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Nucleation Theory and Dynamics of First-Order Phase Transitions in Finite System

H. Ulbricht, F. Schweitzer, and R. Mahnke

Wilhelm-Pieck-Universität Rostock, Sektion Physik, Universitätsplatz 3, DDR-2500 Rostock, GDR

1. Introduction

If we consider a vapor at equilibrium, then a certain change of the thermodynamic parameters (e.g. a supercooling at a given density; see Fig. 1) is able to remove the system into a nonequilibrium state. The vapor thus becomes supersaturated and a phase transition can occur in the system.

Inside the binodal region, the mechanism of such a first-order phase transition is the homogeneous nucleation, if impurities are absent. In general, we can divide the process of phase separation into three stages: nucleation, growth and coarsening. During the first stage, in the supersaturated vapor small nuclei are formed by thermal fluctuations. The critical size of these embryos is caused by the formation of their surface. Overcritical nuclei can grow to form large macroscopic domains (droplets, see also Fig. 2), undercritical nuclei diminish again.

If we take into account a depletion of the vapor in a finite system, that means the vapor pressure decreases because of nucleation, at a certain value of supersaturation no more overcritical droplets are able to arise and the growth process of the established droplets is dominating. For a more decreased vapor pressure the growth is converted to a competition process of the droplets, that is the so-called Ostwald ripening.

Despite intensive research over a period of about sixty years, a number of problems concerning the theoretical description of the
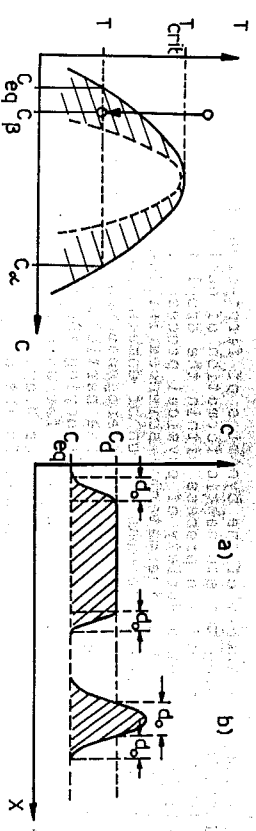

Fig. 1 Phase diagram of a gas-liquid system. The system is quenched from the one-phase equilibrium to a metastable state (binodal region). c_A is the vapor density at the metastable state, c_{eq} the equilibrium vapor density, c_α the liquid density at the given temperature
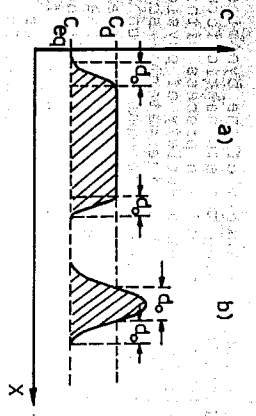
Fig. 2 Density profile of a "classical" droplet (a), with linear dimensions much larger than the correlation length (or interface thickness) d and of a "nonclassical" droplet (b) of smaller size, where interfacial and surface region are no longer clearly distinguishable /10/

nucleation process remain not finally solved yet. Some of these problems are the calculation of the formation energy of critical clusters, the proper consideration of the depletion of the initially metastable phase, the kinetic description of the relaxation into the stable state of the coexisting phases and the influence of the finiteness of the system.

Several models have been pointed out to clarify this situation (/1-3/, see also /4,5/). The classical nucleation theory mainly tends to calculate the stationary nucleation rate for the formation of overcritical droplets in an infinite system using a one-parametric description of the droplets. This theory was modified recently by several authors /6-10/ completing the droplet model. By means of a continuous description of the phase-separating system /11-14/ a more general level of the theory is reached that allows the determination of some kinetic properties near the critical point /15-17/. Recently, computer simulations have given a useful demonstration of the earlier stages of the nucleation process and of the time-dependent cluster evolution /18-20/. They also allow the calculation of the formation energy of microclusters /21/.

For the late stage of the phase transition, the asymptotic solution of the kinetic equations can be obtained from the theory of Ostwald ripening /22-24/. A generalization of this result is given by recent authors applying thermodynamic investigations /25,26/. A thermodynamic analysis can lead to a deeper insight into the process of phase separation, in particular, it gives general results for the existence of stable droplets in principle and their dependence on the thermodynamic parameters of the system, like particle number, system size, pressure and temperature /27-29/.

The classical and other nucleation theories suppose an infinite system neglecting the alteration of the system properties caused by the nucleation process. In finite systems, on the contrary, the limited system size and/or particle number yields a rather complicated evolution of the droplet distribution (see also /30/). Another important contribution to a better description of the kinetic and the stationary properties is that of a proper theory of surface effects, because the surface tension has a great influence on the formation of critical droplets. While classically the capillarity approximation is used, modern theories apply curvature-depending surface tensions resulting from statistic /21,31/ or thermodynamic /32,33/ investigations.

A complete theory of the dynamics of first-order phase transitions, including the stochastic formation of nuclei as well as the late stage competition process within the droplet ensemble, would be very helpful for a variety of physical processes. Many areas of current interest in the material sciences involve the simultaneous diffusional growth and dissolution of domains in a matrix /34/.

In this paper we describe a heterogeneous system with a finite volume consisting of monomers (free particles) and different drops (n-mers) as bound states. After studying the stochastic and kinetic evolution of one droplet, we find for an ensemble of drops under constrained conditions that larger drops grow at the expense of smaller drops, which disappear. So the Ostwald ripening as a competition process quite similar to the selection in bio- or eco-systems is related to the theory of selforganization /35/.

2. Stochastic Evolution of One Droplet in a Finite System

In the following we consider the stochastic evolution of a droplet in a supersaturated vapor. The thermodynamic constraints of the system we fix as follows:

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

where N is the overall particle number, V the volume and T the temperature of the system. The thermodynamic parameters must be chosen in such a way, that the pressure for the (supposed) ideal vapor

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

is much larger than the equilibrium pressure p_∞ of the saturated vapor. If we define an initial supersaturation

$$y_0 = \frac{p - p_\infty}{p_\infty} , \qquad (2.3)$$

then $y_0 > y_{cr}$, where y_{cr} is a critical supersaturation as pointed out in chapter 3, gives one permission that a nucleation process can occur. If we take into account the alteration of the pressure due to nucleation, the actual supersaturation $y(t)$ decreases with time, starting from y_0.

We suppose that a single droplet was formed in the system and evolves due to the following kinetic mechanism:

$$A_1 + A_1 \quad \frac{w^+}{w^-} \quad A_1$$
$$(N-1)A_1 \quad \frac{w^+}{w^-} \quad (N-1-1)A_1 , \qquad (2.4)$$
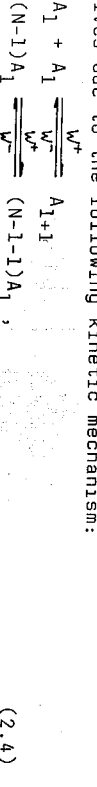
where l is the number of particles bound in the droplet ($1 \le N$). Both reactions (2.4) are coupled by the limitation of the overall particle number.

The evolution of the droplet is assumed to be a Markovian birth and death process. If we define $P(1,t)$ as the probability to find the droplet with l particles at a given time t, the following master equation describes the time dependence of $P(1,t)$ /36/:

$$\dot{P}(1,t) = w^+(1-1)P(1-1,t)+w^-(1+1)P(1+1,t)-P(1,t)[w^+(1)+w^-(1)]. \qquad (2.5)$$

w^+ and w^- are the transition probabilities per unit time as also introduced in (2.4). We define them in agreement with former investigations /30,37/ as follows:

$$w(N-1+1,1-1|N-1,1) = w^+(1) = \alpha 1^{2/3} \frac{N-1}{V}$$
$$w(N-1-1,1+1|N-1,1) = w^-(1) = \alpha 1^{2/3} \frac{1}{\lambda_1^3} \exp\left(\frac{f_1-f_{1-1}}{kT}\right), \quad 2 \le 1 \le N \qquad (2.6)$$

with the mass m and $f_1 = -Al + B1^{2/3}$ is a potential function with $f_1 = 0$. A and B are constants, given by /38/:

$$A = -\ln \frac{p_\infty}{k_B T} \lambda_1^3 , \qquad B = 4\pi \left(\frac{4\pi}{3} c_\alpha\right)^{-2/3} \sigma . \qquad (2.7)$$

α is a constant with respect to the special properties of the droplet like the liquid density c_α [particles/m³], the surface tension σ [N/m] and the temperature T [K] is

$\lambda_1 = h(2\pi m k_B T)^{-1}$ is the de Broglie wave length of a free particle with the mass m and $f_1 = 0$. A and B are constants, given by /38/:

Note, that in the case l=1 it holds /30/:

$$w^+(1) = \alpha \frac{N(N-1)}{V} ; \quad w^-(1) = 0 . \qquad (2.8)$$

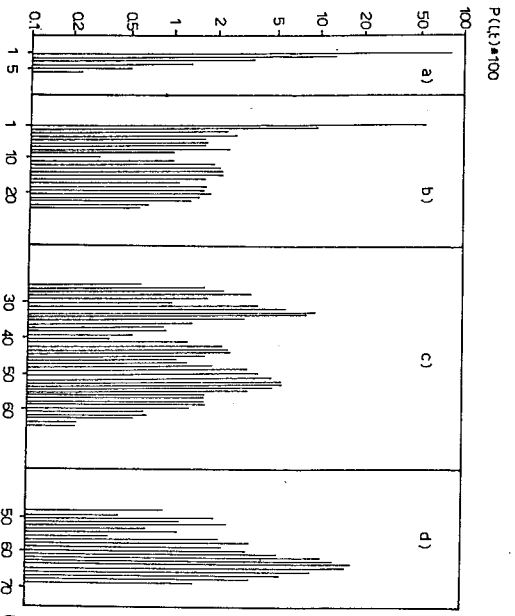The transition probabilities for processes different from (2.4) are set equal to zero.

P(l,t)*100

Fig. 3 Time evolution of a vapor-liquid phase transition in a finite system. $P(l,t)$ is the probability of the droplet to be in state l. Four different evolution stages, averaged over 500 elementary processes, are shown corresponding to the (reduced) time a) 7500; b) 16000; c) 29500; d) 33000.
vapor: ethanol, T = 290 K, N = 150, V = 2,75·10⁻²³ m³

A computer simulation with the given transition probabilities is demonstrated in Fig. 3 for several stages of the evolution of the droplets.

We can separate two characteristic time scales of the process (see also /40-42/). In a short time regime a quasistationary distribution for the vapor phase is established around l=1, while in a long time regime a distribution around the second stable state evolves by means of the non-poissonian fluctuations. The development of this stable state just corresponds to the phase transition, because the second maximum of $P(l,t)$ is due to the droplet phase. Transition between the two stable states are possible and will be discussed in the following.

3. Equilibrium Distribution and Bistability

The master equation (2.5) allows us to introduce a probability flux

$$J(l-1,l) = w^+(l-1)P(l-1,t) - w^-(l)P(l,t) ,\qquad (3.1)$$

which is analogous to the classical nucleation rate. In the stationary case it holds:

$$J(l-1,l) = J(l+1,l) = J^s = const \qquad (3.2)$$

With this condition we receive the stationary probability distribution in a way given by BECKER and DÖRING /1/ (see also ref. /6/):

$$P^s(m) = P^s(1) \prod_{j=l+2}^{m} \frac{w^+(j-1)}{w^-(j)} - J^s(\sum_{k=1}^{m-1} q_k) ,\quad m > 1 \quad with \qquad (3.3)$$

$$q_k = \frac{1}{w^+(k)} \prod_{j=l+1}^{m} \frac{w^+(j-1)}{w^-(j)} .$$

For $P^s(m) = 0$, that means, m is an absorber state, we get with l=1 the stationary probability flux

$$J^s = P^s(1)\left\{\sum_{k=1}^{m-1} \frac{1}{w^+(k)} \prod_{j=2}^{k} \frac{w^+(j-1)}{w^-(j)}\right\}^{-1} . \qquad (3.4)$$

The equilibrium distribution $p^0(l)$ we obtain from (2.5) with the condition of detailed balance /36/:

$$w^+(l)P(l,t) = w^-(l+1)P(l+1,t) \qquad (3.5)$$

that means consequently $J^s = 0$. From (3.3) it yields:

$$P^0(l) = P^0_N(1) \prod_{j=2}^{l} \frac{w^+(j-1)}{w^-(j)} \qquad (3.6)$$

with the normalization

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

Figure 4 shows that the equilibrium distribution $p^0(l)$ is able to be bimodal in dependence on the thermodynamic parameters.
The existence of two stable states of $p^0(l)$ represents the co-existence of the liquid and the vapor phase in equilibrium. The first maximum of $p^0(l)$ defines the stable droplet size l_{st}, while the second maximum of $P^0(l)$ (not to be seen in Fig. 4) is related to the minimum of $P^0(l)$.

P⁰(l)*100

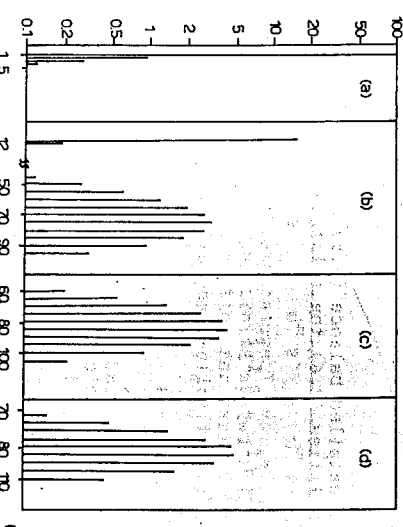Fig. 4 Equilibrium distribution $P^0(l)$ for various values of the system volume V. The maximum states are relative to the vapor (l=1) and the droplet (l=l_st). In dependence of the system size we find a coexistence of the droplet and the vapor
vapor: ethanol, T = 290 K, N = 150
a) V = 2,75·10⁻²³ m³; b) V = 2.5·10⁻²³ m³; c) 2.25·10⁻²³ m³
d) V = 2.00·10⁻²³ m³ /38/

critical droplet size l. Both values of the thermodynamic parameters l_{cr} and l_{st} strongly depend on the values of the thermodynamic parameters /29,39/. From a stochastic point of view, transitions between the two stable states are possible if $P^o(l)$ is bimodal. The mean first passage time for the transition between two states l and m ($m > l$) can be calculated as follows:

$$\tau(l \to m) = \sum_{j=l}^{m-1} \frac{1}{w^+(j)\, P^o(j)} \sum_{k=1}^{j} P^o(k) . \qquad (3.7)$$

In Tab. 1 there is demonstrated the dependence of the mean first passage time on the initial supersaturation y_o (2.3), which caused the distinction of the second stable state of $P^o(l)$.

Tab. 1 Mean first passage time to reach the critical state l and the stable state l_{st} in dependence on the system volume V and supersaturation y_o /39/.

V $(10^{-23} m^3)$	y_o	l_{cr}	l_{st}	$\tau(l \to l_{cr})$	$\tau(l \to l_{st})$
2.0	4.79	9	93	372.7	830.5
2.25	4.15	12	85	1607.3	3333.1
2.5	3.63	15	75	7237.6	16616.4
2.75	3.21	21	63	51761.4	119631.6

Further we want to discuss the problem under which thermodynamic constraints the bimodality of $P^o(l)$ is just diminishing. That means a stable droplet is impossible to exist then and we find only a one-phase equilibrium state. From the extremum condition for the equilibrium distribution

$$P^o(l_E) = P^o(l_E + 1) , \qquad (3.8)$$

we get with the condition of detailed balance (3.5) and with the introduced transition probabilities (2.6) the relation:

$$\ln\left(\frac{1}{l+1}\right)^{2/3} + \ln \frac{N-1}{V} \lambda_t^3 = \frac{1}{k_B}\{f_{l+1} - f_l\} . \qquad (3.9)$$

For the extremum states of $P^o(l)$ it follows approximately:

$$\ln \frac{(N-1)k_B T}{P_\infty V} = \left(\frac{2\sigma}{c_\alpha k_B T}\right)\left(\frac{4\pi}{3} c_\alpha\right)^{1/3} l^{-1/3} . \qquad (3.10)$$

A further discussion of (3.10) /38/ leads to the condition (3.11) that gives a relation between the critical values of the thermodynamic parameters N, V and T for which the bimodality of $P^o(l)$ is lost:

$$N\left\{\ln \frac{N k_B T}{P_\infty V}\right\}^4 = 4\left(\frac{4\pi}{3} c_\alpha\right)\left\{\frac{4}{3}\frac{2\sigma}{c_\alpha k_B T}\right\}^3 . \qquad (3.11)$$

Note, that the equilibrium pressure P_∞, the surface tension σ and the particle density c_α of the liquid depend on the temperature too. From (3.11) results a critical overall particle number N_c respectively a critical system size V as well as a critical temperature T of the system, where a stable coexistence of a droplet in the vapor is just impossible. This fact is just a consequence of the finiteness
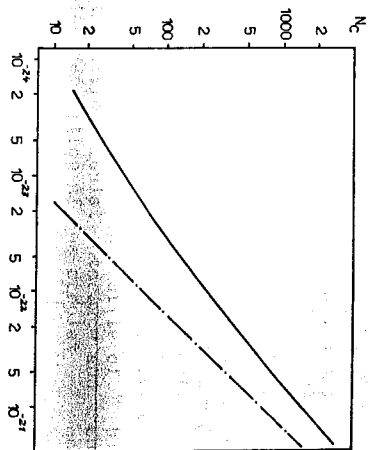
Fig. 5 Critical overall particle number N_c vs. system volume V. Only for $N > N_c$ is a coexistence of the finite system possible. The dashed-dotted line gives the saturation particle number $N_\infty = P_\infty V/k_B T$ /38/
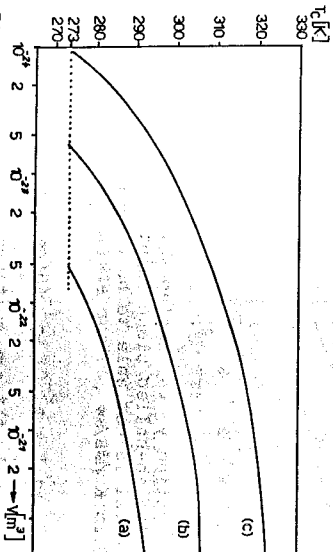vapor: ethanol, T = 280 K

Fig. 6 Critical temperature T_c vs. system volume V. If $T > T_c$, the binodal region of the finite system is left and no nucleation can be obtained. T is plotted for various overall particle densities:
a) $N/V = 2\ 10^{24}\ m^{-3}$; b) $N/V = 4 \cdot 10^{24}\ m^{-3}$; c) $N/V = 8\ 10^{24}\ m^{-3}$ /38/
vapor: ethanol

of the system. The region where a two-phase coexistence of the system is possible is shown in Fig. 5 and Fig. 6. We want to underline, that the critical temperature of the binodal region depends on the system size too, this fact should become important for small systems.

The existence of critical thermodynamic parameters for the nucleation process permits the calculation of a critical supersaturation of the finite system /38/

$$y_c = \frac{P_\alpha - P_\infty}{P_\infty} = \exp\left\{\left(\frac{\frac{4\pi}{3} c_\alpha}{\frac{N_c}{4}}\right)^{1/4}\left(\frac{4}{3}\frac{2\sigma}{c_\alpha k_B T}\right)^{3/4}\right\} - 1 . \qquad (3.12)$$

For the initial supersaturation $y < y_c$ the system possesses only one stable state due to the vapor phase. An overcritical droplet is not able to be formed because the pressure of the system decreases faster due to the attachment of free particles by the droplet, than the droplet reaches the overcritical size. This effect is caused by the finiteness of the system.

For $y > y_c$ a stable droplet is possible to exist. That means y_c has to be reached at least initially to insert the nucleation process. y_c gives the so called cloud point for the phase transition in the finite system.
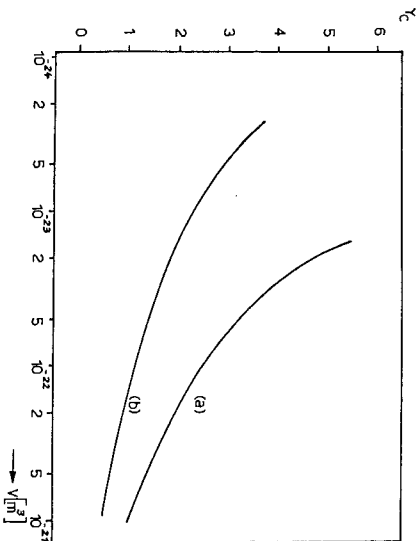
The value of y_c are given in Fig. 7.

Fig. 7 Critical supersaturation y_c vs. system volume V. y_c gives the onset of nucleation, the so-called cloud point. For $y < y_c$ a critical droplet is not able to be established. a) T = 280 K; b) T = 312.15 K /38/ vapor: ethanol

4. Basic Equations of the Competitive Growth Problem

Apart from the concept discussed above, the time evolution of the phase transition can be described by means of a concentration field $c(r,t)$, which has to fulfill a reaction-diffusion equation or a similar functional master equation /44/. To avoid the difficulties in solving these equations, we consider a model where spherical droplets are located in the otherwise homogeneous vapor. Figure 8 (compare Fig. 2) indicates that our assumption of the droplet with a constant density c_α is no longer valid for small droplets. If the droplet radius r has the magnitude of the interface thickness g (explicitly if $r \leq d/2$) the droplet model breaks down, because there are no incompressible bulk regions. Then one has to take into account a changing density c_α like in Montroll's approach /45/. For a typical liquid-vapor system the capillary length is

$$d_0 = 2 \delta (c_\alpha k_B T)^{-1} \sim 10^{-9} \text{ m} = 1 \text{ nm}. \qquad (4.1)$$

In the following we use macroscopic values for the constants c_α (density of monomers within the droplet) $c_{eq}(\infty)$ (equilibrium concentration of monomers), δ (surface tension of the droplets), T
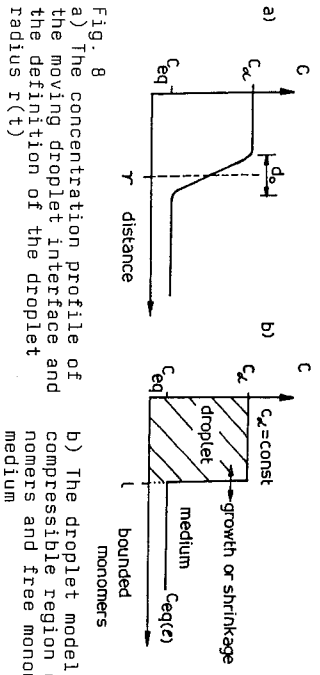
Fig. 8
a) The concentration profile of the moving droplet interface and the definition of the droplet radius r(t)
b) The droplet model with an incompressible region of bound monomers and free monomers in the medium

(temperature), D (diffusion coefficient of monomers) coming from experimental data. Now our basic quantities describing the system are

$$c(t) = M_\beta(t)/V \qquad \text{concentration of free monomers} \qquad (4.2)$$

$$f(1,t) = N(1,t)/V \qquad \text{cluster density distribution function} \qquad (4.3)$$

where $M_\beta(t)$ is the number of the free monomers in the volume of the system V and $N(1,t)$ the number of droplets with 1 bounded particles respectively. The time-dependent supersaturation characterizing the monomer phase thus can be written in the form

$$y(t) = (c(t) - c_{eq}(\infty))/c_{eq}(\infty) > 0 , \qquad (4.4)$$

where $c_{eq}(\infty)$ is the concentration of monomers in equilibrium with an infinitely large droplet (planar surface) : $c_{eq}(\infty) = p_{eq}/k_B T$.

To establish appropriate scales, we may introduce a "characteristic unit of time"

$$t_0 = c_\alpha d_0^2 (c_{eq}(\infty)D)^{-1} \sim 10^{-9} \text{ s} = 1 \text{ ns} \qquad (4.5)$$

for defining a reduced time $\tau = t/t_0$ instead of the dimensional time t, and a "characteristic unit of system size"

$$V_0 = (4\pi/3)d_0^3 c_\alpha/c_{eq}(\infty) \approx 10^{-23} \text{ m}^3 = 10^4 \text{ nm}^3 \qquad (4.6)$$

to make use of a reduced volume $\omega = V/V_0$ instead of the system size V.

We choose the number 1 of bounded monomers as the relevant variable for a droplet, but the other quantities describing an 1-mer can be easily defined as follows:

$$r(1) = (c_\alpha 4\pi/3)^{-1/3} 1^{1/3} \qquad \text{radius}$$
$$k(1) = (c_\alpha 4\pi/3)^{1/3} 1^{-1/3} = 1/r(1) \qquad \text{curvature}$$
$$v(1) = c_\alpha^{-1} 1 \qquad \text{volume}$$
$$A(1) = 4\pi (c_\alpha 4\pi/3)^{-2/3} 1^{2/3} \qquad \text{surface} \qquad (4.7)$$

We mention, that the distribution function (4.3) is normalized to the total droplet density (N_α - number of all drops)

$$\int_0^\infty f(1,t)dl = N_\alpha/V$$

and for the first moment of the distribution function we get the total number of bounded monomers M_α per volume

$$\int_0^\infty l f(l,t) dl = M_\alpha(t)/V .$$

In the following, we formulate the basic equations of the competitive growth problem. The droplet distribution function (4.3), which changes due to condensation and/or evaporation of monomers only, satisfies a continuity equation of the form

$$\frac{\partial f(l,t)}{\partial t} + \frac{\partial}{\partial l}(vf(l,t)) = j(t) ,$$ (4.8)

The production-decay term j in (4.9) vanishes when nucleation or such phenomena like coagulation, splitting, etc., are neglectable. We introduce new droplets of a given size class, which introduce

$$dl/dt = V(l,y) .$$ (4.10)

Conservation of matter implies that for a closed system the total number N of monomers (either free or bound) is fixed

$$c(t) + \int_0^\infty l f(l,t) dl = N/V ;$$ (4.11)

or with (4.4)

$$y(t) + (c_{eq}(\infty))^{-1} \int_0^\infty l f(l,t) dl = y_o ,$$ (4.12)

where $y_o = (N/V - c_{eq}(\infty))/c_{eq}(\infty)$ = const is the overall supersaturation. In a recent paper of VENZL the parameter y_o is time dependent for treating open systems /46/.

It is well known that growing and dissolving drops obey kinetic laws resulting from solutions of the diffusion equation. Employing the quasistationary approximation we assume that an individual drop grows (or dissolves) if the monomer concentration is greater (or less) than the equilibrium value. Therefore the growth law (4.10) which embodies much of the physics reads in the so-called interface kinetic limited case

$$dl/dt = v_{ik}(l,y) = D_o d^{-1}(c(t)-c_{eq}(l)) ,$$ (4.13)

where the equilibrium monomer concentration $c_{eq}(l)$ over a curved surface with curvature k(l) is

$$c_{eq}(l) = c_{eq}(\infty)\exp(d_o k(l)) \approx c_{eq}(\infty)(1+d_o k(l)) .$$ (4.14)

This curvature-dependent expression is the GIBBS-THOMSON equation indicating that atoms will flow from regions of high to low curvature.
From (4.13), (4.14) we obtain

$$dl/dt = D c_{eq}(\infty) d_o^{-1} A(l)(y(t)-d_o k(l))$$ (4.15)

and after introducing the critical droplet size l_c by

$$l_c(t) = (c_\alpha 4\pi/3)(d_o/y(t))^3 = c_{eq}(\infty) v_o y^{-3}$$ (4.16)

we are able to reformulate the kinetic law (4.10) in the form of the well-known droplet equation

$$dl/dt = Dc^{eq}(\infty)(c_\alpha 4\pi/3)^{1/3} A(l)(l^{-1/3} - l_c^{-1/3}) ,$$ (4.17)

which makes apparent the typical bistability situation with opposite behaviour of drops below and above the critical value l_c. We want to underline, that due to the conservation of monomers /4.11/ the critical droplet size is changing in time. Let us finally introduce a new measure of the droplet size in units of l_c by the dimensionless variable

$$z = 1/l_c .$$ (4.18)

Therefore the basic equations (4.9-11) written in dimensionless variables (4.4), (4.18) and reduced time τ are

$$\frac{\partial F(z,\tau)}{\partial \tau} + \frac{\partial}{\partial z}(v(z,y)F(z,\tau)) = 0 ,$$ (4.19)

$$y(\tau) + \frac{v_o}{y(\tau)^3} \int_0^\infty z F(z,\tau) dz = y_o ,$$ (4.20)

$$dz/d\tau = v(z,y,\dot y) = 3y^2 z^{2/3}(1-z^{-1/3}) + 3y^{-1} z (dy/d\tau) ,$$ (4.21)

with the scaled cluster distribution $F(z,\tau) = l_c^2 f(l,t)$ instead of (4.3). This coupled nonlinear integro-differential system can serve as the starting point for the analysis of the competitive growth problem of different droplets /35/.

5. Growth of one Droplet in a Closed System

Here we want to investigate the deterministic behaviour of one single droplet in a changing medium which agrees with the stochastic description (chapter 2,3). From the basic equations (4.19-21) we get in this simple case

$$dz/d\tau = \dot z = 3y^2 z^{2/3}(1-z^{-1/3}) + 3y^{-1} z(dy/d\tau) ,$$ (5.1)

$$y + z/(\omega y^3) = y_o ,$$ (5.2)

showing the kinetics $\dot z = v(z,y,\dot y)$ (5.1) and the conservation of monomers (5.2). Recalling the parameter $\omega = V/V_o$ (4.6) as reduced system size we reformulate (5.1), (5.2) in the following form

$$dz/d\tau = (3/\omega)y^{-2} z^{2/3}(1-z^{-1/3})/(\omega y^4 - 3z)$$ (5.3)

$$dy/d\tau = -(3/\omega)y^{-1} z^{2/3}(1-z^{-1/3})$$ (5.4)

and with (5.2) $z = \omega y^3(y_o-y)$ we find

$$dy/d\tau = 3\omega^{-2/3}(y_o-y)^{1/3} - 3\omega^{-1/3}(y_o-y)^{2/3} .$$ (5.5)

The analysis of the development of one droplet (5.3), (5.4) or (5.5) in dependence of the volume ω is shown in Fig. 9 and Fig. 10. For fixed overall supersaturation $y_o = 2$ we find a critical volume $\omega_c = 4^4/(3^3 y_o^4) = 16/27 = 0,5926$ (or $v_c = 3,1\cdot10^{-23} m^3$). For very small systems ($\omega < \omega_c$) we observe free monomers only, but for $\omega > \omega_c$ the coexistence of droplets and monomers is obvious. Overcritical droplets grow to their stable size.
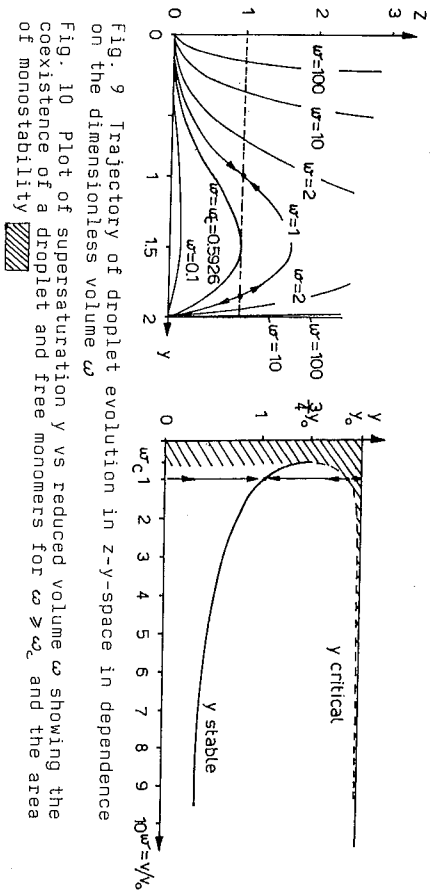
Fig. 9 Trajectory of droplet evolution in z-y-space in dependence on the dimensionless volume ω

Fig. 10 Plot of supersaturation y vs reduced volume ω showing the coexistence of a droplet and free monomers for $\omega \geq \omega_c$ and the area of monostability

6. Competitive Growth of an Ensemble of Droplets

To find solutions of the basic equations formulated in chapter 4 seems to be impossible. However, if the droplet ensemble consists of s kinds of drops with different sizes $1_1; \ldots; 1_i; \ldots; 1_s$ let us consider the discrete case. So we are able to obtain a system of ordinary nonlinear differential equations governing the constrained growth of droplets with $s \geq l$ components /35/. Note that the index i is now the number of a component; we get a system of equations (6.1,6.2) which can be solved numerically

$$\frac{dl_i}{d\tau} = c_\alpha\, d_0\, A(1_i)\left\{ d_0(\langle k\rangle - k(1_i)) - \frac{c_{eq}(\infty)V}{c_\alpha\, d_0} \frac{1}{A_\alpha}\frac{dy}{d\tau}\right\}$$

$$(i = 1,2,\ldots,s) \qquad (6.1)$$

with

$$\frac{dy}{d\tau} = - \frac{c_\alpha\, d_0}{c_{eq}(\infty)V} A_\alpha(\tau)\left\{ y_0 - \frac{c_\alpha}{c_{eq}(\infty)V}V_\alpha(\tau) - d_0\langle k\rangle\right\} \quad . \qquad (6.2)$$

Here we abbreviate as follows: $A_\alpha(\tau)$ - total surface of all droplets, $V_\alpha(\tau)$ - total volume of all droplets, $\langle k\rangle$ - mean curvature of the droplet ensemble.

The equations describe 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)). If the supersaturation is high enough, the droplets have the chance to grow up. Since the raw material is limited the system will reach at first a so-called internal equilibrium. When the flow between the liquid phase and the vapor is decreasing to zero, a competitive ripening process takes place. In this selection game the smaller droplets with $k(1_i) > \langle k\rangle$ must dissolve to give mono- mers to the bigger ones which increase. Since the mean curvature $\langle k\rangle(\tau)$ is a slowly decreasing function of time in the limit $\tau \to \infty$ only one component of the droplet phase is present and the station- izing system has reached its stable stationary situation (Fig. 11). It is obvious that our resulting equations (6.1,6.2) are a rea- listic physically motivated example for natural selforganization. It was pointed out by EIGEN /47/ and others /48/ that Darwinian evolution can be characterized by an extremum principle, which de- fines the behaviou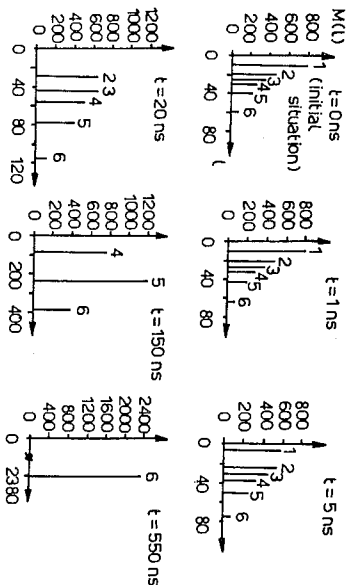r of selfreplicative units. Under stated selec- tion constraints in bio- or ecosystems (compare the constant over- all organization) the population numbers of all but one species will disappear. In the Fisher-Eigen model of prebiotical evolution

$$\frac{dx_i}{dt} = (E_i - \langle E\rangle)\,x_i \qquad \text{with} \qquad \sum_{i=1}^{s} x_i = c \qquad (6.3).$$

the species with the highest reproduction rate $E_m = \text{Max}\{E_1;\ldots,E_s\}$ (selection value) will increase to the finite value C and all others must die out ($x_i \to 0$ for $i \neq m$). Note that in both cases (Fisher-Eigen model with population average fitness $\langle E\rangle$, Ostwald ripening of droplets 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 /49/. As we demonstrated, there is an inter- esting analogy in modeling phase transitions on the one hand and evolution processes in biophysics on the other.

Fig. 11 Time evolution of a droplet ensemble showing the monomer distribution function $M(1,t) = 1 \cdot N(1,t)$. Numerical solution of (6.1,6.2) with s=6 groups of drops

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Dynamic Chaos in Ensembles of Structures and Spatial Development of Turbulence in Unbounded Systems

A.V. Gaponov-Grekhov and M.I. Rabinovich

Institute of Applied Physics, Academy of Sciences of the USSR, SU-Gorki, USSR

1. Development of Chaos in Ensembles of Dynamic Structures

1.1. Dynamic Structures

Development of spatial instabilities in nonequilibrium dissipative media is often a cause of regular formations which appear as ensembles of identical (or similar) elementary cells or dynamic structures. Rolls observed in thermoconvection in a plane-horizontal layer, Taylor vortices in the Couette flow between rotating cylinders, large vortices in underwater jets, wakes and other shear flows are examples of such dynamic structures. The onset of developed turbulence in a nonequilibrium medium is often preceded by several stages of gradual complication and transformation of the structures. For example, structures with individual or collective degrees of freedom excited against the background of a regular ensemble. First, as a rule, the structures begin to oscillate: for example, bending oscillations of convective rolls or azimuthal waves in Taylor vortices or in toroidal vortices in underwater jets appear. Then, with a further increase in supercriticality, the coupling between the neighbouring elements weakens and the resulting nonequilibrium medium can be considered (in a certain range of parameters) as a discrete ensemble of interacting oscillating structures.

1.2. Example. Chaotic Self-Modulation of Two-Dimensional Structures on the Surface of a Fluid at Parametric Excitation

Let us consider transition to turbulence via chaotic modulation of two-dimensional structures on the surface of a viscous fluid in a periodically oscillating homogeneous field of gravity /1/. Transition to chaos in our experiments was observed on a horizontal surface with about 10^4 cells-oscillators. Irrespective of the shape of the boundaries, turbulence occurred against the background of two-dimensional structures due to their self-modulation that was random in space and time. We used a layer of silicon oil 0.5 cm thick on a plane surface of a vibrator. The surface of the fluid was photographed in reflected light with subsequent space Fourier analysis of the image contrast using an optical spectrum analyser.

As the oscillation amplitude of the cells increased the following transitions were observed. A regular grating with square cells appeared at the first critical value of the vibration amplitude R cr. The grating was formed by two pairs of parametrically excited travelling waves (photo a) in Fig. 1). These pairs of waves propagated orthogonally, irrespective of the shape of the cell boundaries, thus forming a tetrahedron.

A further increase in R resulted in the appearance of modulation waves with a space period of the order of the cell size. The direction of their propagation coincided with that of the parametrically excited waves forming the tetrahedron. With a still further increase