \frac{d(\frac{\Phi}{V})}{dV}$$

and it becomes evident that

$$f(R) \approx \text{const} \frac{1}{L} \cdot \frac{d\Phi}{dV} \quad (8b)$$

can be used /7/ when δ^2 is nearly a constant or $V d(\Phi/V)/dV$ is a small number as compared with $d\Phi/dV$. Of particular interest for the phase formation in solids is also the classical example /8/ of strains, produced, when a number z of B atoms is introduced into an initial volume V_0 , so that $V - V_0 = z v_B^0$ (see also /6/). Then /6,8/ the energy to enlarge the cluster from V_0 to V is

$$\Phi = \pi_0 \left(\frac{V - V_0}{V_0} \right)^2 \cdot V_0 \quad (9)$$

and (as in eq. (8) $V^* = V - V_0$ or via eq. (8b))

$$f(R) \approx \text{const} \frac{1}{L} \cdot \frac{V - V_0}{V_0} \quad (10)$$

is an increasing function of the volume V .

Thus $f(R)$ has two possible effects in eq. (3): either a trivial decrease of the volume growth rate (when $\Phi/V \approx \text{const}$) or (and this is of particular significance) $f(R)$ is an increasing function of V and a complete stop of growth and a saturation of the y - t curve is to be expected.

2. In the vicinity of T_g glassforming melts behave as viscoelastic media. In /7/ a detailed molecular model of the segregation process in a viscoelastic glassforming matrix is described, the building units of which have a diffusion coefficient D_M much smaller than the diffusion coefficient D_B of the segregating molecules (e.g. of AgCl type). Taking into account both mentioned types of generation of elastic strains it can be shown that in such a process of segregation

$$f(R) = \pi_1 \left[\left(\frac{v_A^0 - v_B^0}{v_B^0} \right)^2 + \frac{\pi_2}{\pi_1} \cdot \frac{(V - V_0)}{4\pi R^2 \ell \Psi\left(\frac{D_M}{D_B}\right)} \right] \quad (11)$$

where π_1 and π_2 are constants determined by the elastic moduli of both phases and $\Psi(D_M/D_B)$ is a function of the D_M/D_B ratio. ℓ being a characteristic distance. At $V > V_0$ the first term in eq. (11) can be neglected. Thus a dV/dt function is obtained in the form

$$\frac{dV}{dt} \approx \Delta \frac{1}{\eta} \Delta p - \frac{\pi^* (V - V_0)}{\eta \cdot \Psi\left(\frac{D_M}{D_B}\right)} \quad (12)$$

where Δp is the driving force of the process and $\eta \sim kT/D_M$ is the viscosity of the glassforming matrix and π^* is determined by the elastic moduli. It can be shown, that eq. (12) is in fact an extended form of the well known Kelvin-Voigt equation /9/ describing the time dependence of retardation processes in viscoelastic media. Thus the interconnection of processes of the phase formation and the rheological behaviour of glassforming melts with both an elastic and viscous component becomes obvious.

3. In the process of Ostwald ripening $dC/dr|_{r=R}$ in eq. (3) is determined by a factor of the type $\frac{1}{R} \left(\frac{1}{R_k} - \frac{1}{R} \right)$, where R_k is the radius of the critical nucleus at a given supersaturation. Thus, when elastic effects can be neglected ($f(R)=0$) eq. (3) can be written in the form /3/

$$\frac{dV}{dt} = \text{const } D_B \left[\left(\frac{V}{V_k} \right)^{1/3} - 1 \right] \quad (13)$$

and the volume vs time ($V-t$) and number of particles vs time ($N-t$) dependence follow the well known Lifshitz-Slyozov equations

$$\bar{V}(t) - \bar{V}_0 = \text{const } D_B t \quad (14)$$

$$1/N(t) - 1/N_0 = \text{const } D_B t \quad (15)$$

In considering strain effects in the Ostwald ripening process it can be shown that eqs. (3) and (13) give with the $f(R)$ -function (14)

$$\begin{aligned} \frac{dV}{dt} &= \text{const } D_B \left[\left(\frac{V}{V_k} \right)^{1/3} - 1 \right] - \frac{\pi^* (V - V_0)}{e \psi \left(\frac{D_M}{D_B} \right)} \approx \\ &\approx \text{const } D_B \left[\left(\frac{V}{V_k} \right)^{1/3} - 1 \right] \exp(-t/\tau) \end{aligned} \quad (16)$$

where the relaxation time τ is determined by D_M , D_B and an elastic modul. Thus instead of eqs. (14) and (15) the kinetics of the ripening process is described by

$$\bar{V}(t) - \bar{V}_0 = \text{const } D_B \tau (1 - e^{-t/\tau}) \quad (17)$$

$$1/N(t) - 1/N_0 = \text{const } D_B \tau (1 - e^{-t/\tau}) \quad (18)$$

A detailed investigation of the kinetics of growth of AgCl-clusters in a sodium borate melt described in /10/ results in the conclusion that in fact the $V-t$ curve shows a saturation as given by eq. (17) (Fig.1). From the initial slope of this curves (at $t \rightarrow 0$ eq. (17) is equivalent to (14)) D_B can be determined. From the $\log D_B$ vs $1/T$ plot it is obvious (Fig.2), that the activation energy U_{DB} for the diffusion of AgCl in our model glass does not depend on the composition and is equal to

the value U_D for the migration of Ag^+ -ions in various glasses ($U_D \approx 30$ kcal/mol). The value of the activation energy U_M for the self-diffusion coefficient of the glassy matrix itself turns out to be of a much higher value ($U_M \approx 150$ kcal/mol) and $D_B \approx 10^5 D_M$. Thus the premises of the theoretical model as expressed by the eqs. (11) and (12) fully correspond to the experimental situation. Fig.3 illustrates the $N(t)$ dependence for our AgCl model glass corresponding in its decreasing Ostwald ripening part to eq.(18). It was shown that the rise of the $N(t)$ -curve corresponds to Zeldovich type non-steady state effects /11,22/. More details of the calculations given here in brief and on the experimental procedure etc. may be found in /5,7,10,15/. In /7/ also the time development of the concentration profile in the vicinity of a growing complex is given when $f(R) = \text{const}/R$ and when $f(R) = (V - V_0)/V_0 R$.

Figure Captions

- Fig.1 Kinetics of Ostwald ripening of AgCl-clusters in a sodium borate melt at temperatures indicated at each curve in °C. Solid lines drawn through the experimental points (cube of diameter d vs time t) according to eq. (17).
- Fig.2 Data on the diffusion coefficient of AgCl and Ag^+ -ions in different glassforming melts in Arrhenius coordinates; 1- D_0 for AgCl in our sodium borate melt from eq. (14) and (17) and initial slope of d^3-t curves; 2- D_0 for AgCl in borosilicate melt according to eqs. (14) and (17) to measurements by Fanderlik /13/; 3 to 4 and 5 to 11: Direct determinations of the diffusion coefficient D of Ag^+ -ions in borosilicate and alkalisilicate glasses according to measurements by Tsekhomskij et al. /14/.
- Fig.3 Number N of clusters vs time curves for formation (increasing initial part of curves) and for ripening process of AgCl phase in sodium borate melt.

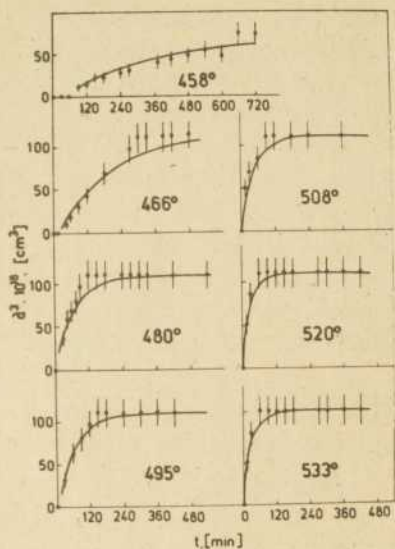


Fig. 1

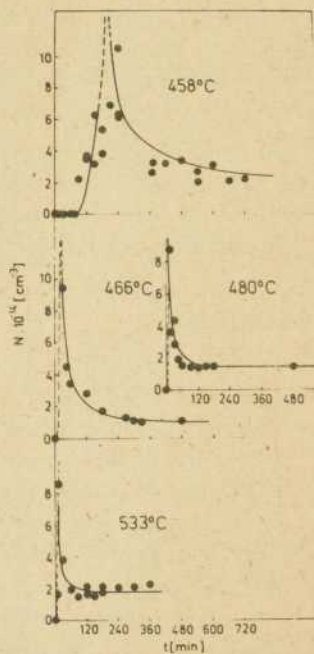


Fig. 3

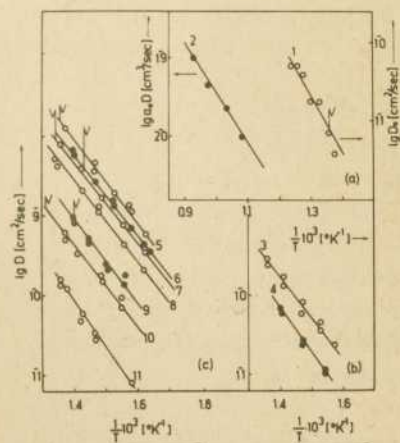


Fig. 2

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Verfasser

Prof. I. Gutzow, Dr. R. Pascova
Institute of Physical Chemistry
Bulgarian Academy of Science

S o f i a 1040
Bulgaria

Dr. J. Schmelzer
Wilhelm-Pieck-Universität Rostock
Sektion Physik

DDR - 2500 R o s t o c k
Universitätsplatz 3

Prof. B. Popow
Higher Institute of Chemical
Technology

S o f i a 1166
Bulgaria

Special Stochastic Measures as Critical Quantities in Non-equilibrium Phase Transitions

F. SCHLÖGL

1. Introduction

As already discussed in earlier papers of the author /1/ the bit-number cumulants of a probability distribution over the microstates of a system are sensitive to interior correlations between parts of the system. The second of these cumulants, the bit-number variance, is sensitive in a higher degree than the first one, the informational entropy /2/. Of special interest are the bit-number cumulants of the probability distributions in Gibbs phase space of the microstates described by the canonical variables of Hamilton mechanics. Equilibrium entropy is a first cumulant and specific heat is a second cumulant of this type. The sensitivity of the bit-number variance is the reason for the dramatic critical behaviour of specific heat in an equilibrium phase transition.

Therefore it seems interesting to examine the bit-number variance of nonequilibrium probability distributions near a critical point of nonequilibrium phase transitions. This was done, as described in the following, for some systems with such transitions.

2. Critical Quantities in Equilibrium and in Nonequilibrium Phase Transitions

It was pointed out by several authors /3-7/ that in certain physical systems of different kind cooperative effects can be observed which, notwithstanding that they occur far away from any thermal equilibrium, show properties closely analogous to those of equilibrium phase transitions. We then speak of "nonequilibrium phase transitions". In the following we will deal with such transitions which can be observed in the diagram of

steady (stationary) states of an open system. (We do not speak of structures in time). In case of a non-equilibrium phase transition the steady state diagram, in particular with respect to singularities, look like an equilibrium state diagram of a system with a phase transition. This equilibrium state diagram is given by the "thermal state equation". By this the critical behaviour of certain quantities is already determined, like the singularity of the order parameter and of certain susceptibilities (so we call derivatives of a thermal quantity with respect to another one). Yet not determined by the thermal state equation is the behaviour of specific heat. For this we need the caloric state equation as an independent information. We can obtain all these informations by the knowledge of the energy as function of thermal variables.

In nonequilibrium we do not know a quantity which plays an analogous role like free energy in equilibria. I mean a thermodynamic function which distinguished steady states far away from any equilibrium by its extrema and which gives an analogous additional information like the caloric equation for equilibria (the principle that steady states are distinguished by minimum entropy production is valid only in linear thermodynamics near an equilibrium).

Specific heat is a special susceptibility. It is the derivative of energy E with respect to temperature T :

$$c = \partial E / \partial T \quad (2.1)$$

Temperature is the thermal adjoint to energy. Energy is the generator of time-shift against which an equilibrium is invariant, unlike steady nonequilibrium states which belong to an environment changing with time. Temperature is distinguished in equilibrium phase transitions as a natural control parameter. This distinction does no more exist in nonequilibria. - Specific heat is also proportional to the variance of energy in a canonical ensemble:

$$c \sim \langle (\Delta E)^2 \rangle \quad (2.2)$$

And this provides a key to find an analogous quantity in nonequilibria.

3. Bit-number Cumulants

We consider a sample set of events which are uniquely characterized by a set

$$\xi = (\xi_1, \xi_2, \dots) \quad (3.1)$$

of continuous parameters ξ_i . A special case which will be considered later is that these events are microstates of a physical system in Gibbs phase space. Then the set ξ is the set of the canonical variables q_i and their adjoint momenta p_i . Let

$\mathcal{S}(\xi)$ be the probability density of the events in ξ -space. We call

$$b(\xi) = -\log \mathcal{S}(\xi) \quad (3.2)$$

the corresponding bit-number because it is related to the number of bits which are necessary to select the event ξ if $\mathcal{S}(\xi)$ is already known. The mean value of b

$$\langle b \rangle = \int d\xi \mathcal{S} b \quad (3.3)$$

is Shannon's informational entropy, a fundamental measure of the distribution \mathcal{S} in information theory [8].

This mean value of b is the first cumulant of b . We can define bit-number cumulants Γ_k of any order k by the expansion

$$\log \langle e^{db} \rangle = \sum_{k=1}^{\infty} d^k \Gamma_k / k! \quad (3.4)$$

These stochastic measures Γ_k are distinguished by the following two features:

- (a) They are additive for uncorrelated subsystems.
- (b) They are invariant with respect to volume conserving transformations of ξ -space.

The feature (a) allows to use the differences

$$\Gamma_k - \Gamma_k^I - \Gamma_k^{II} \quad (3.5)$$

as an ordered system of measures for the correlations between two subsystems I, II of which the system is composed. The feature (b) makes Γ_k invariant against Liouville motion in Gibbs phase space.

The following statement shows that the second cumulant T_2 is more sensitive to the onset of correlations than the first one, the information entropy T_1 . We consider a given distribution

$S_{i_1, i_2} \dots$ of a system which is composed of subsystems the states of which are $i_1, i_2 \dots$. The probability distribution of the first subsystem is the marginal distribution

$$S_{i_1} = \sum_{i_2, i_3 \dots} S_{i_1, i_2, \dots} \quad (3.6)$$

In an analogous way we define marginal distributions S_{i_1} for any subsystem. The product of all of them

$$S_{i_1, i_2, \dots}^0 = S_{i_1} S_{i_2} \dots \quad (3.7)$$

is the distribution in which the probability densities S_{i_1} for the subsystem are unchanged but all correlations between them are suppressed. We call it the uncorrelated distribution to

$S_{i_1, i_2} \dots$. We always can write

$$S_{i_1, i_2, \dots} = (1 + \varepsilon_{i_1, i_2, \dots}) S_{i_1, i_2, \dots}^0 \quad (3.8)$$

where ε describes the correlations in a given microstate. For small ε , say for the onset of correlations it turns out that T_2 depends on ε in first order already whereas T_1 depends but in second order.

4. Bit-number Variance as Thermodynamic Quantity

A macroscopic thermal equilibrium state can be described by a set of variables M^v which in statistical theory are mean values of phase functions $M^v(\xi)$ in Gibbs phase space ξ . The adequate probability distribution in ξ -space belonging to maximum entropy $\langle b \rangle$ is

$$\xi = \exp [\Phi - \lambda_v M^v]. \quad (4.1)$$

The underlining tilda denotes the phase functions. Greek sub- and superscripts occurring twice in a product are summation dummies. As a rule M^v are extensive and λ_v intensive variables describing the same macrostate. The construction of ξ in the form (4.1) is interpreted by Jaynes /9/ as the method of "unbiased guess". We call this ξ a generalized canonical

ensemble. It is well known that the same macrostate can be described alternatively by a microcanonical, canonical, or a grand canonical ensemble. This means that we can use different \mathcal{L} with less than the whole set M^ν for the same macrostate. So we have generally to distinguish between M^ν entering into \mathcal{L} as phase functions, this is as random quantities, and those M^ν entering as fixed parameters. Correspondingly Γ_2 becomes different for the different \mathcal{L} . The specific heat is such a Γ_2 and becomes thus different for let us say constant volume than for constant pressure.

It is found by examples that this kind of specific heat shows the most dramatic critical behaviour in equilibrium phase transitions which is Γ_2 to a \mathcal{L} in which the order parameter is a random variable M^ν .

Now we have to ask for an adequate probability distribution describing a given macroscopic nonequilibrium state with local and time dependent macroscopic variables $M^\nu(\underline{x}, t)$. These variables then are densities in three-dimensional geometric space \underline{x} . In the so-called Schrödinger picture these variables are interpreted as mean values of phase space functions $\tilde{M}^\nu(\underline{x}; \mathfrak{f})$ in a time dependent probability distribution $\mathcal{L}(t; \mathfrak{f})$. If we apply Jaynes method of unbiased guess, starting with the instantaneous mean values $M^\nu(\underline{x}, t)$, we obtain the so-called "local equilibrium distribution"

$$\mathcal{L}^L(t) = \exp [\Phi(t) - \lambda(t) \cdot \tilde{M}] \quad (4.2)$$

where we use the symbolic abbreviation

$$\lambda \cdot \tilde{M} = \int d^3x \quad \lambda_\nu(\underline{x}) \tilde{M}^\nu(\underline{x}) \quad (4.3)$$

This $\mathcal{L}^L(t)$, however, deficient because no knowledge about the dynamics is included into the construction. Therefore this $\mathcal{L}^L(t)$ is not able to describe correlations and transport phenomena correctly.

The construction of a suitable distribution \mathcal{L} belonging to the nonequilibrium state was first proposed by H. Mori /10/, which indeed has given good results in transport theory and similar questions. This construction implies that the time scale of the

microscopic processes is distinctly separated from that of macroscopic processes. This is a standard condition for the applicability of a thermodynamic description. If it is fulfilled, then there exists a large plateau of intermediate times τ . In such a time τ the system is practically isolated and therefore its dynamics in Gibbs phase space is a Liouville motion. $\underline{\xi}$ at time t is constructed by the application of this dynamics during a time τ on the local equilibrium distribution $\underline{\xi}^L$ at the earlier time $t - \tau$. By use of the Liouville operator \mathcal{L} this is

$$\underline{\xi}(t) = e^{-i\tau\mathcal{L}} \underline{\xi}^L(t-\tau). \quad (4.4)$$

The result of this construction is identical with expressions based on different arguments later by McLennan /11/ and Zubarev /12/. Due to the supposed time scale separation the result is independent of the choice of τ if only on the plateau. $\underline{\xi}$ belongs practically to the same mean values $M^{\nu}(\underline{x}, t)$ as $\underline{\xi}^L$, yet the two distributions are very different. In $\underline{\xi}$ all interior correlations are fully developed which were suppressed in $\underline{\xi}^L$. Now the invariance property (b) mentioned in the preceding chapter becomes important. Due to it all bit-number cumulants T_k for $\underline{\xi}$ are the same as for $\underline{\xi}^L$ at the earlier time. They are functionals of the variables λ_{ν} , M^{ν} and therefore practically the same at time t and $t - \tau$. This means, due to the time scale separation, the T_k are the same for $\underline{\xi}$ as for $\underline{\xi}^L$. This is an important and nontrivial justification of the local equilibrium approximation for all T_k . Thus the bit-number variance for the Mori distribution is

$$T_2 = - \int d^3x d^3x' \lambda_{\mu}(\underline{x}) \lambda_{\nu}(\underline{x}') \delta M^{\mu}(\underline{x}) / \delta \lambda_{\nu}(\underline{x}'). \quad (4.5)$$

The derivative in this expression is a functional derivative in space. In macroscopic systems composed of different homogeneous parts as a rule the correlation lengths are so small that these derivatives become local derivatives with the exception that correlations going through the interfaces between the parts lead to derivatives of variables of one part with respect to variables of a neighbored part.

For systems with a nonequilibrium phase transition T_2 formed with the distribution in which the order parameter is a random quantity is a distinguished candidate for a characteristic critical behaviour. It will be discussed in what follows for some special systems.

5. Some Examples

In the following we give some examples which have been discussed in more detail in ref. /2/. They are simple models for systems with a nonequilibrium phase transition in a macroscopic description which has the character of a mean field approximation. In the neighbourhood of the critical point we can reduce the state equation into an approximate standard form. For the equilibrium systems this is the thermal state equation, for the nonequilibrium systems it is the equation of the steady states far away from any equilibrium. The standard form is

$$m^{\zeta} + \tau m = h - c \tau \quad (5.1)$$

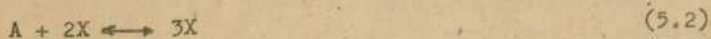
where m, τ, h are the deviations of certain thermodynamic variables from the critical value expressed in adequate reduced units. These variables usually are called in the following way: m is associated with the "order parameter", τ with the "control parameter", and h with the "external field". c is a fixed coefficient, exponent ζ is 3 or 2. As already mentioned, in equilibrium phase transitions the control parameter is always temperature. In the nonequilibrium examples the control parameter is different for the different systems and no more generally distinguished.

1.) Weiss ferromagnet. It shows a second order equilibrium phase transition. Temperature T is control parameter, magnetization M order parameter, magnetic field H is external field, c vanishes, ζ is three. T_2 has to be formed for the magnetic field ensemble in which M is a random quantity. Thus T_2 is specific heat c_H for fixed magnetic field.

2.) Van der Waals Gas-Liquid System. It shows a first order equilibrium phase transition between two coexistent phases.

T is control parameter, volume V is order parameter, pressure p is external field, c is nonzero, ζ is three. T_2 has to be formed for the pressure ensemble and thus becomes equal to specific heat for fixed pressure.

3.) Chemical Reaction Model. Described in detail in ref. /13/. Reaction scheme is



Concentrations of A, B, C are fixed by adequate feedings of the reactor. Autocatalytic component X can vary and moreover diffuse. The system shows close analogies to the gas-liquid system. The coexistence of two phases, that means a low and a high concentration of X in different domains in space, is possible. These domains have the tendency to assume spherical shape like droplets on bubbles. The coexistence value of concentration C depends on the surface curvature in a similar way like vapour pressure. And yet more analogies exist. Here concentration B is control parameter, X order parameter, C external field, c is nonzero, ζ is three. T_2 has to be formed for the grand canonical ensemble where the concentrations are random variables. T_2 is a typical new thermodynamic quantity.

4.) Ballast Resistor. This system was studied as an example of a nonequilibrium phase transition by several authors /14-16/. It shows close analogies to example 3 in the special one-dimensional case. The domains are parts of the wire with high or low temperature as two phases. Here electrical current I is control parameter, temperature T of the wire order parameter (and not control parameter!), temperature T_0 of the environment is external field, c is nonzero, and ζ is three. T_2 has to be formed for the system composed of the wire and the environment and belongs to two different temperatures T, T_0 of these parts. Their energies E, E_0 are random quantities.

5.) Schematic Laser Model. This model is described in ref./17/ as a two-level one-mode laser with simple properties. The number N of excited molecules and the number n of photons are assumed to fulfil the equations

$$\partial N / \partial t = -(N - N_0) / \mathcal{T} - G n N \quad (5.4)$$

$$\partial n / \partial t = -k n + G n N \quad (5.5)$$

with the additional assumption that the molecular relaxation time \mathcal{T} is so short that N becomes a unique function of the instantaneous value n . This leads to

$$\partial N / \partial t = (k - G N) (N - N_0) / N_0 \quad (5.6)$$

The stationary solutions show a nonequilibrium phase transition. N_0 describing the pumping rate is control parameter, N is order parameter. Here external field and c are zero, \mathcal{G} is two. T_2 has to be formed for the combined system of the excited molecules with an energy and temperature proportional to N and the pumping radiation with an energy and temperature proportional to N_0 .

In table I the quantities are listed which are control parameters, and external field for the different examples.

Table I

| | control par. | order par. | extern. field | \mathcal{G} | |
|------------------|-----------------|---------------|------------------|---------------|------------|
| Weiss ferromagn. | M | T | H | 3 | $c = 0$ |
| Laser model | N | N_0 | - | 2 | |
| V.d. Waals | V | T | P | 3 | $c \neq 0$ |
| Chem. model | X | B | C | 3 | |
| Ballast res. | T | I | T_0 | 3 | |

We can divide these systems in two classes, one with vanishing c and one with nonvanishing c . This is the usual classification of second and first order phase transitions.

The result of the detailed analysis now is that T_2 indeed is singular if passing the critical point. Moreover, it behaves in each of the two classes uniformly. It makes a finite step for vanishing c and behaves like $|\tau|^{-1}$ for nonvanishing c .

This uniformity only can be expected in the mean field framework which therefore is advantageous for the comparison of the

different systems. We have to expect that a more detailed description of the internal correlations would bring individual differences. We can also not exclude that the study of more systems already in the mean field description would lead to a more detailed division in classes of common critical behaviour of T_2 . Nevertheless, the here stated uniformity already is non-trivial if we look for the very different physical character of the variables listed in table I in one column. Even in another respect the behaviour of the systems is different. For the here considered nonequilibrium systems the leading singularity in the expression of eq. (4.5) arises from cross derivatives with $\mu \neq \nu$. In the two equilibrium systems, however, such cross terms are cancelled by corresponding terms in the term $\mu = \nu = 0$. Only this term and no cross term brings the singularity. It should be stressed that, in spite of these essential differences, the measure T_2 behaves in the mentioned uniform way.

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Verfasser

Prof. F. Schlögl
RWTH Aachen

BRD - 5100 Aachen
Templergraben 55

New Aspects of Instabilities and Chaos in Laser Systems

G. WALLIS

Introduction

The phenomena to be described occur in nearly all types of laser systems, though with large differences in pump intensity: in single-mode and multi-mode lasers, in lasers with homogeneously or inhomogeneously broadened lines, in lasers with or without external drive or feedback, in lasers with and without saturable absorbers. As in all other dynamic system with similar instability behaviour, the observed effects are results of internal selforganization, possibly by interplay with an external triggering. They appear above a second threshold, the first one being the threshold between incoherent emission and stable laser activity. The main characteristics are gradually enhanced: selfpulsing of the laser output under constant laser conditions regular at first, then irregular and chaotic with growing intensity, or bistability going to multistability, hysteresis included, frequency pulling and locking, phase locking also. What we can expect in the phenomena above it, therefore comprehends the whole arsenal of chaos theory applied to all instable dynamic systems with determined asymptotics: Poincaré mappings and their picturesque clouds of points (sometimes of spiral structure in the laser case), interval mappings or area mappings (sometimes specific circle maps or mappings of the complex plane), strange attractors (fractals), the rippled curves of Ljapunov exponents, and the large amount of bifurcation diagrams (comp. the excellent overview of Leven and the other instructive topical lectures of this conference). Concerning the power spectrum it has been found out that it is useful to determine the routes to chaos (period doubling or subharmonics generation, appearance of incommensurable frequencies and so on) more than to characterize the state of chaos itself.

In the last time some new aspects have been added to this. On the one hand there is the use of homoclinic and heteroclinic orbits as well as homoclinic explosions and homoclinic bifurcations, in their relevance to changes from prechaotic to chaotic states or to changes between chaos types (spiral type to screw type e.g.). On the other hand we have the new method of attractor determination from time series. After years of intensive and sometimes expensive numerical work to grasp the multiplicity and plurality of chaos phenomena, some revival of analytical methods, further developed in the mean time, took place. Punctually the numerical results gave some hints where analytic methods promisingly could be applied. We will give some comments to this subject in the case of the real and complex Lorenz equations, playing some restricted but fundamental role for laser systems (Maxwell-Bloch equations).

Of most practical importance in the future probably will be the new concept of determining existence and dimension of fractal attractors from time series of direct experimental data, i.e. without knowledge of the underlaying dynamic equations describing the system. This shurely will be of great value for concrete, nonidealized laser systems, where the complete system of equations either is not really known or is to complicated even for long computing times of fast machines.

All these methods stem from classical systems. Concerning lasers we should finish with a short remark on classical and quantum chaos. Unfortunately nearly nothing can be said about applications of instabilities and chaos in laser systems.

A guide through the large field of literature on the standard aspects of instabilities and chaos in lasers, as mentioned above, may be learned from /1-3/ and especially from the topical issue of Josa B (Jan. 1984) /4/. This has the character of a compound status report, showing the strongly growing activities on basic dynamics under real experimental or even technical conditions of opto-electronics or all-optical devices. In /4/ also the work done in our group is represented, namely that of Brunner, Fischer and Paul on regular and chaotic behaviour

of multi-mode laser (p. 202) and that of Müller and Glas on bi-stability, regular self-pulsing, and chaos in lasers with external feedback (p. 184). On the other hand only minor overlapping analysis may be found there concerning types of basic equations and main orbit structures (as compared e.g. with the case of instabilities and chaos in chemical systems /5/), leading to possible classifications of laser systems and phenomena concerning chaos structures, answering by this the question of the usefulness of such an analysis. Comparable efforts may be seen in the investigations of the Navier-Stokes equations with different degree of truncation (multi-mode approximation).

From a mathematical point of view the main difficulties and surprising phenomena are drawn from the fact, that not only the local behaviour of systems of nonlinear (NL) ODEs has to be described, difficult enough, but that to a large extent the global character of their solutions has to be determined. Books like that of Andronov, Vitt and Khaiken /6/, of Arnold /7/ and of Guckenheimer and Holmes /8/ therefore should be recommended to add some knowledge of the newly developed body of analytical methods, at least for 2D and 3D problems, to that of numerical and experimental results. To the main problem of predict the global behaviour from local ones we will come back in chapter 2 for a special case at least.

1. The Basic Equations for Laser Instabilities and the Lorenz/Maxwell-Bloch Systems

In the simplest case the basic quantities are the field strength E , the polarization P and the inversion D . For single-mode operation of a resonant, homogeneously broadened laser ($\partial E / \partial z = 0$ in the Maxwell-Bloch system) we have the Haken version /9/ of that system ($E \sim q_1$, $P \sim q_2$, $D \sim q_3$):

$$\begin{aligned} \dot{q}_1 &= -d q_1 & | & + q_2 \\ \dot{q}_2 &= -\beta q_2 & | & + q_1 q_3 \\ \dot{q}_3 &= d_0 - q_3 & | & - q_1 q_2 \end{aligned} \quad (1)$$

showing, more directly than in the Lorenz version, the existence of two conserved quantities if the coupling terms (pumping

and damping) on the left of the broken line are neglected:

$$q_1^2 + q_2^2 + q_3^2 = R^2 = \text{energy} \quad (\text{sphere})$$

$$q_2^2 + (q_3 - 1)^2 = S^2 = \text{pseudo-spin} \quad (\text{shifted cylinder})$$

$$q_3' = q_3 - 1 \quad (2)$$

In this case of coherent interaction of atoms and field the solution is determined by the cross sections of the sphere and the cylinder (two separated trajectories for $R > 1 + S$, one closed trajectory for $R < 1 + S$). Switching on the terms on the left of the broken line, we get a "breathing" of both the sphere and the cylinder, giving rise to the more complicated behaviour possible for the solutions of the Lorenz equation, which is equivalent to (1) setting $X = bq_1$, $Y = (b^2/5)q_2$, $Z = r -$

$$(b^2/5)q_3', \quad d = 5/b, \quad \beta = 1/b, \quad d'_0 = r5/b^2 = rd\beta, \quad t' = \beta t:$$

$$\begin{aligned} \dot{X} &= -5X + 5Y \\ \dot{Y} &= rX - Y - XZ \\ \dot{Z} &= -bZ + XY \end{aligned} \quad (3)$$

This form more directly shows the basic symmetry $(X, Y, Z) \rightarrow (-X, -Y, Z)$, leading to the two fixed points besides $(0, 0, 0)$.

The first generalization includes amplitude and phase of E and D by choosing X and Y complex, also $r = r_1 + ir_2$ and $a = 1 - ie$, if dispersive effects are relevant too:

$$\left. \begin{aligned} \dot{X} &= -5X + 5Y \\ \dot{Y} &= rX - aY - XZ \\ \dot{Z} &= -bZr^{1/2}(X^*Y + XY^*) \end{aligned} \right\} \quad \dot{\underline{X}} = \underline{F}(\underline{X}; \underline{\mu}) \quad (4)$$

having the rotational symmetry

$$\underline{R}(\underline{d}) \underline{F}(\underline{X}, \underline{\mu}) = \underline{F}(\underline{R}(\underline{d})\underline{X}; \underline{\mu}) \quad (5)$$

with the rotation matrix $\underline{R}(\underline{d}) \cdot \underline{R}(\underline{\beta}) = \underline{R}(\underline{d} + \underline{\beta})$, replacing the non-zero fixed points of the real equation by a limit cycle (comp. /10, 11/).

From this one has the impression, that all the complicated bifurcation structure of the real Lorenz equation, as well as the its strange attractor, filling a book /12/ not even exhausting the whole richness of the phenomena in the full 3D space of

the parameters \bar{G} , r and b may be pronounced by the truncation of the rotational invariance of the complex Lorenz equation to the mirror symmetry on the real plane $(X, Y) \rightarrow (-X, -Y)$.

(4) gives a system of five real ODEs:

$$\begin{aligned} E &\rightarrow (x_1 + ix_2), \quad P \rightarrow (y_1 + iy_2), \quad D \rightarrow 1 + z \\ \dot{x}_1 &= -\bar{G}x_2 + \bar{G}y_1 \\ \dot{x}_2 &= -\bar{G}x_1 + \bar{G}y_2 \\ \dot{y}_1 &= rx_1 - y_1 - x_1z \\ \dot{y}_2 &= rx_2 - y_2 - x_2z \\ \dot{z} &= -bz + x_1y_1 + x_2y_2 \end{aligned} \quad (6)$$

This may be reduced again to three real ODEs, but different from the real Lorenz equation, if the adiabatic approximation for the polarization $y_1 = y_2 = 0$ is allowed ($y_1 = (r-z)x_1$, $y_2 = (r-z)x_2$):

$$\begin{aligned} \dot{x}_1 &= -\bar{G}(1-r+z)x_1 \\ \dot{x}_2 &= -\bar{G}(1-r+z)x_2 \\ \dot{z} &= -bz + (r-z)(x_1^2 + x_2^2) \end{aligned} \quad (7)$$

which may be reduced by $\xi = x_1^2 + x_2^2 \sim |E|^2 = I$ to

$$\begin{aligned} \dot{\xi} &= 2\bar{G}(r-1) - 2\bar{G}\xi z \\ \dot{z} &= r\xi - bz - \xi z \end{aligned} \quad (8)$$

This 2D system shows that, by adiabatic elimination of the polarization, chaos and irregularities are eliminated too. If they appear in this approximation they are originated by additional effects as external feedback or signal injection and so on.

There exists a large body of literature about the basic equations including such effects as inhomogeneous line broadening, detuning and triggering with the difference frequency to enhance the growth rate of instabilities and by this to lower the second threshold significantly, furthermore waves propagating in both directions of the optical system, influence of transversal modes and other effects mentioned in the introduction.

A comprehensive survey on the additional terms and equations, by which the Maxwell-Bloch system has to be generalized, may be drawn from the youngest survey found in /4/. In the case of inhomogeneously broadened gas lasers the basic equations have to be accomplished by integrals containing the velocity distribution of the atoms and the influence on the polarization and the population, transforming the ODEs to integral-differential equation. This shows that the question of numbers and types of basic equations for laser instabilities must be considered carefully in each experimental situation. On the other hand one can see that the procedure of attractor determination from time series as discussed in the next paragraph might be of some interest also for the interpretation of experimentally observed non-stable laser operation.

2. Attractor Determination from Time Series - Application to Laser Chaos

As in other dynamic systems there may arise also in active optical devices the case only known is the time series of one single system quantity (property) $x_0(t)$, mostly the laser output intensity (emitted radiation). What is proposed consists in the possibility to describe the evolution of the system behaviour in a k D phase space, i.e. by a system of ODEs, k in number. Not known is the connection between the measured $x_0(t)$ and the orbit $Y(t) = \{y_1(t) \dots y_k(t)\}$ in the phase space. What may be hoped, nevertheless, is to give some estimates for the asymptotic behaviour by determining the existence and dimension $d \leq k$ of an attractor. The procedure developed for this in /13-15,17/ works as follows: We go from t to $\{t_1 \dots t_N\}$ if $x_0(t)$ is measured continuously, or take the measured $x_0(t_1)$ directly. Then we choose some τ , incommensurable with $t_{1+j} - t_1$ in the continuous case or not, and put together the following samples:

$$\begin{array}{ccc} x_0(t_1) & \dots & x_0(t_N) \\ x_0(t_1+\tau) & \dots & x_0(t_N+\tau) \end{array} \quad (9)$$

$$\underbrace{x_0(t_1+(n-1)\tau)}_{\underline{X}_1^{(n)}} \dots \underbrace{x_0(t_N+(n-1)\tau)}_{\underline{X}_N^{(n)}}$$

and build the vectors $\underline{X}_i^{(n)}$ of them. They span a substitute nD phase space, possibly embedding the attractor. Again the connection between the $\underline{X}_1^{(n)}$ and $\underline{Y}(t_1)$ is not known. So we are in a situation which falls into the category of an attempt to say something interesting about chaotic systems with very incomplete information. What may be help in this case may be searched for in the field of correlation analysis. Taking a mesh width (cube length) r and looking for the number of points $\underline{X}_1^{(n)}$ falling into these cubes, we have with the step function Θ and the wellknown correlation function

$$C_n(r) = \frac{1}{N^2} \sum_{1 \neq j=1}^N \Theta(r - |\underline{X}_1^{(n)} - \underline{X}_j^{(n)}|) \quad (10)$$

depending, besides on N , also on n . The corresponding correlation dimension is then given by

$$d_n = \lim_{r \rightarrow 0} \lim_{N \rightarrow \infty} \frac{\log C_n(r)}{-\log r} \quad (11)$$

So we arrive at a n -series of dimensions $d_1, d_2 \dots d_n$ which may be compared with the sequence of dimensions in systems with a rescaling hierarchy of Mentschel and Procaccia /16/. If they converge to a certain finite value, this demonstrates the existence of an attractor determining the asymptotics of the system in contrast to the stochastic case. What are the generic conditions which must be fulfilled by the system in order the attractor dimension in this substitute phase space, drawn from the correlation within one time series, to be representative for that in the true phase space? The answer may be selected from the "Main Theorem" in Taken's fundamental paper /14/, which connects the limit capacity $D(L^+(p))$ of the limit set $L^+(p)$ of all measuring points p with the so-called cardinality

$C_{n,s}$, replacing the correlation integral $C_n(r)$ in (10). By this at least one method has been found to connect global properties of the solution of ODEs with local ones, i.e. by means of such quantities as correlation integrals or cardinality.

This method of attractor determination has been applied to the time series of the emission of a Xe-He-Laser on the $3,51 \mu\text{m}$ line (4 mA excitation current) /18/, consisting in 512 data points, taken by a Tektronix fast transient digitizer (10-bit resolution) within a period of about 250 nsec. A direct application of the procedure mentioned above results in Fig. 4b of /18/. An enlargement of the part $n = 1$ to $n = 10$ is given in Fig. 1 here. It shows that the transition to the final values $d_n \lesssim 3$ is very smooth and is finished only at $n^* \approx 7$. This may indicate that the dimension k of the original phase space may be also equal n^* , which could be realized with a complex Lorenz equation and two directions of propagation for the fields (7 real equations).

The points in our Fig. 1 show the results of a test case using a time series taken from a pure sin-fuction, checking the reliability of the limited number of only 500 points. Included are also the results of /17/ for the case of a random number time series (white noise), which has been proved in /18/ also. Concerning the "fractal" character of chaotic attractors and its connection with the Lyapunov dimension comp. also /19/.

3. Usefulness and Limitations of Analytic Methods for Describing Chaotic Behaviour in Laser Systems

The method of attractor determination from time series may be set on sound analytic grounds without limitations by the phase space dimension. From this its practical importance follows, since laser systems as other practical dynamic systems mostly have five dimensions or more. Concerning analytic methods to describe and determine topologic properties of orbits in higherdimensional phase spaces, the comparison of the book of Andronov, Vitt and Khaiken /6/ from 1966, morely devoted to planar flows, with that of Guckenheimer and Holmes /8/ from 1983 clearly shows, what efforts have been necessary to extend

the previous work by one dimension only: an uncountable set of new phenomena may occur in 3D phase space compared with planar nonlinear oscillations. The final chapter of /8/ only gives some hints on fourdimensional flows and then immediately shifts to "large systems" with an infinite number of degrees of freedom, as may be derived from partial differential equations (PDEs), using a suitable version of the center manifold theorem.

So, concerning dynamic systems in 5D or 7D phase spaces we are left with

- (i) numerical and experimental results for special parameter combinations, and
- (ii) some (unreliable) hints from 2D and 3D analysis.

This concerns the classification of planar nonwandering limit sets and their structural stability as well as the structural stability of attractors for the 2D case. The three classes of planar nonwandering limit sets are /6/: (i) fixed points, (ii) closed orbits, and (iii) unions of fixed points and trajectories connecting them. Peixoto's theorem /8/ restricts structural stable planar flows to the case of (i) a finite number of hyperbolic fixed points and closed orbits, (ii) no orbits connecting saddle-points, and (iii) only fixed points and periodic orbits, which leads to the Morse-Smale system, if, in addition, all stable and unstable manifolds intersect transversally.

The corresponding statements for the 3D case are not so concrete. The very new phenomena in that case are due to the appearance of strange attractors, i.e. of invariant limit sets (attractors) which contain a transversal homoclinic orbit. The condition for 3D homoclinic orbits (connecting a singular point with itself for $t \rightarrow \pm \infty$) is governed by Silnikov's theorem. Similar results for the nD case with $n > 3$ seem, up to now, not available.

Concerning the concrete case of the Lorenz/Maxwell-Bloch system in addition to /12/ the analytic approximation of its fractal attractor by invariant manifolds /20/, the investigation of its analytic structure /21/ and other /22-26/ should be mentioned. Extremely useful will be the analysis of the bifurcation scheme

of the semiclassical equations describing a ring laser /23/.

Conclusion

Looking back to our introduction we will try to connect the phenomena described here with those at other physical systems (comp. /27/ e.g.). Since the Maxwell-Bloch system contains, in another approximation, also the Sine-Gordon equation, there arises the question concerning the interplay between solitons and chaos in NL optical systems /28-30/. Arecchi /31/ relates chaos and a generalized concept of multistability in quantum optics. The connection of chaos and multiple photon absorption /32/ is a special optical case of the general problem of quantum chaos. We only give a (surely incomplete) list of papers /33-52/ and add an elementary remark.

The main question concerns the chance that classical chaos survives in quantum systems, i.e. what are the special properties of quantum systems whose classical limits exhibit deterministic chaos. In other words: What limitations give the uncertainty relations to the Cantor set property of fractal attractors? The answer may be found in handling the auto-correlation in time of the wave function (since in quantum systems one cannot use the concept of trajectory) and the approach of the frequency spectrum to a continuum /51/. A quantitative answer may come from a method using the random walk test.

The limitation of the rotating-wave approximation by chaotic behaviour is discussed in /53/.

Quantum fluctuations about the Lorenz attractor and the use of Wigner distributions of the quantized Lorenz model have been investigated in /54/ and /55/ (comp. also /56/).

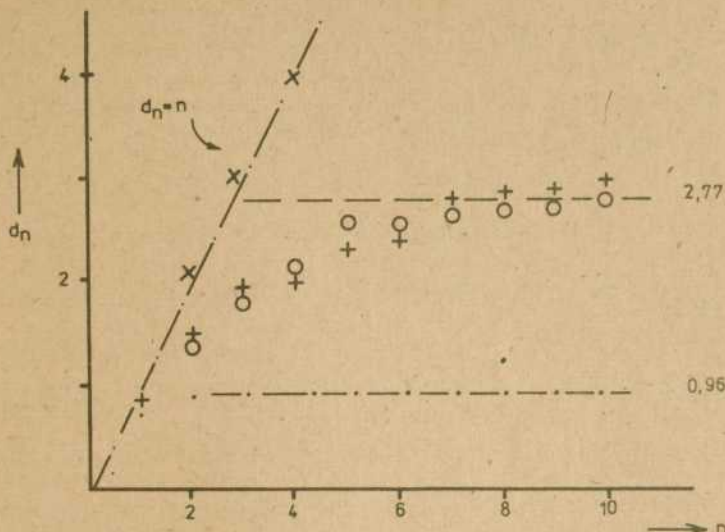


Fig.1 Determination of attractor dimension d_n as function of embedding dimension n

- + } inhomogeneously broadened single-mode gas laser
- o } (Xe-He at 3,51 μm) /18/
- test case of sinusoidal time series (2 MHz)
- x white noise /17/

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Verfasser:

Prof. G. Wallis
Akademie der Wissenschaften der DDR
Zentralinstitut für Optik und
Spektroskopie

DDR - 1199 Berlin-Adlershof
Hudower Chaussee 6

The Kinetics of Ostwald Ripening as a Competitive Growth in a Selforganizing System

R. MAHNKE and R. FEISTEL

It is shown that the kinetics of an ensemble of coarsening particles of different sizes is a competition process, which is quite similar to the selection in biological or ecological systems. A comparison to the theory of selforganization is given.

1. Introduction

In general, the time evolution of any first-order phase transformation process can be divided into three regimes. In the first stage, called nucleation, the new phase α is formed out of the metastable mother phase β . A large number of small droplets (nuclei with a restricted distribution of sizes) will be created. After this formation stage the nuclei grow rapidly at the expense of the surrounding phase β . At the end of this very fast growth process the two phase mixture has reached internal quasi-equilibrium. In the following late stage, called coarsening or Ostwald ripening (see for a recent review /1/), the new phase α evolves in such a way, that larger droplets grow at the expense of smaller ones, which disappear. The situation in this long-time regime is very close to the description of selforganization under constrained conditions.

Treating a finite ensemble of coarsening droplets we are able to give fully time-dependent numerical solutions of the equations describing the second (growth) and third (ripening) stage of phase transformations.

Our evolutionary model (fig.1) is based on the following conditions. Considering spherical droplets we introduce a droplet size distribution function $N(n,t)$ where n is the number of monomers (atoms) bounded within the droplet. We choose the size n

as relevant variable, but equivalent descriptions are possible (e.g. droplet radius $r = (c_d 4\pi/3)^{-1/3} n^{1/3}$). In contrast to the bounded states of the d phase the surrounding β phase consists of free monomers only. The time dependent monomer density $c_\beta(t) = M_\beta(t)/V_\beta$ may change by condensation or evaporation of atoms. We neglect spatial correlations and use the incompressibility condition $c_d = \text{const.}$

2. Basic Equations of Coarsening

The theory of Ostwald ripening in a closed system deals with the following three general assumptions (compare [2]).

(a) Continuity equation

$$\frac{\partial N(n,t)}{\partial t} + \frac{\partial}{\partial n} (\psi N(n,t)) = 0 \quad (1)$$

On the right hand side of (1) we neglect spontaneous nucleation or coagulation phenomena (no production term). In this case the total number of droplets is fixed.

(b) Conservation of monomers

$$\int_0^\infty n N(n,t) dn + M_\beta(t) = M_{\text{total}} = \text{const} \quad (2)$$

In a finite system we have a limited number of monomers which either free particles in the β phase or bounded in drops of the d phase. In a supersaturated situation we will find a flux of monomers from the matrix (β phase) into the droplets phase.

(c) Growth law

$$\frac{dn}{dt} = \psi(n, c_\beta(t)) \quad (3)$$

The velocity of a growing or dissolving droplet embodies much of the physics of the ripening problem and must be carefully constructed. Assuming that an individual drop grows (or dissolves) if the monomer concentration is greater (or less) than the equilibrium concentration we use the reaction limited growth rate according to the Fickian diffusion law

$$\psi_{rl}(n, c_\beta(t)) = D l_0^{-1} A(n) (c_\beta(t) - c_{eq}(n)) \quad (3.1)$$

where $A(n)$ is the surface of a size- n -droplet, $l_0 = 2\gamma/c_d kT$ a constant length (capillarity length) and D the diffusion

coefficient.

The equilibrium monomer concentration $c_{eq}(n)$ over a curved surface with curvature $k(n) = 1/r$ reads

$$c_{eq}(n) = c_{eq}(\infty) \exp(l_0 k(n)) \approx c_{eq}(\infty) (1 + l_0 k(n)) \quad (3.2)$$

This curvature dependent expression is the well known Gibbs-Thomson equation indicating that atoms will flow from regions of high to low curvature.

The solution of the coupled nonlinear differential equations (1)-(3) seems to be impossible. However, if the droplet ensemble consists of s kinds of drops with different sizes n_1, \dots, n_s only, let us consider this discrete case. Using the ansatz

$$N(n, t) = \sum_{i=1}^s N_i \delta(n - n_i(t)) \quad (4)$$

and inserting in the Liouville equation (1) we get

$$\frac{dn_i(t)}{dt} = \mathcal{V}_{r1}(n_1, \dots, n_s, c_\beta(t)) \quad (i=1, \dots, s) \quad (5)$$

Due to the conservation of matter (2) the system of kinetic equations (5) becomes nonlinear. In the case of reaction limited growth (3.1) together with the linearized version (3.2) our exact basic equations governing the constrained growth of precipitates with $s \geq 1$ components read

$$\frac{dn_i}{dt} = \frac{D}{l_0} A(n_i) \left\{ c_{eq}(\infty) l_0 (\langle k \rangle - k(n_i)) + \frac{l_0}{D} \frac{\Phi(t)}{A_d(t)} \right\} \quad (6.1)$$

($i = 1, \dots, s$)

with

$$\Phi(t) = \frac{D}{l_0} A_d(t) \left\{ \frac{M_{total}}{V_\beta} - \frac{c_d V_d(t)}{V_\beta} - c_{eq}(\infty) - c_{eq}(\infty) l_0 \langle k \rangle \right\} \quad (6.2)$$

This is a system of first-order differential equations with the abbreviations

$$A(n_1) = 4\pi (c_d 4\pi/3)^{-2/3} n_1^{2/3}$$

surface of a droplet with n_1 atoms

$$k(n_1) = (c_d 4\pi/3)^{1/3} n_1^{1/3}$$

curvature of a droplet with n_1 atoms

$$\langle k \rangle = \frac{\sum k(n_1) N_1 A(n_1)}{\sum N_1 A(n_1)}$$

mean curvature of the whole droplet ensemble

$$A_d(t) = \sum_{i=1}^{\infty} N_i A(n_i)$$

total surface of phase d

$$V_d(t) = c_d^{-1} \sum_{i=1}^{\infty} N_i n_i$$

total volume of phase d (volume of all drops)

and coefficients D (diffusion constant), c_d (density of bounded monomers), $c_{eq}(\infty)$ (equilibrium concentration of free monomers over a flat interface), V_β (volume of the system), M_{total} (total number of monomers) and l_0 (capillarity length, typical values in nanometers). It describes the rapid growth (second term on r.h.s. of (6.1)) and the slow selection process (first term on r.h.s. of (6.1)). The flow $\Phi(t)/A_d(t)$ (6.2) is the flux density of raw material into the ensemble of drops. If the supersaturation is high enough (that means $\Phi(t) \gg 0$) all clusters have the chance to grow up ($\dot{n}_1 > 0$). Since the raw material is limited the two phase system will reach at first a so called internal equilibrium, a nonstationary situation where the d -phase as a whole global system (meanfield description) is in a quasi-equilibrium with its surrounding β -phase. When the flow between the two phases $\Phi(t)$ is decreasing to zero, a competitive ripening process takes place. In this selection game the smaller clusters with $k(n_1) > \langle k \rangle$ must dissolve to give monomers to the bigger ones which increase. Since the mean curvature $\langle k \rangle(t)$ is a slowly decreasing function of time in the limit $t \rightarrow \infty$ only one component in the droplet phase is present and the selforganizing system has reached its stable stationary situation.

For the set of parameters $D = 10^4 \text{ nm}^2/\text{ns}$, $c_d = 10^2 \text{ monomers/nm}^3$, $V_\beta = 10^6 \text{ nm}^3$, $l_0 = 0,35 \text{ nm}$, $c_{eq}(\infty) = 10^{-4} \text{ monomers/nm}^3$, $M_{total} = 2500 \text{ monomers}$ results obtained from the analysis of (6) are shown in fig.2 and 3. After about one nanosecond the growing system has reached internal equilibrium and in the following long-time regime of selection the dynamic system will approach the stable fixed point.

3. Conclusions

It is obvious that our resulting basic equations (6) are a realistic physically motivated example for natural selforganization. As was pointed out by Eigen /3/ and others /4/ that Darwinian evolution can be characterized by an extremum principle, which defines the behaviour of selfreplicative units. Under stated selection constraints in bio- or ecosystems (compare the constant overall organization (2)) the population numbers of all but one species will disappear. In the Fisher-Eigen model of prebiotical evolution

$$\frac{dx_1}{dt} = (E_1 - \langle E \rangle)x_1 \quad \text{with} \quad \sum_{i=1}^s x_i = C \quad (7)$$

the species with the highest reproduction rate $E_m = \text{Max} \{E_1, \dots, E_s\}$ (selection value) will increase to the finite value C and all others must die out ($x_i \rightarrow 0$ for $i \neq m$). Note that in both cases (Fisher-Eigen model with population 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 only by an overall dilution flux which corresponds to the mean-field concept of many body physics /5/. As we demonstrated, there is an interesting analogy in modeling phase transitions on the one hand and evolution processes in biophysics on the other. Directions for future work /6/ are investigations with special potential like elastic fields to determine the coarsening behaviour of solid-solid phase transformations.

Figure Captions

- Fig.1 Evolutionary model of phase transition between a metastable mother phase β (freemonomers) and the coarsening phase d (spherical drops of different sizes)
- Fig.2 Reaction limited growth and competition of a droplet ensemble of two components ($s=2$)
- a) Time dependence of droplet sizes n_1 and n_2
 - b) Trajectory in phase space showing the symmetry breaking between growth and ripening regime

Fig.3 Time evolution of an droplet ensemble showing the monomer distribution function $M(n,t) = n N(n,t)$. Numerical solution of eq. (6) with $s=6$ groups of drops.

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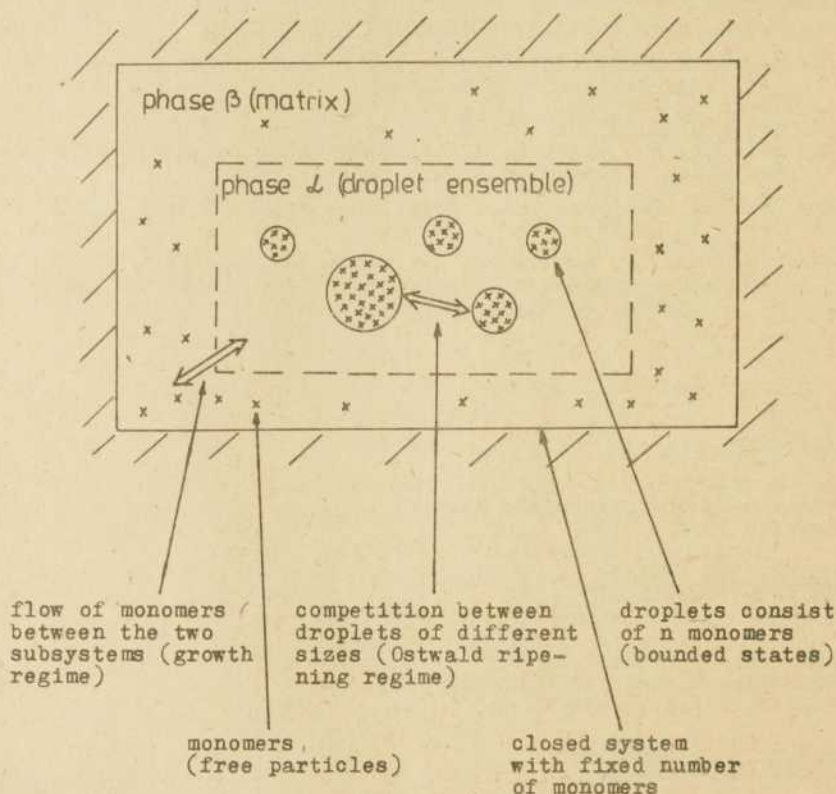
Dr. R. Mahnke
Wilhelm-Pieck-Universität Rostock
Sektion Physik

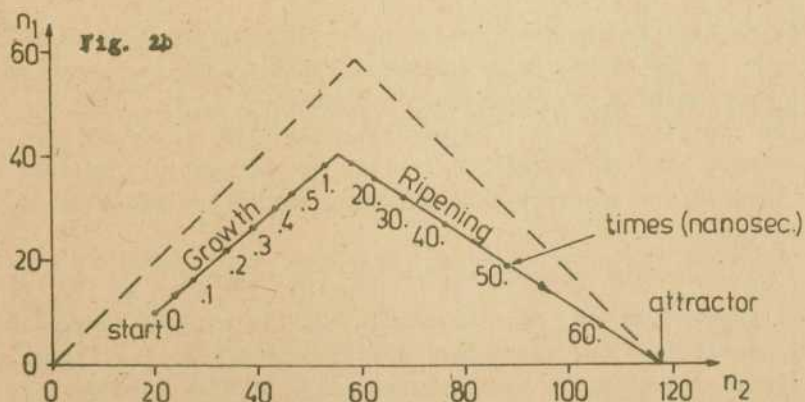
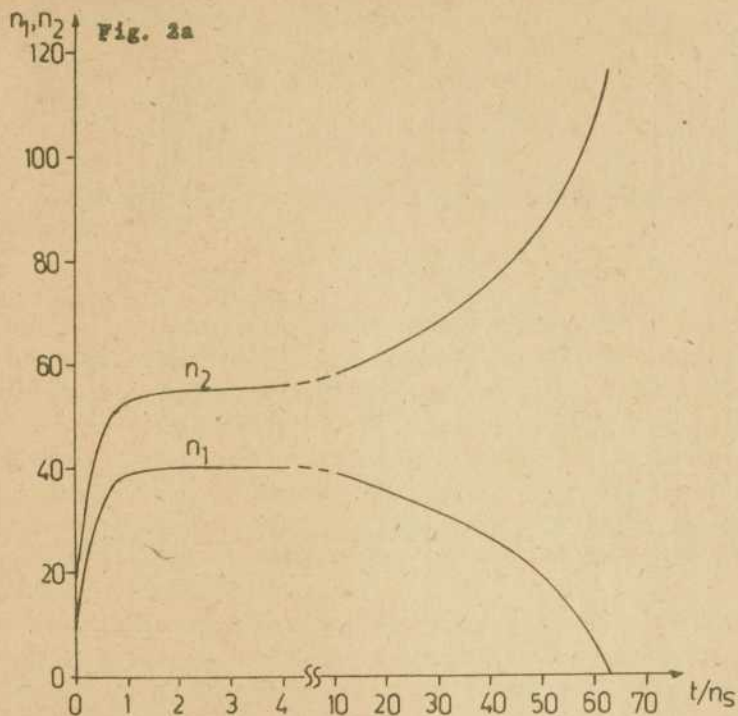
DDR - 2500 Rostock
Universitätsplatz 3

Doz. Dr. R. Feistel
Humboldt-Universität zu Berlin
Sektion Physik, Bereich 04

DDR - 1040 Berlin
Invalidenstraße 42

Fig. 1





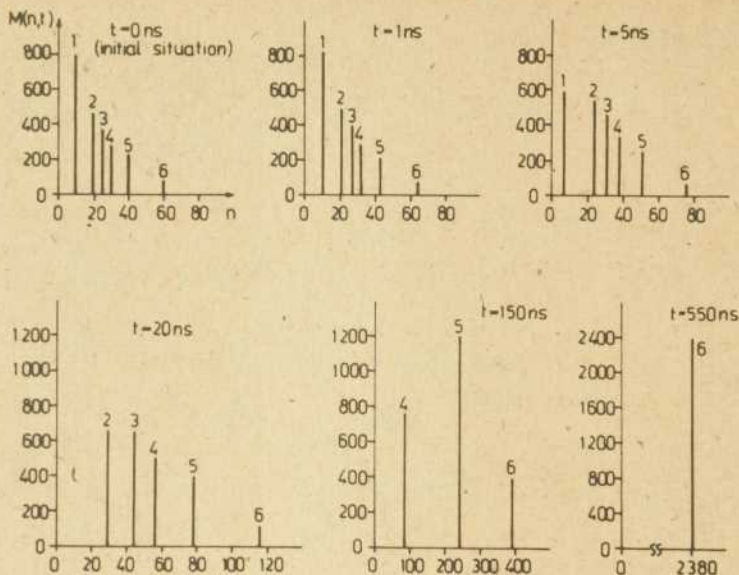


Fig. 3

Appendix

Here we want to show the relationship between the traditional growth law in the interface kinetic limited case (eq. 3.1) and the corresponding thermodynamic potential.

If we consider the limit of sufficiently slow interface kinetics such that the growth is limited by the reaction process to incorporate monomers into the particle we use the time dependence (3.1, 3.2)

$$\dot{n} = (D/l_0)A(n)(c_p(t) - c_{eq}(\infty) - c_{eq}(\infty)l_0k(n)) \quad (A1)$$

This growth law (A1) and the similar diffusion limited growth law result from the stationary solution of a reaction-diffusion field around a single spherical particle of size n subject to the boundary condition (3.2) at the surface and the concentration c_p at large distances from the centre. Introducing the

critical droplet size n_c by

$$n_c(t) = (c_d 4\pi/3) (1_0/y(t))^3 \quad (A2)$$

with the supersaturation

$$y(t) = (c_\beta(t) - c_{eq}(\infty))/c_{eq}(\infty) \quad (A3)$$

we reformulate (A1) without any further approximations in the following form

$$\dot{n} = D c_{eq}(\infty) (c_d 4\pi/3)^{1/3} A(n) \left(\frac{1}{n_c^{1/3}} - \frac{1}{n^{1/3}} \right) \quad (A4)$$

From (A4) it is apparent, that droplets with $n < n_c$ shrink and those with sizes $n > n_c$ will grow. The stability analysis shows that the stationary state $n = n_c$ is unstable and we find a typical bistability situation with opposite behaviour of drops below and above the critical value n_c . We want to mention that due to the conservation of monomers (eq. 2) the critical droplet size is changing in time and it is sometimes convenient to measure the droplet size in units of the critical value n_c by a dimensionless variable $x(t) = n/n_c$.

Now we want to construct the thermodynamic potential G corresponding to the driving force n . Taking into account the traditional connection between force and potential by the gradient we use the ansatz

$$\dot{n} \sim A(n) \cdot \left(- \frac{\partial G}{\partial n} \right) \quad (A5)$$

and calculate G inserting (A4) in (A5). The result can be summarized in the following relationship between kinetics and thermodynamics

$$\dot{n} = - \frac{D c_{eq}(\infty)}{kT l_0} A(n) \frac{\partial G}{\partial n} \quad (A6)$$

with the potential (free enthalpy; up to an arbitrary constant)

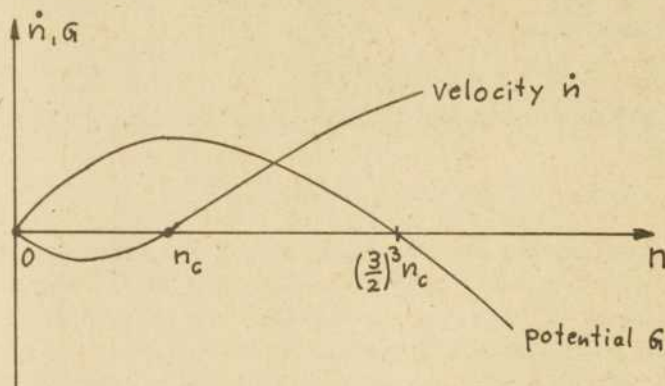
$$G(n, c_\beta(t)) = - \mu n + G A(n) \quad (A7)$$

and the chemical potential

$$\mu = kT \ln \frac{c_\beta(t)}{c_{eq}(\infty)} \approx kT \frac{c_\beta(t) - c_{eq}(\infty)}{c_{eq}(\infty)} \quad (A8)$$

In the figure the driving force \dot{n} and the potential G are shown over size n for a fixed situation of the β -phase.

Fig.: Driving force \dot{n} and corresponding potential G vs cluster size n



In conclusion we suggest instead of the special growth law (3.1, 3.2) a more general formula

$$v_a(n, c_\beta(t)) = \frac{D}{l_0^{a+1}} \frac{A(n)}{k(n)^a} (c_\beta(t) - c_{eq}(n)) \quad (A9)$$

The parameter a can be positive, zero or negative and gives for special values the well known examples. The growth laws used in the literature are the diffusion limited case ($a = -1$) and the interface kinetic limited case ($a = 0$). It may be interesting to take into account also the choice $a = 1$.

On the Macrodynamics of Evolution: The Synchronous Hyperbolic Increase of Specific Dissipation and Information-Capacity - A Quantitative Empirical Study of the Phylogenesis from Bacteria to the Highly Technologized Man

G. GEBHARDT

1. Basic - Assumptions Based on the Physically Founded Theory of Selforganization

1.1. Approach

Since there is no hope of achieving solutions of a multidimensional system of non-linear, partial and stochastic differential equations that could describe the spatial-temporal development $q(r,t)$ of qualitative changes of living organisms in a reductionistic way the principle - well tested in synergetics - of modelling the development of complex systems with the help of (mostly highly aggregated) order-parameters $u(t)$ /10/ was used:

Usually it is assumed that evolution-processes \bar{q} are initiated at time t_0 by fluctuations (example: mutations on the molecular-genetic level versus variations of the state of environment) caused by (small) spatio-temporal symmetry breaking perturbations \bar{q}'_0 from a locally homogenous and temporary stable stationary initial-state \bar{q}_0 :

$$\bar{q}(t) = \bar{q}_0 + \bar{q}'(t_0) \quad (1)$$

After that an order-parameter $u(t)$ that has to be identified governs the subsequent development, e.g. according to

$$\bar{q}(t) = u(t) \bar{q}'(t_0) \quad (2)$$

It is possible to distinguish fluctuations firstly as to whether they transform in the order-parameter equation

$$d u(t) / dt = \lambda u(t) \quad (3)$$

some eigenvalues (or more generally Ljapunov-exponents /10/ λ_1 from $\lambda_1 < 0$ (\bar{q}_0 remains stable - homeostasis) into $\lambda_1 \geq 0$.

Such dynamic states with λ_{1+} (i.e. a selfamplification of \bar{q}' (t_0)) determine the further irreversible evolution of the system according to the slaving-principle /10/ as a self-motion directed away from the initial state (homeorhesis) because of (2) and (3) as

$$\bar{q}'(t) = \exp(\lambda_{1+}t) \cdot \bar{q}'(t_0) \quad (4)$$

Secondly, fluctuations will cause innovations in a dissipative structure if they increase an (external) control parameter d to some discrete critical values d' . d stands for the pumping power of entropy-export out of the evolving system, i.e. its distance from thermodynamic equilibrium.

Obviously in this case qualitatively new dynamic states materialize as suggested by the behaviour of iterative ($n \rightarrow n+1$) solutions of different model equations of the non-linear (N) kind $q_{n+1} = N(q_n, d)$.

Mostly with increasing d -values the solutions will pass through bifurcation-cascades /8,27/ with the following stations: mono-stable fixed-points \rightarrow multiple steady states \rightarrow limit cycles \rightarrow tori \rightarrow strange attractors \rightarrow deterministic chaos /26/. Generally, during the process mentioned, the number Σ of distinctive dynamic states that $\bar{q}'(t)$ can assume is increasing from Σ_{initial} (at d_{initial}) to Σ_{final} (at d_{final}).

Such bifurcations are well known from phylogenesis.

If homeorhesis is accompanied by bifurcations along with an increase of the diversity of states during the evolution of the system the term heterorhesis should be used. This term implies the endogenous continuously progressing change as essence of the evolution of matter.

As the distance of $\bar{q}(t)$ from the initial state \bar{q}_0 (see eq.(1)) need not be restricted to small deviations the order-parameter equation (3) should generally contain non-linear terms with respect to u . Therefore, we have to use the ansatz

$$d u(t)/dt = c u(t)^k \quad (5)$$

with $k \geq 1$ as evolution-exponent for phenomenological investigations of the dynamics of real order-parameters according to

Mende's hypothesis for structure-building evolution processes /23/.

At least the following two fundamental evolution-indicators have to depend functionally on the unidentified order-parameter $u(t)$ or can be identically with it because both - in the same way as $u(t)$ - are primarily dependent on the external control-parameter d .

1.2. Two Highly-Aggregated and Empirically Ascertainable Measures of Evolution: Specific Dissipation, Information-Capacity

It is firstly suggested by the theory of non-equilibrium thermodynamics and of dissipative structures /24,13,5,1,Poppel/ also as by generalized reflections /17,18,21,16,25/ that the mass-specific dissipation Ψ as a measure of the distance from thermodynamic equilibrium should increase at innovative leaps during heterorhesis. When Ψ is increasing it can be expected to be amplified resulting from the "evolutionary feed-back" /24/ because the exogenous fluctuations are acting more intensively on the system over the newly developed channels of metabolic interactions with environment /19/, cf. the lower cycle of the scheme in chapter 1.3.

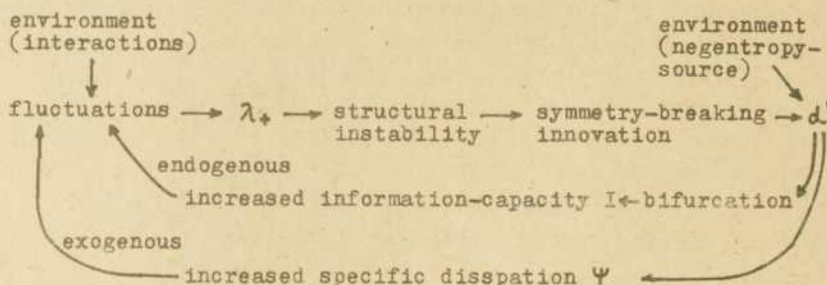
Secondly the information-capacity I /5/ measuring the dynamic diversity Σ of the states q_1 of an evolving system as

$$I = \log_2(\Sigma_{\text{final}} / \Sigma_{\text{initial}}) \text{ in bit} \quad (6)$$

is a further measure of the heterorhesis-progression /20/, although it does not state anything about the correlations between the states, i.e. complexity, which again can be regarded as the degree of order (Gatlin).

Various model investigations suggest the hypothesis that the probability of endogenous generation of fluctuations increases when the diversity Σ is growing (cf. the inner cycle of the following scheme).

1.3. Hypothesis of an Evolutionary Hypercycle Generating Heterorhesis



According to this reaction-scheme suggested by the physically founded theory of self-organization you can expect a feed-back being stronger than simple autocatalytic along with a dynamics of the two indicators proceeding more rapidly than exponentially ($k > 1$ in eq.(5)) /6/ provided the model helps to reflect the actual evolutionary innovative processes correctly. That hypotheses will have to be put to the test on the following section.

2. Results of the Empirical Analyses of Macroevolutionary Dynamics

In the case of the analysis of the biotic evolution experimentally obtained values (calorimetry, gasexchange intensity, mostly from Lamprecht and Zotin /15/) of the specific power of the basal-metabolism - that is identical with the specific dissipation Ψ_{1g} - a after completing the growth stage at steady state - of animal organisms representing different phylogenetic stages of evolution were coordinated to its time of origin t in the course of phylogenetic development. Such relevant time-dates have been made available by paleontology, e.g. /7/; see fig.1.

In the same way values of information-capacity I as the sum of genetic, neural and brain - fixed information-capacities (starting with data from /5/ that were considerably extended after /14,12 et al./ were coordinated with the respective times of the phylogenetic origin t of the organisms (see fig.2).

The same method was applied also to such basic empirical indicators of the evolution of society which make it possible to measure qualitatively different stages of development in a quantitatively commensurable manner.

For the main developmental stages like hominids, hunters and gatherers, neolithic agriculture, antiquity with emerging urbanization, medieval modes of production, energy balances were evaluated in retrospect /4/ and from the beginning of capitalism up to the present time exact statistics concerning energy consumption and population - demographic trends have been available /28/ for calculating $\Psi(t)$, cf. fig.3 and notes 5) and 6) in table.1.

The social information-capacity has been measured indirectly (cf. fig.4 and note 8) on table 1).

The data-sets $\{\Psi, t_1\}$ and $\{I_1, t_1\}$ have been fitted with the well known growth-functions (least square deviations). The approximations were evaluated by correlation-coefficients r .

Exponential functions ($k = 1$ in eq.(5)), e.g., have to be rejected whereas hyperbolic approximations provided highly significant correlations ($r > 0,97$) at the probability of error being below 1%.

The best approximating hyperbola has been computed by iterative variations of the unknown singularity-time t_∞ in the logarithmized hyperbolic solution of eq.(5) (see note on fig.1) with the following selection of that solution which provides a maximal r /9/.

All possible combinations of the single points (see figures) extremely perturbed within their confidence intervals caused maximal differences of computed evolution-exponents of $\Delta k/k \leq \pm 0,08$. While k seems to be an evolutionary invariant t_∞ depends very sensitively on stochastic variations of single points and hence it does not represent the essence of evolutionary macrodynamics.

The main results are summarized in the following table and commented on in additional notes. Further parameters are noted in the figures.

Table 1: Results of analysis

| Stage | time-interval documented by data in years | | parameters of best approximation acc. to eq.(5) | | | indicator of in- formation-capacity | | |
|---------------------|---|--------------------|--|-------|-----------|--|-------|----------|
| | from | to | indicator of specific dissipation $k_W(t)$ | r | fig. note | $k_I(t)$ | r | fig,note |
| biotic evolution | -3,8·10 ⁹ | -1.10 ⁴ | 1,34 | 0,974 | 1 1)3)4) | 1,28 | 0,989 | 2 2)3) |
| social evolution | -2·10 ⁶ | 1980 | 3,42 | 0,979 | 3 5)6)7) | 3,39 | 0,988 | 4 6)8) |

Notes on table 1:

1) The following allometrically determined relations are valid:
The overall metabolic power of an organism is identical with its
overall dissipation at steady state $\Psi(m,a) = a \cdot m^c$.

Mass-specific, dissipated metabolic power $\psi(m,a) = a \cdot m^{c-1}$.

Significance of the first term (a): intensive parameter of meta-
bolic activity, species-specific, depending as $a(t)$ on the phy-
logenetic developmental stage. Significance of the second term:
extensive influence. Mass exponent c is determined geometrical-
ly by surface-volume-relationship. Estimated experimentally at
 $c = 0,75$ (Kleiber's rule). Comparisons between phylogenetically
different species are significative only if influence of differ-
ent mass is eliminated as

$$\psi_{1g} = \psi(m, a(t)) \quad m=1g = a(t) = \Psi m^{-c}, \quad m \text{ in } g.$$

2) Indicators for $I(t)$: genetically - number of DNA-pairs of
nucleatides per cell, cerebrally - brain-volume.

3) In spite of the nearly synchronous run of $\psi_{1g}(t)$ and $I(t)$
as dynamic frame encompassing macroevolutionary step-like qua-
litative leaps (Goldschmidt, Simpson, Waddington, Gould,
Maynard Smith, Stanley, Riedl) the equivalent of information-ca-
pacity and energy dissipation $\beta = I(t) / \psi_{1g}(t)$ has been found to
be the function of the level of phylogenetic development and
therefore of evolutionary time: $\beta = \beta(t)$. β grows from 10^{11} bit/
 Wg^{-1} at the beginning of biogenesis to $2,25 \dots 5,71 \cdot 10^{14}$ bit/
 Wg^{-1} during anthropogenesis, following a hyperbolic function
with $k=1,84$.

4) Since about 10^8 years, at stage of primates, $\psi_{1g}(t)$ is levelling off to the steady state according to hyper-logistic evolution-dynamics /23/. Assumed reasons: ecological donator-limitation. The growth of the activity of intrasomatic dissipation during phylogenesis makes it necessary to increase the anatomic and physiologic complexity and hence the number of different structural elements. Phylogenetic development is in fact correlated with an increasing body-weight from 10^{-16} g to 10^{+6} g. Such a tendency needs a simultaneously increasing intake of food and the rate of captured prey, respectively. That means an increasing donator-area per organism because of the limited evolutionary source-intensity of photosynthesis caused by astrophysically determined, constant entropy-export from the earth's surface.

If the intrasomatic strategy of metabolism had been the only strategy by further evolutionary stages the sustainable population-density would have had to decline. Consequently inter-individual interactions as precondition for reaching the next higher level of organization (sociogenesis) would have been rendered more difficult.

Only after the fundamental structural innovations, the extrasomatic organization of metabolism (erected carriage, use of hands, tools and fire, social division of labour etc.) and of cognition (speech, anticipative intellect, social transfer of experiences, writing, book-printing, computers etc.) had occurred about two million years ago, the above-mentioned stagnation was overcome.

5) Measured as primary-energy consumed per capita. It is assumed that the required free energy dissipation for sustaining the productive and consumptive functions of a society (i.e. its metabolism), related to the number of its members, is an indicator analogous to the specific biotic dissipation ψ_{1g} , which could have been related in the same way to the number of cells as molar measure. Argument: the evolutionary stages of purpose performing work using the ability of cognition, i.e. the successive modes and techniques of production, are undoubtedly characterized by the simultaneously increasing inflow of free-energy

by harnessing natural powers (antropogenic entropy-export!). This tapped energy-potential is converted into different kinds of purposefully channelled final-energy by the use of appropriate technologies suitable to amplify progressively stronger the intelligently invested trigger- or control-energy, respectively /17,22,21/.

6) That evolution-indicator is given for the upper envelope curve, which is defined by those national economies having reached the highest level of specific power input at a certain time. In fig.3 the results of study for different important nations are given: The later an industrialization started the higher the evolution-exponent k obtained in the investigation (e.g. Japan and socialist countries: $k > 4$).

7) More detailed analyses are suggesting that a levelling off into the steady-state has occurred already according to the model of hyperlogistic "evolon-dynamics" /23/.

However, if the purposes realizing part of final-energy is investigated with respect to the historic evolution of efficiencies or of elasticity-coefficients, respectively, an endogenous (surplus?) compensation of exogenous retarding forces (e.g. limitations of resources) can be established.

8) Instead of social information-capacity $I(t)$ - for which continuous data are not available - the number E of basic innovations depending on it is analyzed cumulatively up to time t as empirical indicator. There are well defined criteria of selecting for deciding which innovations are basic ones with regard to its potential to change given modes of production or life styles /11/. Assumed reason: A really remarkable extension of knowledge "crystallizes" into basic-innovations.

3. Perspectives

Feschel und Mende /23/ are suggesting that phenomenological (macro-) dynamics is generated by rate-coupled interactions of autocatalytic units of driving forces. These interactions can be modelled as Lotka-Volterra-equation-system. The case $k=2$ may be generated by cascade - like interactions of these units (model

of power-product driving forces) /23/ or by an hypercycle with degree 2 /6/. Higher evolution-exponents k require a higher degree of interaction between autocatalytic units in hypercycles /6/.

The abrupt change-over from $k=1,3$ (biotic evolution) to $k=3,4$ (social evolution) could be caused by a structural "metafluctuation" of complexity of hypostasized hypercycle-structure (cf. chapter 1.3) linked with the change-over from intrasomatic interactions to extrasomatic social organization.

It would be a challenging and rewarding task firstly to design suitable abstract models of driving-force-structures generating the actual dynamics resulting from the present study, and secondly to identify the specific nature, and the functional change of the structural units of driving forces of evolution and the kinds of their interactions in terms of biology and social sciences, respectively.

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Verfasser

Dipl.-Phys. G. Gebhardt
Humboldt-Universität zu Berlin
Sektion Philosophie
Bereich: Philosophische Probleme
der Naturwissenschaften

1080 B e r l i n

permanent address:

Bezirks-Hygiene-Institut Potsdam

DDR - 1500 Potsdam

Küsselstr. 9

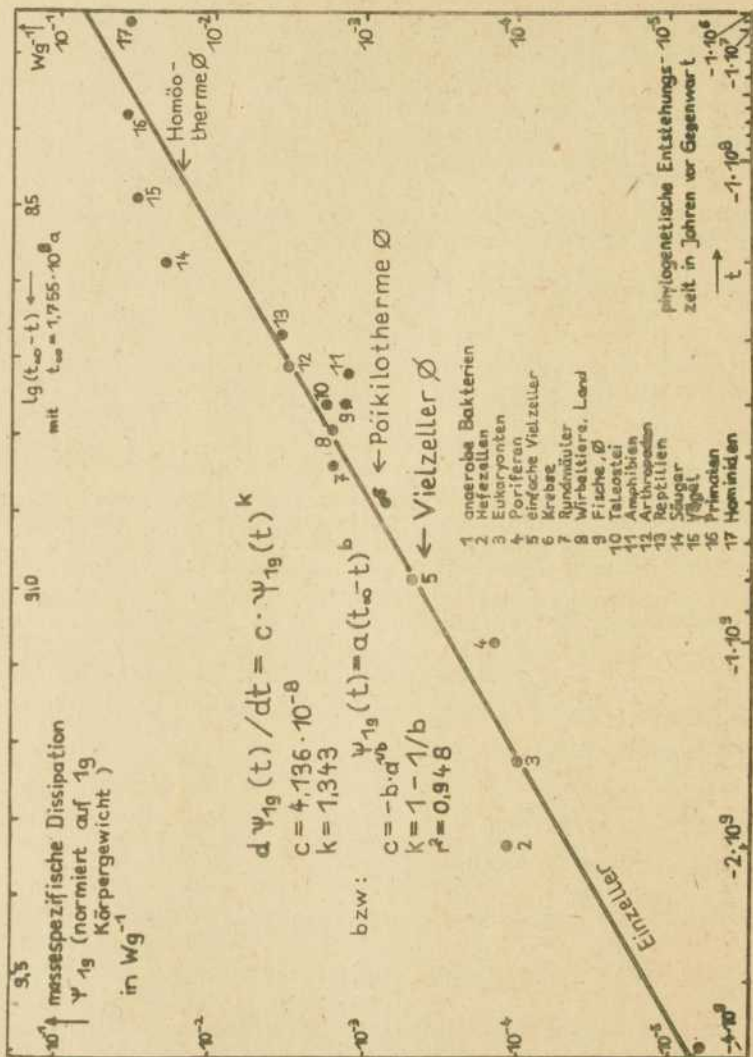


Fig.1: Linearized representation of the time dependent increase of (mass-)specific dissipation over the whole course of biotic evolution

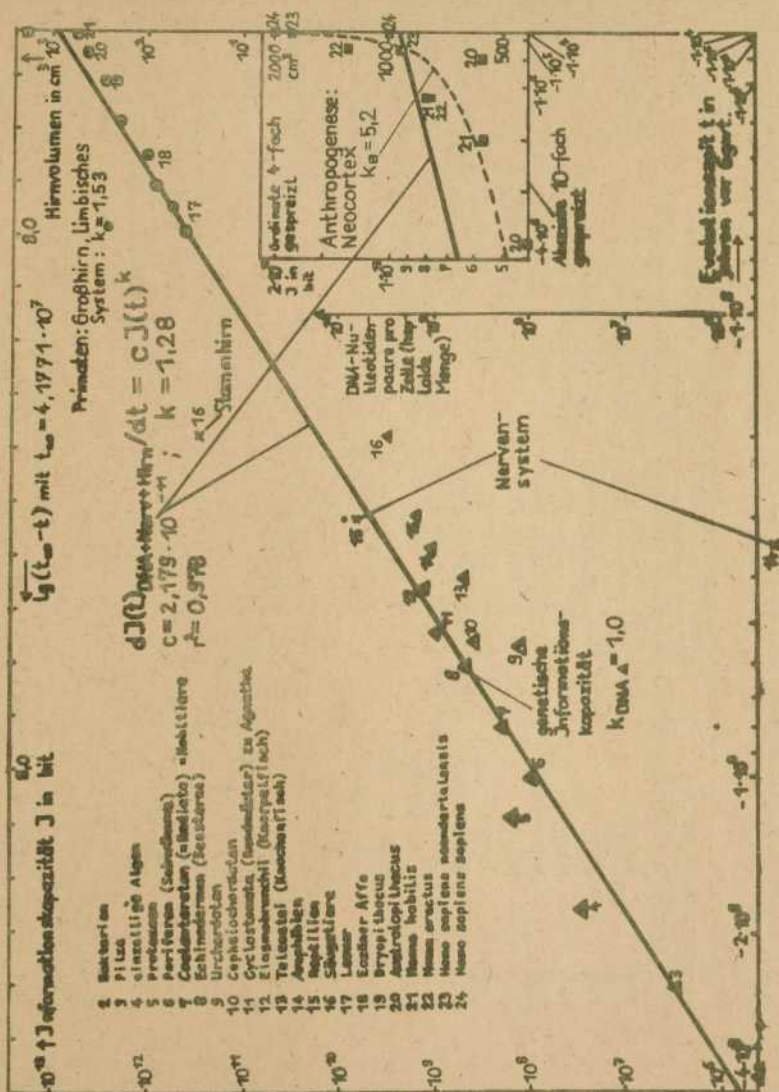


Fig.2: Linearized representation of the time dependent increase of information-capacity over the whole course of biotic evolution

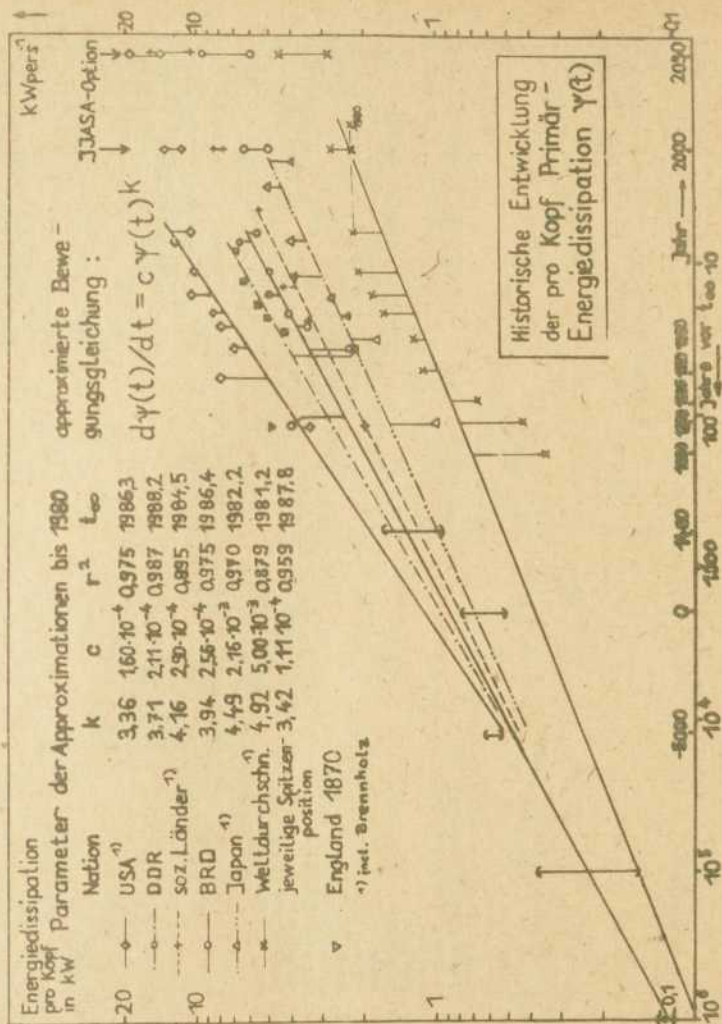


Fig.3: Linearized representation of the time dependent increase of (energy-)specific dissipation over the whole social development

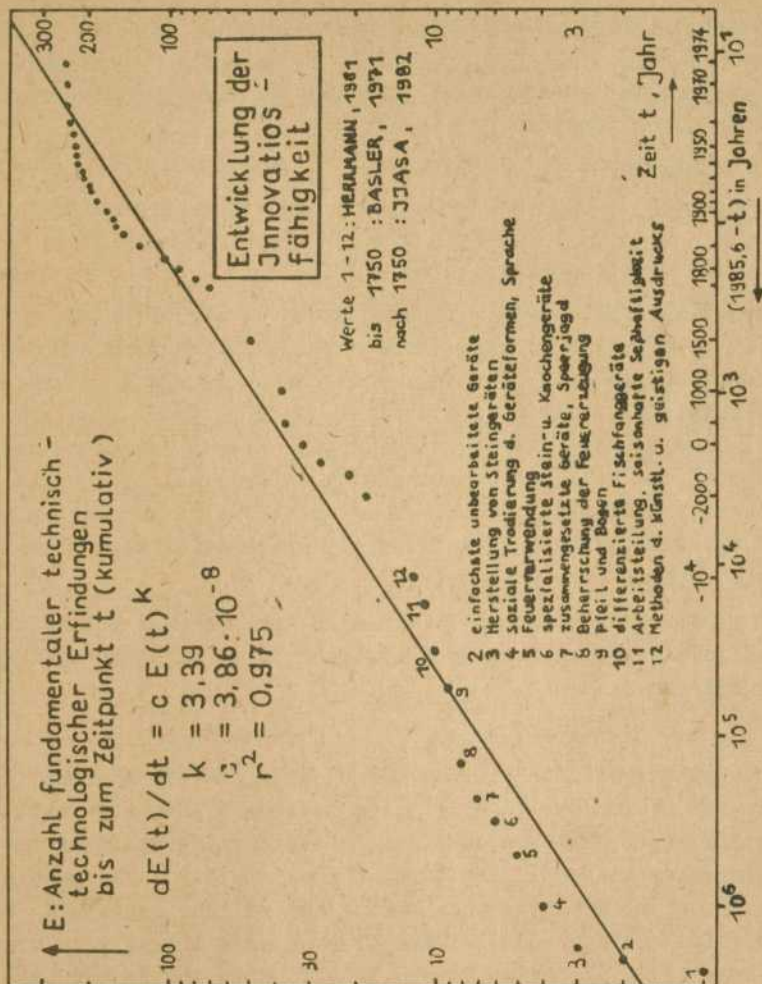


Fig.4: Linearized representation of the time dependent increase of information-capacity over the whole social development

Curvature Dependent Surface Tension and the Work of Formation of Critical Clusters

J. SCHMELZER

1. Introduction

One of the thermodynamic presumptions of the classical nucleation theory, its modifications and generalizations consists in the existence of a critical cluster size r_k . In a macroscopic description clusters with a radius $r_d > r_k$ grow, clusters with a radius $r_d < r_k$ shrink and disappear /1,2/. The exact calculation of the work of formation of such critical clusters W is one of the finally not solved yet problems in nucleation theory /3,4/. This is an unsatisfying situation since the nucleation rate depends strongly on W .

As it was already shown by Gibbs /5/ the work of formation W of sufficiently large critical clusters in an infinite system can be expressed by

$$W = \frac{1}{3} \sigma O \quad (1)$$

O being the surface area of the cluster, σ the surface tension. One way to improve this relation to obtain adequate results also for small clusters consists in the consideration of the curvature dependence of the surface tension /5-7/. The problems connected with the calculation of the surface tension σ as a function of the radius of the cluster were intensively discussed by us in preceding papers /8-12/. Here the results are applied to determine the work of formation of the critical clusters, if the surface tension σ depends on the radius r . The position of the dividing surface is assumed to be well-defined but no special choice is done at first.

We always assume in the following that the system is in a metastable initial state, that the size of the system is sufficiently large, so that a depletion of the medium or changes of the

temperature T due to the development of a critical cluster can be neglected. The influence of depletion effects on the work of formation of the critical clusters is analyzed in detail in /13/.

2. Curvature Dependent Surface Tension-General Equations

According to the thermodynamic theory of heterogeneous systems developed by Gibbs /5/ (see also /8,15/) the variations of the superficial energy U_0 , entropy S_0 , number of moles n_{i0} in the course of a deformation of a surface element with the surface area $d0$, the principal curvatures c_1 and c_2 are given by

$$dU_0 = TdS_0 + \sum \mu_i dn_{i0} + \sigma d0 + C_1 dc_1 + C_2 dc_2 \quad (2)$$

μ_i is the chemical potential of the i -th component, C_1 and C_2 are quantities determined by the independent variables chosen for the description of the system.

For spherical clusters of the new phase ($c_1=c_2=c=1/r$) equ. (2) reads:

$$dU_0 = TdS_0 + \sum \mu_i dn_{i0} + \sigma d0 + Cdc \quad C=C_1+C_2 \quad (3)$$

An integration of this equation results in:

$$U_0 = TS_0 + \sum \mu_i n_{i0} + \sigma 0 \quad (4)$$

A derivation of this equation and a comparison with eq. (3) leads to the most general form of the Gibbs adsorption equation /14/:

$$S_0 dT + 0d\sigma + \sum n_{i0} d\mu_i = Cdc \quad (5)$$

If according to Gibbs definition $C=0$ the surface of tension is chosen as the dividing surface then eq. (5) is reduced to

$$S_0 dT + 0d\sigma_s + \sum n_{i0} d\mu_i = 0 \quad (6)$$

The variation of the inner energy U of the heterogeneous system consisting of one cluster in the otherwise homogeneous surrounding medium can be expressed by /8,15/:

$$dU = -p_d dV_d - p_p dV_p + \sum \mu_i dn_i + TdS + \sigma d0 + Cdc \quad (7)$$

V_d and V_p are the volumes of the cluster (d) and the medium (p), p_d and p_p are the pressures in both phases.

For an isolated isochoric system the inner energy is the characteristic thermodynamic potential and as one equilibrium condition it follows from eq. (7)

$$p_d - p_\beta = \sigma \frac{dO}{dV_d} + C \frac{dc}{dV_d} \quad (8)$$

Here it was used that for spherical clusters the curvature c and the surface area O or the volume V_d are not independent variables.

The eqs. (2)-(4) and (7)-(8) are valid independent on the special choice of the dividing surface. Their application leads to some complications since in addition to σ a second unknown, in general, quantity C appears. In two cases, however, Cdc can be expressed by the surface tension σ via eq. (5), first, if isothermal real processes in one-component systems are considered and, second, if the position of the dividing surface is varied the physical state of the system being unchanged. Only in these both cases eq. (5) leads to

$$Od\sigma = Cdc \quad (9)$$

In the first case eq. (8) reads

$$p_d - p_\beta = \frac{2\sigma_e}{r_e} + \frac{d\sigma_e}{dr_e} \quad (10)$$

σ_e is the value of the surface tension corresponding to the equimolecular dividing surface with a radius r_e . In the second case the generalized Young-Laplace equation (11) is obtained /7/:

$$p_d - p_\beta = \frac{2\sigma}{r} + \left[\frac{d\sigma}{dr} \right] \quad (11)$$

the brackets indicating the special type of variation considered /16/.

Two conclusions can be derived at once. First, the definitions of the surface of tension as proposed by Gibbs ($C=0$) on one side and Ono and Kondo ($[d\sigma/dr]=0$) on the other side are equivalent (see also /17/). Second, the equations (11) and (6) or (10) and (6) are incompatible. Based on this second conclusion it was shown by us /12/ that some new approaches to the problem of curvature dependent surface tension /18-19/ are, to our opinion, not acceptable. The origin of the confusion consists

in the fact that in the basic equations used by Vogelsberger et al. /18/ for the description of the surface effects the superficial numbers of moles n_{10} are omitted (see, e.g., /22/ eqs. (2), (3), (6), (7) and other equations based on them).

3. Incompressibility of the Clusters and Curvature Dependent Surface Tension

The general results outlined in section 2 are now applied to the problem of the curvature dependence of surface tension of a one-component system under isothermal conditions. Choosing, as it is usually done, the surface of tension as the dividing surface eq. (6) reads:

$$0d\sigma_s + n_0 d\mu = 0 \quad (12)$$

Together with the necessary equilibrium conditions

$$\mu_\alpha = \mu_\beta = \mu \quad ; \quad p_\alpha - p_\beta = \frac{2\sigma_s}{r_s} \quad (13)$$

this equation gives the possibility to obtain a general thermodynamic equation for the curvature dependence of the surface tension σ_s related to the surface of tension with a radius r_s /9-12/. Here another point is to be mentioned which is of importance for the calculation of the work of formation of the critical clusters. The chemical potential of the cluster phase can be expressed as a function of the molar density ρ_α and the temperature T . Assuming incompressibility of the cluster phase the surface tension σ_s is only a function of the temperature, and, therefore, for isothermal processes a constant. The assumptions of an incompressibility of the cluster and a curvature dependence of the surface tension are, consequently, incompatible. A calculation of the work of formation of the critical clusters implying both assumptions is meaningless.

If instead of the surface of tension another arbitrary but well-defined dividing surface is chosen then the eqs. (12)-(13) have to be replaced by the following expressions for the calculation of the curvature dependence of σ , n_0 and C :

$$0d\sigma + n_0 d\mu = C d\sigma \quad ; \quad p_\alpha - p_\beta = \frac{2\sigma}{r} + C \frac{d\sigma}{dV_\alpha} \quad (14)$$

$$\mu_\alpha = \mu_\beta$$

Again, such a calculation cannot be performed without additional assumptions, knowledge concerning the system considered /9-12/.

4. The Work of Formation of the Critical Clusters

The work of formation of a critical cluster can be expressed, generally, as the difference between the characteristic thermodynamic potential of the heterogeneous system, consisting of the cluster in the otherwise homogeneous medium and the metastable initial state /20/. It is given by

$$W = (p_\beta - p_d) V_d + \sigma_0 + \sum_{i=1}^k (\mu_{id} - \mu_{i\beta}) \tilde{n}_{id} \quad (15)$$

if the cluster has a higher density comparing with the surrounding medium and by

$$W = (p_\beta - p_d) V_d + \sigma_0 + \sum_{i=1}^k (\mu_{id} - \mu_{i\beta}) n_{id} \quad (16)$$

otherwise /15/. Here the abbreviation

$$\tilde{n}_{id} = n_{id} + n_{io} \quad (17)$$

is used. Taking into account the equilibrium condition $\mu_{id} = \mu_{i\beta}$ in both cases the work of formation of the critical clusters can be expressed by

$$W = (p_\beta - p_d) V_d + \sigma_0 \quad (18)$$

These equations do not depend on the special choice of the dividing surface since in the expression for the superficial inner energy U_0 , and, consequently, in the expressions for the other thermodynamic potentials the quantity C does not appear. Taking into account the general equilibrium condition (8) eq. (18) can be transformed into

$$W = \frac{1}{3} \sigma_0 - V_d C \frac{dc}{dv_d} \quad (19)$$

As special cases we obtain

$$W = \frac{1}{3} \sigma_s \sigma_0 \quad (20)$$

if the surface of tension is chosen as the dividing surface ($C=0$) or

$$W = \frac{1}{3} \sigma_e \sigma_0 - V_d \frac{d\sigma_e}{dr_e} \quad (21)$$

for the equimolecular dividing surface (see also /21/).

In the derivation of eq. (18) only expressions for the thermodynamic potentials and the necessary equilibrium conditions were used. Another method can be applied for the determination of the work of formation of the critical clusters considering W (eqs. (15) and (16)) as a function of the number of moles n_{1d} and the volume V_d of the cluster and applying the necessary equilibrium conditions, e.g.,

$$\frac{\partial W}{\partial V_d} = 0 \quad (22)$$

Since sometimes it is questioned if such a determination is consistent with the method applied above the equivalence is shown explicitly starting with eq. (15). The derivative of W reads

$$\begin{aligned} \frac{\partial W}{\partial V_d} = & -V_d \frac{\partial p_d}{\partial V_d} + \sum_{i=1}^k n_{id} \frac{\partial \mu_{id}}{\partial V_d} + \sum_{i=1}^k \frac{\partial \tilde{n}_{id}}{\partial V_d} (\mu_{id} - \mu_{i\beta}) + \\ & p_\beta - p_d + 0 \frac{\partial \sigma}{\partial V_d} + \sigma \frac{\partial \theta}{\partial V_d} + \sum_{i=1}^k n_{i\sigma} \frac{\partial \mu_{id}}{\partial V_d} \end{aligned} \quad (23)$$

According to the Gibbs-Duhem equation

$$SdT - Vdp + \sum_{i=1}^k n_{1d} d\mu_1 = 0 \quad (24)$$

and the condition of inner stability underlying the thermodynamic description the eq. (25)

$$-V_d \frac{\partial p_d}{\partial V_d} + \sum_{i=1}^k n_{1d} \frac{\partial \mu_{1d}}{\partial V_d} = 0 \quad (25)$$

is always fulfilled /8/. In addition, it follows from eq. (5) that the derivative of W can be written as

$$\begin{aligned} \frac{\partial W}{\partial V_d} = & \sum_{i=1}^k \frac{\partial \tilde{n}_{id}}{\partial V_d} (\mu_{id} - \mu_{i\beta}) + \\ & p_\beta - p_d + \frac{2\sigma}{r} + G \frac{dc}{dV_d} \end{aligned} \quad (26)$$

Eq. (22) is fulfilled only if the necessary equilibrium conditions (8) and (27)

$$\mu_{1d} = \mu_{1\beta} \quad (27)$$

hold. Therefore, this second method of determination of the work of formation of the critical clusters is consistent with the first.

5. Application to Nucleation Processes in One-Component Systems

Starting with the general equations (15) and (18) we would like to show now, which additional assumptions are implied to obtain the equations

$$W = \frac{16\pi}{3} \frac{\sigma^3}{s_d^2 (\mu_p(p) - \mu_d(p'))^2} \quad (28)$$

$$\ln \frac{p}{p'} = -\frac{2\sigma}{s_d RT} \frac{1}{r} \quad (29)$$

usually applied in the classical nucleation theory and its modifications (see also (23)). p is the external pressure or the pressure in the medium, p' the equilibrium pressure for a co-existence of both phases at a planar interface.

We restrict ourselves here to the case that the cluster has a higher comparing with the surrounding medium density. Using the introduced notations eq. (15) can be written now as

$$W = (p - p_d) V_d + \sigma O + (\mu_d(p_d) - \mu_p(p)) \tilde{n}_d \quad (30)$$

To obtain from it eq. (28) first \tilde{n}_d has to be replaced by n_d . If, furthermore, incompressibility of the cluster is assumed then μ_d can be written as

$$\mu_d(p_d) = \mu_d(p) + \frac{1}{s_d} (p_d - p) \quad (31)$$

and eq. (30) reads

$$W = \sigma O + (\mu_d(p) - \mu_p(p)) n_d \quad (32)$$

The necessary equilibrium condition (22) immediately leads to eq. (28) then. Replacing $\mu_d(p)$, approximately, by $\mu_d(p')$, taking into account eq. (33)

$$\mu_d(p') = \mu_p(p') \quad (33)$$

and assuming further the medium being an ideal gas

$$\mu(p) = \mu^+ + RT \ln \frac{p}{p^+} \quad (34)$$

we get finally

$$W = \frac{16\pi}{3} \frac{\sigma^3}{s_d^2 [RT \ln \frac{p}{p^+}]^2} \quad (35)$$

To derive eq. (29) we start again from the equilibrium condition (27) and eq. (31). Substituting $\mu_d(p)$ through $\mu_d(p')$ we

get with eq. (33)

$$\mu_a(p) - \mu_a(p') = \frac{1}{s_a} (p - p') \quad (36)$$

Again, the assumption of an ideal gas has to be used and, furthermore, the surface of tension has to be chosen as the dividing surface to obtain the Gibbs-Thomson equation in the form (29) from eq. (36). Therefore, a number of approximations (incompressibility of the cluster, ideal gas, neglect of some terms) and a special choice of the dividing surface are implied to derive the eqs. (28) and (29).

Since as it was shown in section 3 the assumptions of an incompressible cluster and a curvature dependence of the surface tension are incompatible in the applications of the eqs. (28) and (29) the capillarity approximation has to be used.

If instead of the surface of tension another dividing surface is chosen then the Gibbs-Thomson equation reads (see eq. (8))

$$\ln \frac{p}{p'} = \frac{1}{s_a} \left\{ \sigma \frac{dO}{dv_a} + c \frac{dc}{dv_a} \right\} \quad (37)$$

Taking into account the underlying the derivation of eq. (36) assumption of the incompressibility of the cluster $d\mu$ in eq. (14) is equal to zero and independent on the choice of the dividing surface Cdc is equal to $Od\sigma$. Therefore, eq. (37) can be transformed into

$$\ln \frac{p}{p'} = \frac{1}{s_a} \frac{d}{dv_a} (\sigma O) \quad (38)$$

not only for the equimolecular dividing surface, as pointed out by Parlange /21/, but in general. It has to be underlined once more, however, that the equations derived in this section in contrast to the equations (19)-(21) are not exact results since additional approximations are used for their derivation. To obtain exact results for the work of formation of the critical clusters it is necessary to start with the equations (19)-(21) and the equilibrium conditions (8) and (27) directly.

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Verfasser

Dr. J. Schmelzer
Wilhelm-Pieck-Universität Rostock
Sektion Physik

DDR - 2500 Rostock
Universitätsplatz 3

Short Communication

On the Kinetics of Phase Formation in Photochromic Glasses by Means of X-ray Scattering

U. LEMBKE, R. MAHNKE

The nonequilibrium kinetic theory of metastability either in its field-theoretic approach (Ginzburg-Landau functional) or in the simple form of the physically motivated droplet model deals with observable thermodynamic parameters and bulk transport coefficients. Special attention is paid to test these calculations experimentally by observing nucleation, growth and the coarsening process (Ostwald ripening) in different materials.

We restrict our attention to a two-component fluid in which one of the components, the solute, may be visualized as diffusing in the background of the other component, the solvent. Describing the mixture of molecular clusters by a droplet-size-distribution function N the theoretical approach is given elsewhere /1/. Here the relations to experimental results by investigations of glasses are shown.

The phase formation of lightsensitive microcrystallites within photochromic glasses was investigated by small-angle X-ray scattering (SAXS). The SAXS was measured for samples, which were treated thermally for different times (temperature $T = 610^\circ\text{C}$). The analysis of the scattering data was performed by Hankel transformation. The correlation function /2/

$$C(r) = \frac{1}{4\pi^2} \int_0^\infty s \tilde{I}(s) J_0(sr) ds \quad (1)$$

and the particle diameter distribution function

$$N^*(\frac{D}{2}) = - \frac{d}{dr} \left[\frac{d^2 C(r)}{dr^2} / r \right]_{r=D} \quad (2)$$

where r is the distance in real space, D is the particle diameter, $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$, λ is the wavelength, θ is the scattering

angle, $\tilde{I}(s)$ is the collimation distorted scattering intensity and J_0 is the Bessel function, were calculated using a technique, which is based on the sampling-theorem of information theory [3]. From

$$C(0) = w (1-w) (\Delta \xi)^2 \quad (3)$$

and from X-ray diffraction measurements for the determination of the composition of the silverhalide mixed crystals and the electron density difference $\Delta \xi$ between matrix glass and crystallites is obtained. $N(D)$ is normalized in that way that the total volume of all particles is equal to the volume fraction w :

$$N(D) = \frac{N^*(D) \cdot w}{\frac{\pi}{6} \int_0^\infty D^3 N^*(D) dD} \quad (4)$$

Consequently the volume distribution function $\frac{\pi}{6} D^3 N(D)$ represents the fraction of w , which is contributed by all crystallites with diameter D .

The development of the volume distribution with increasing time of thermal treatment is shown in figure 1. Pay attention on the fact resulting from the analysis according to equation (3) that

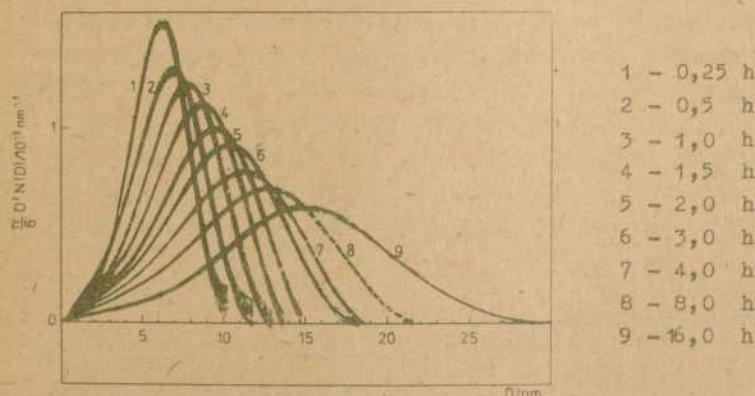


Fig.1: The volume distribution function of the light-sensitive microcrystallites in a photochromic glass, $T=610^\circ\text{C}$ (the error bands are indicated by a gray background)

respectively, the volume fraction w

already after the first treatment of 0.25 h the maximum volume w was reached, and it remains constant. This is demonstrated in the figure, because according to equation (4) the area under the volume distribution function is constant.

The development of the volume distribution function with increasing time clearly demonstrates the ripening process taking place in the glass: the vanishing material in the region of small particles is accumulated at the bigger particles (equality of the area differences left and right between two treatment states). The analysis of the increasing mean diameter with treatment time delivers $D \sim t^{1/3}$. Therefore, the growth mechanism within the investigated glass is diffusion limited ripening /4/.

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Verfasser

Dipl.-Phys. U. Lembke, Dr. R. Mahnke
Wilhelm-Pieck-Universität Rostock
Sektion Physik

DDR - 2500 Rostock
Universitätsplatz 3

Short Communication

Selbstorganisation und stimulierte Organisation kooperativer
Nichtgleichgewichtssysteme

A.A. KALNIN

Die gegenwärtige Situation bei der Untersuchung von dissipativen Strukturen (DS) und Strukturen, die auf Grundlage des Boltzmannschen Mechanismus (Gleichgewichtsstrukturen) (GS) entstehen, besteht darin, daß diese gewissermaßen als Antipoden betrachtet und dementsprechend nicht in ihrem Zusammenhang untersucht werden. Jedoch bildet sich faktisch jede DS immer in Medien mit einer Boltzmannschen Komponente der Elementstrukturierung aus und jede GS unterliegt Störungen irgendwelcher äußeren Einflüsse. Die Stabilität der DS ist mit der Stabilität ihrer Grenzbedingungen verbunden. Die Stabilität der GS dagegen hängt davon ab, ob die äußeren Störungen eine kritische Größe überschreiten. In realen offenen Systemen besteht somit eine Wechselwirkung zwischen den beiden Mechanismen der Strukturierung von Elementen, deren Untersuchung eine große Bedeutung für das Verständnis der Evolution offener Systeme hat.

Wir definieren nun die reflexiven Strukturen (RS) (vgl. Abb.1) und die Voraussetzungen ihrer Entstehung. Reflexive Strukturen sind solche Strukturen, die durch das Einwirken der Felder

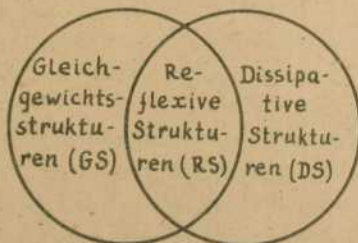


Abb. 1:
Die relative Lage
reflexiver Strukturen

dissipativer Strukturen auf eine Gleichgewichtsstruktur entstehen. Wie zu sehen ist, kann man die RS weder zur Klasse der Gleichgewichtsstrukturen, da sie nur unter Nichtgleichgewichtsbedingungen existieren, noch zur Klasse der DS zählen, da sie durch stetige Deformation der Gleichgewichtsstrukturen entstehen können.

Die Entstehung von RS erfordert folgende Voraussetzungen:

1. Das Vorhandensein der Boltzmannschen Komponente der Elementstrukturierung.
2. Die Suszeptibilität der Basis gegenüber den Feldern der DS muß der Bedingung $\eta > 0$ genügen.
3. Die charakteristische Zeit der Umverteilung der generalisierten Masse $\tau^{(B)}$ muß größer als die Übergangszeit der DS in eine alternative Mode $\tau^{(D)}$ sein.

Die letzte Bedingung ist offensichtlich, da zum Beispiel lokale Veränderungen der Dichte der Flüssigkeit zu einer Veränderung des Reliefs in der Oberfläche in der flüssigen Schicht führen, jedoch die Relaxation des Reliefs zu schnell vonstatten geht, so daß es der Veränderung der Dichte folgt, ohne "Spuren" in der Basis zu hinterlassen.

Von großem praktischen Interesse ist folgendes Problem: Welchen Einfluß hat eine lange Zeit im System existierende RS auf die Ausbildung und Evolution einer DS? Es ist bekannt, daß die Grenzbedingungen aktiv auf die Herausbildung einer Mode der DS wirken. Man kann bekräftigen, daß in dem Fall, wenn die Existenzzeit der RS, die unter Einfluß der Mode M einer DS gebildet wurde, groß ist, die Mode M der DS unter dem Einfluß dieser RS rekonstruiert wird, wenn die äußeren Bedingungen des Nichtgleichgewichtszustands reproduziert werden. In einem solchen Fall kann man die RS als eine innere Speicherstruktur des Systems und die Rekonstruktion der DS unter Einfluß der RS, als eine stimulierte Organisation eines kooperativen Systems im Nichtgleichgewichtszustand betrachten.

Diese Aussage wurde einer experimentellen Bestätigung unterworfen. Das Wesen des Experiments ist in der Abb. 2 erklärt. In einem flachen zylindrischen Gefäß wird die Bildung einer DS Rayleigh-Benard durch Erhitzen des Bodens des Gefäßes hervorgerufen. Der Temperaturgradient entsteht dabei aufgrund des

natürlichen Wärmeaustausches ($dT/dz=7K/cm$, $\bar{T}=328K$). Nach längerem Übergangsprozeß zu einer stationären Konvektionsstruktur wurden auf die Oberfläche kleinste schwimmende Teilchen gleichmäßig aufgebracht. Unter dem Einfluß der Strömung bewegten sich die Teilchen zu den Linien, an denen sich die entgegengesetztgerichteten Strömungen treffen, wo sie sich vereinigten und nach Ablauf einer bestimmten Zeit eine geordnete Konfiguration entstand, welche eine RS ist. Faktisch ordneten sich die Teilchen so, daß der Reibungseinfluß auf die dissipativen Prozesse minimal ist. (Abb. 2a) Um die organisierende Wirkung der RS auf

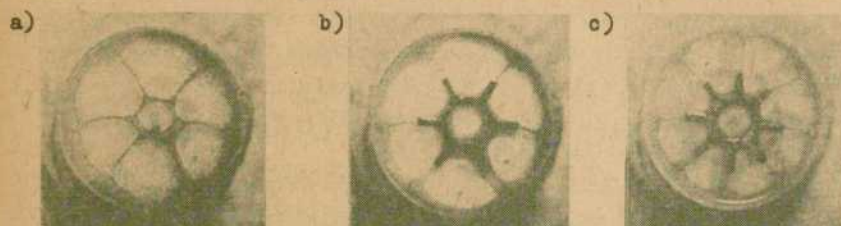


Abb. 2: Die Bildung von RS auf der Grundlage der Verschiebung und Vereinigung in konvektiven Strömungen schwimmender Teilchen (a); die Rekonstruktion der DS nach dem Modell der RS (b); und die Entstehung einer stimulierten Mode der DS unter Einfluß einer Imitation der RS (c).

die Konfiguration der konvektiven Strömungen zu zeigen, wurde eine Kopie der RS aus dünnem Phenoplast auf die Oberfläche der Flüssigkeit aufgebracht. Um die Übersichtlichkeit der Demonstration des Rekonstruktionsprozesses zu erhöhen, wurde nur der Teil der RS benutzt, der die wesentlichsten Informationsmerkmale in sich trägt (Abb. 2b). Bei Reproduktion des Temperatureinflusses, der während der Herausbildung der RS vorlag, wird die DS rekonstruiert, was sich an der stimulierten Winkelorientierung der Elemente zeigt, die anhand des Reliefs der schwimmenden Teilchen zu beobachten war. Faktisch fand außerdem ein Komplettieren der RS statt. In einem anderen Versuch wurde die Stimulierung der Mode mit einer großen Anzahl von elementaren Konvektionsströmungen mit Hilfe eines Keimes untersucht, der die RS imitierte (Abb. 2c).

Diese Versuche gestatten den Schluß, daß das statische Relief der RS in der Lage ist, die RS unter entsprechenden Nichtgleichgewichtsbedingungen des Systems zu rekonstruieren. Der

physikalische Rekonstruktionsmechanismus der DS besteht in dem aktiven Einfluß der RS auf die Richtung der Evolution des Systems auf der Grundlage des Einwirkens der RS auf die Fluktuationsprozesse.

Hauptresultate:

1. Beim Studium der Strukturbildung in offenen Systemen ist die Einführung einer besonderen Klasse von Strukturen - der reflexiven - nötig, die zu einer Rekonstruktion von DS fähig sind, d.h. zur Anregung eines Systems von Prozessen nach einem quasistatischen Relief.
2. Die Generierung von RS ermöglicht die Realisierung von Funktionen von verteilten assoziativen Speichern, die auf kooperativen Erscheinungen basieren, wobei assoziative Umwandlungen durch die Schaffung eines auswählenden Nichtgleichgewichts der kooperativen Systeme geschaffen werden.
3. Die Strukturreflexion muß als adaptive Struktur- und Formbildung unter der Einwirkung von Informationssignalen verstanden werden, wobei in diesen Prozessen eine Regenerierung der RS erreicht wird, wenn ihre Beschädigungen unbedeutend sind.
4. Für eine erfolgreiche Realisierung der Methode sind Materialien nötig, in denen eine DS erzeugt werden kann, die kleine Schwellenleistungen und große verbundene und "abgeleitete" Felder besitzt, wobei die Materialien zum Einschreiben der DS eine große Suszeptibilität gegenüber diesen Feldern sowie eine große räumliche Auflösung besitzen müssen.
5. Die Methode der Strukturreflexion erlaubt es, die Evolution als Einheit der Prinzipien der Organisation und Selbstorganisation von kooperativen Nichtgleichgewichtssystemen zu betrachten.

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Verfasser

Dr. A.A. Kalnin, Elektrotechn.Inst., Leningrad, UdSSR

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DDR - 2500 Rostock

Universitätsplatz 3

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applied also to such basic empirical indicators of society which make it possible to differentiate different stages of development in a quantifiable manner.

mental stages like hominids, hunters and agriculture, antiquity with emerging urban modes of production, energy balances were not /4/ and from the beginning of capitalism time exact statistics concerning energy consumption - demographic trends have been available $\Psi(t)$, cf. fig.3 and notes 5) and 6)

on-capacity has been measured indirectly (on table 1).

and $\{I_1, t_1\}$ have been fitted with the well known (least square deviations). The approximation by correlation-coefficients r .

($k = 1$ in eq.(5)), e.g., have to be realistic approximations provided highly significant ($r > 0,97$) at the probability of error being

ing hyperbola has been computed by iterative known singularity-time t_∞ in the logarithmization of eq.(5) (see note on fig.1) with the of that solution which provides a maximal r

tions of the single points (see figures) within their confidence intervals caused of computed evolution-exponents of k seems to be an evolutionary invariant positively on stochastic variations of single does not represent the essence of evolution-

summarized in the following table and complementary notes. Further parameters are noted in