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Irreversible thermodynamics and true thermal state dynamics in view of generalised solid-state reaction kinetics

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Abstract

Reaction dynamics of processes involving solids are extensively studied by thermal analysis methods. They are often solved almost naively by analogy with apparently gradientless homogeneous reactions. Other oversimplified approximations involve the regular shape of reacting particles that are assumed to be circles or spheres regardless of their true texture (stereology). This model never matches the results of traditional morphology observations. This article points the direction where a more rigorous solution should go by introducing a more actual state of the sample but, unfortunately, is yet unable to show the practical way how to actually bring in the challenge of entire introducing fluxes incorporation which solution makes difficult mathematical problem but it enables wide options of state of the system. Practical examples are illustrated on the flux-dependent growth of dendrites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemical reaction; Diffusion; Solid-state; Gradients; Fluxes; Temperature fluctuation; Unstable interface; Dissipations; Irreversibility; Stereology; Bifurcations; Solidification; Undercooling; Non-equilibrium growth; Dendrites

1. Introduction

> *Motto: "reading literature on kinetics of solid-state processes and, in particular, the papers on non-isothermal kinetics, one cannot help noticing the similarities between Science and Religion" Brown [1].*

Reaction dynamics of processes involving solids are extensively studied by thermal analysis methods [1,2], i.e. under conditions where the heat flow is supplied to or absorbed from the investigated sample by means of a surrounding thermostat which is under temperature control (regulated at constant or under spontaneous heating/cooling). There is a vast amount of data published on such "non-isothermal" kinetics of solid-state processes frequently treated on the basis of oversimplified (and customarily isothermal) modelling [3–7]. It became a subject of criticism and discussion, e.g. [1,6–11], which we do not want to repeat, other than stressing that real solid-state reactions are often too complex to be described in terms of single pairs of Arrhenius parameters and a traditional set of simple reaction orders, i.e. rational exponents representing our models of the reaction mechanism under study [4–7]. Even the participation of the most evident flux-diffusion is seldom recognised, other than by the appearance of overall (characteristic) time-dependent terms [10].

However, the modern tools of thermal physics make available powerful mathematical models associated with the reality of natural processes that are never at

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equilibrium nor without gradients by appreciating the decisive role of thermal fluxes. In the scientific intent (publications) of non-isothermal kinetics it, however, has not been applied yet but in the more urgent technological processing, such as industrially significant arc melting or welding, its solution became a real necessity to overcome feasible manufacturing difficulties. In particular, we can generally assume that at some distance from the reaction zone where the solidification is taking place, the molten material undergoes irregular (turbulent) motion. It creates a mushy zone consisting of cascade of branches and side branches of crystals and interspacial melts that remains lying between the original reactant (fluid) and the product (fully solidified region). Some chemical admixtures of the alloy solution are concentrated in the interspacial regions and ultimately segregated in the resulting microtexture pattern. Such a highly irregular microstructure of the final solid can become responsible for alternative properties, e.g. reduced mechanical strength that is a costly factor thus worthy for an active search as to resolve the intricacy of the processes involved. It follows that small changes in the surface tension, microscopic temperature fluctuations or non-steady diffusion may determine whether the growing solid looks like a snowflake or like seaweed. The subtle way in which tiny perturbations at the reacting interface are amplified then become important research topics bringing necessarily into play a higher mathematics. The challenge of theorists turns out to be the prediction of spacing of the final crystalline array which requires computations how the initially stationary flat interface accelerates in response to the moving temperature gradient, how local concentrations (e.g. impurities) adjust to this motion, how the flat interface destabilise and became branched, how the resulting crystalline twigs interact with each other and how the branched array coarseness and ultimately finds a steady-state configuration. In every details it is not an easy task at all.

A real solid-state reaction under thermoanalytical investigation, even those most ideal one, is intrinsically more complicated than most of us would like to believe. As emphasised above, we will have to deal with these complications, usually caused by actual localisation of generated heat, liquids and gases (or other freely moving products) if we are to achieve new levels of performance. The conceptual underpinnings for much of our more advanced perception of phase transformations have thus to use complicated mathematics that is curiously employed to describe both the pattern formation in crystal growth and the so called symmetry breaking (the origin and distribution of elementary particles in the early Universe). Therefore, such an intricate approach is not too welcome in the ordinary practice of chemical kinetics and its further application to daily kinetic evaluations has not been assumed as yet. Our contribution tries to point the direction where we should go but, unfortunately, is yet unable to show the practical way how to actually bring in the challenge of entire fluxes incorporation which solution thus sustains the imminent task for both the advanced research to take part during this new century and the newly educated generation of young thermodynamists to undertake it.

2. Current approach

Our originally proposed theory, based on generalised (near-equilibrium) thermodynamics applicable to thermal treatment and analysis, employed conditions of constant heating [4,11,12] (i.e. constant first derivatives, particularly those regarding the change of temperature, $\mathrm{d}T/\mathrm{d}t$, assuming that $\mathrm{d}^2T/\mathrm{d}t^2 = 0$) supposing only the straightforward heat interaction between the sample and regulated thermostat. It does not involve the actual effect of heat liberated and/or absorbed by the reacting sample itself so that it is herewith extended to areas so far not commonly applied in the traditional domain of thermal analysis, although it is most pertinent to its feature of "real heating and/or cooling" phenomena (where the second derivatives can often be non-zero, in general notation $\mathrm{d}^2x/\mathrm{d}t^2 \neq 0$). Moreover, classical sphere of thermodynamic definitions of stability are inapplicable to the determination of the morphology of growing interfaces, and current extensions have not yet furnished a fully acceptable alternative. The simplest assumption made is that the morphology which appears is the one which has the maximum growth rate and/or minimum undercooling (or less commonly overheating). This assumption can be justified on the basis of minimum (non-equilibrium) entropy production. In contrast to aspects of the classical thermodynamics, these new "true flow" features, which should be taken into account in all actually studied thermal processes are the subject of the *thermodynamics of irreversible processes* [12–23] and are thus the issues worthy of discussion.

Classical kinetics of solid-state reactions is mostly performed by assuming physical–geometrical model functions reflecting chemical changes at the flat reaction interface in its systematic advance into the unchanged reactant. These models are derived on the basis of a formal description of geometrically well-defined sample bodies [3–9]. It is assumed that it is possible to transfer concepts from the convenient, simple geometry of homogeneous-like kinetic models (represented by non-dimensional concentration) to idealised heterogeneous (dimension-like geometry) models [6,24,25] (represented by the surface versus volume ratio between the reactant and product phases and based on the derived representation by a dimensionless fractional degree of conversion). Space dimensionality is factually introduced through the formation of a reaction interface and the consequent possibility of multi-dimensional interfacial forward movement—called *growth*. However, the more adequate aspects of *fractal geometry* [24,26] and/or *integral geometry* (stereology) [27,29] have not been put into wider use as yet.

Disregarding the initial process of new phase formation (nucleation) the kinetic models are described in terms of the overall atom attachments to the reaction interface due to either chemical reaction (bond redistribution steps) or interfacial diffusion (reactant supply). A stabilised (steady) state is taken for granted neglecting, however, directional changes (fluctuations). The models also neglect other important factors such as interfacial energy (immediate curvature, capillarity) and particularly, internal/external transport of heat and mass to and from the localised reaction boundary which may result in the breakdown of planar reacting interface, which anyhow, at the end of process, often exhibits complex topology (resulting microstructure). Various activated disturbances are often amplified until a marked difference in the progress of the tips and depressions of the perturbed reacting interface occurs, making the image of resultant structures irregular (unrefinable), see Fig. 1. This creates difficulty in correlating traditional morphology observations with anticipated structures that are

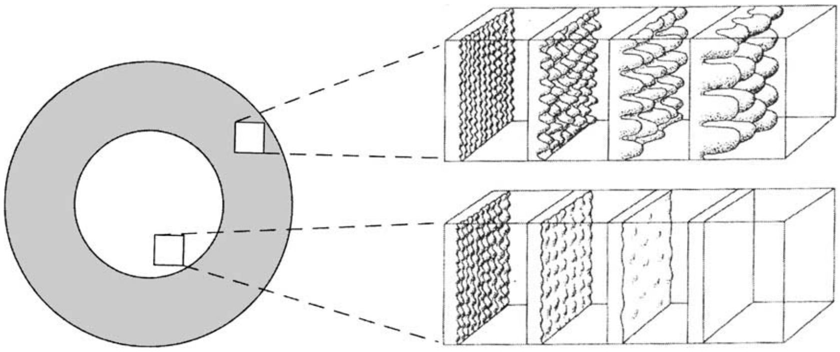

Fig. 1. Initial evolution of an unstable and stable interface. Let us imagine a planar section of a reacting interface (left). During its propagation, any such interfaces will become a subject to random (spatially regular) disturbances caused by temperature fluctuations, variations of grain boundaries, curvature, insoluble subdivisions, concentration fluctuations, energy irregularities, etc. An unstable interface (upper) is distinguished from a stable interface (lower, assumed in all physical–geometrical modelling such as a contracting sphere, left) by its response to such disturbances. Projections may find themselves in a more advantageous situation for growth and therefore increase in prominence. Shadow area of the left magpie can represent either the traditionally, plainly projected and homogeneously layered product or, in our view, perturbation favoured, heterogeneous and thus morphologically vastly structured growth outcome. This is usually the best manifested during the casting of alloys, and/or rapid quenching in general, where a stable interface is only obtained in special cases, such as at the columnar solidification of pure metals or directional solidification during pulling single crystals by the stabilised methods by the Bridgeman or Czochralsky. It seems to operate for all transformations carried out at high rates of cooling/heating, or latent heat extraction/production, where the cooperative outcome of heat, mass (including decomposition products) and viscous (tension) flux initiates local instabilities. We can also meet it in everyday events of snowflakes formation.

usually very different from the originally presupposed (simple, planar) geometry. Depending on the directional growth conditions, so-called *dendrites* (from the Greek '*dendros*' = tree) develop, their arms being of various orders and trunks of different spacing due to the local uneven conditions of heat supply. This process [28–34] is well known in metallurgy (quenching and casting of alloys), water and weather precipitates [35–37] (snow flakes formation, crystallisation of water in plants) but also for less frequent types of other precipitation, crystallisation and decomposition processes associated with dissipation of heat, fluids, etc.

It is always interesting to see how far the use of classical methods can be extended in this non-equilibrium situation. Growth rates, undercoolings and supersaturations are closely related by functions whose forms depend upon the process controlling growth [28,29] (the chemical reaction involved in the atomic attachment, heat and electrical conduction, or mass and viscous flow). In each case, the growth rate increases with increasing degree of undercooling and the perturbation on the reaction interface can be imagined to experience a driving force for such an accelerated growth usually expressed by the negative value of the first derivative of the Gibbs (free) energy change, ΔG, with respect to distance, r. For small undercoolings, we can still adopt the above-mentioned concept of the constancy of the first derivatives [4,12], so that $\mathrm{d}\Delta G$ equals to the product of the entropy change, ΔS, and the temperature gradient, ΔT, which is the difference between the thermodynamic temperature gradient (associated with transformation) and the heat-imposed gradient at the reaction interface as a consequence of external and internal heat fluxes. Because ΔS is often negative, a positive driving force will exist to allow perturbations to grow, only if ΔT is positive. This pseudo-thermodynamic approach gives the same result as that deduced from the concept of zone constitutional undercooling [32] and its analysis is important for the manufacturing of advanced materials (fine-metals, nano-composed assets, growth of quantum-low dimensional possessions, composites and whiskers, tailored textured configurations, growth of biological structures, processes involving water freeze-out in, e.g. cryopreservations, etc.) and thus, it is worth further and more detailed examination.

3. Impact of non-equilibrium thermodynamics

Any treatment of classical thermodynamics begins with some sort of statement of the principle of conservation of energy, E, (1st law) defining the mechanical concept of work and introducing temperature, T, as an integrating factor of a certain differential equations (which apparently eliminates heat from thermodynamics). If we could identify heat, q, with entropy, S, the mysterious 2nd law becomes quite intuitive and very easy to understand when imagining that heat cannot be annihilated in any real physical process. In classical thermodynamics (understood in the yet substandard notation as "thermostatics") we generally accept for processes the non-equality $\mathrm{d}S \geq \mathrm{d}q/T$ accompanied by a statement to the effect that, although $\mathrm{d}S$ is a total differential, being completely determined by the states of system, $\mathrm{d}q$ is not. It has the very important consequence that in an isolated system $\mathrm{d}q = 0$ and entropy has to increase. Because in isolated systems processes move forwards equilibrium, the equilibrium state corresponds to maximum entropy. In true non-equilibrium thermodynamics, the local entropy follows the formalism of extended thermodynamics [13–22] where gradients are included and small corrections to the local entropy appear due to flows making $(\mathrm{d}S/\mathrm{d}t) \geq (\mathrm{d}q/\mathrm{d}t)(1/T)$. The local increase of entropy in continuous systems can be then defined by using the local production of entropy density, $\sigma(r, t)$. For the total entropy change $\mathrm{d}S$, consisting of internal changes and contributions due to interaction with surroundings, i and e, we can define the local production of entropy as $\sigma(r, t) \equiv \mathrm{d}_i S/\mathrm{d}t \geq 0$. The irreversible processes obey the Prigogine evolution theorem about the minimum of the entropy production [22].

Traditionally, the phenomenological description of macroscopic systems is based on a selected number of *observables* accessible by macroscopic measurements. These may be intensive, I (temperature T, pressure P, magnetic field H, etc.) or extensive, X (energy E, entropy S, volume V, mass m, momentum $\boldsymbol{u}$, dimensionless extent of reaction α, etc). Classical thermodynamic systems at (infinitesimal $\mathrm{d}I$ and $\mathrm{d}X$) or near equilibrium including its extension to constant heating [4,11] (assuming real ΔI and ΔX) cannot depict the often disturbing role of heat fluxes, $\mathrm{d}q/\mathrm{d}t$. In most real situations, we can assume local equilibrium, where thermodynamic relations remain valid for the thermodynamic variables assigned to an elementary volume ΔV [14,15]. With each extensive quantity, X, we can associate a density (quantity per unit volume) through the function $x(\boldsymbol{r}, t)$ dependent on position, $\boldsymbol{r}$, and time, t,

$$x(\boldsymbol{r}, t) = \lim_{\Delta V \to 0} \frac{X(\boldsymbol{r}, t)}{\Delta V} \qquad (1)$$

For the total value of the extensive quality

$$X(t) = \int_V x(\boldsymbol{r}, t)\, \mathrm{d}\boldsymbol{r} \qquad (2)$$

where the space integral, $\int_V$, extends over the volume, V, occupied by the system under study.

4. Introducing fluxes

By manipulating various factors that influence the rate of change of $X(t)$ in a non-equilibrium system, we can obtain a balance equation for the density $x(\boldsymbol{r}, t)$ by specifying hydrodynamic derivatives (d/dt a total time derivative) thus maintaining the view of continuum mechanics. The general balance of $x(\boldsymbol{r}, t)$ has the form:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\mathrm{div}\boldsymbol{j}_x + \sigma_x \qquad (3)$$

where σ_x is density of the source of value x, and $\boldsymbol{j}_x$ is the non-convective (dissipative) part of the flux of a particular x (e.g. diffusive flux, thermal flux, viscosity flux, etc. i.e. fluxes responsible for the actual condition of a given region of the reacting interface). In the case of a mass balance or an energy balance, we have

$$\frac{\mathrm{d}\rho_i}{\mathrm{d}t} = -\mathrm{div}\, \rho_i \boldsymbol{u}_i + \nu_i \; (\text{mass balance}) \qquad (4)$$

and

$$\frac{\rho \mathrm{d}E}{\mathrm{d}t} = -\mathrm{div}\boldsymbol{j}_\mathrm{E} + \rho q \; (\text{energy balance as a local form of the first law of thermodynamics}) \qquad (5)$$

where ρ is the total mass density and ρ_i is the partial mass density of the ith subsystem. Some other appropriate fluxes like the momentum density, $\rho_i \boldsymbol{u}_i$ (for individual velocities u_i which principally also include diffusion) or the heat flux $\boldsymbol{j}_\mathrm{E}$, and those expressing the presence of sources or sinks, like rates of chemical reactions ν_i or density of supplied heat, q may also be included. In this generalised thermodynamic view the notion of irreversibility is of the utmost importance and a local field derived from entropy must again obey the Clausius inequality. The temporal change of the total entropy S in some subsystem is due to both the interaction of the system with its surroundings (the entropy flux $\mathrm{d_e}S$) and the internally produced entropy ($\mathrm{d}_i S$). Moreover, $\mathrm{d}S - \mathrm{d}_e S = \mathrm{d}_i S > 0$. In a like manner to Eq. (3) we may write

$$\frac{\rho \mathrm{d}S}{\mathrm{d}t} = -\mathrm{div}\boldsymbol{j}_\mathrm{S} + \sigma \; (\text{local form of the second law of thermodynamics}) \qquad (6)$$

where $\boldsymbol{j}_\mathrm{S}$ and σ are the entropy flux and the entropy production per unit volume, respectively.

Let us consider the extension into the range of nonlinear phenomenological laws where the balance Eqs. (3)–(6) have a general form

$$\frac{\mathrm{d}\Phi_i}{\mathrm{d}t} = f_i(\{\Phi_i\}, \Psi) \qquad (7)$$

where Φ_i and f_i are shorthand notations for the state variables and the rates respectively. In general, f_i are functionals of $\{\Phi_i\}$ because they contain the effect of space derivatives. The symbol Ψ stands for a set of parameters that may enter in the description to define the process. Within the framework of linear nonequilibrium thermodynamics, the mass and entropy balance Eqs. (4) and (6) would give certain forms for f_i as summarised in Table 1 which illustrates the various type of fluxes, that can be involved.

The entropy flux $\boldsymbol{j}_S = \boldsymbol{j}_\mathrm{E}/T - \sum_i \boldsymbol{j}_i \mu_i / T$ and the entropy production take a remarkable bilinear form $\sigma = \sum_a J_a X_a$, where J_a and X_a are conjugate variables known as generalised fluxes and forces associated with the various irreversible processes, see also Table 1. *Generalised forces can be viewed as the driving forces for irreversible phenomena which are manifested through the fluxes* (*e.g. a temperature gradient is associated with a heat flow*). Such gradients may arise transiently, or be maintained systematically, by appropriate boundary conditions (constraints) applied on the surface of the system studied. For the local formulation of irreversible processes, it is necessary to see how the fluxes J_a (which in principle are unknown quantities) are related (if at all) to the forces X_a which, according to Table 1, are known functions of the state variables

Table 1
Fluxes and forces corresponding to irreversible phenomena

Process	Flow/current	Generalised force	Tensor character
Chemical reaction	Reaction rate (w)	Affinity (A_ρ/T)	Scalar
Heat conduction	Energy flow ($\boldsymbol{J}_\mathrm{E}$)	($\nabla T/T$)	Vector
Mass transport	Diffusion current ($\boldsymbol{J}$)	$-(\nabla \mu_i/T)$	Vector
Electrical conduction	Ion current ($\boldsymbol{J}_k$)	$-\nabla(U/T)$	Vector
Viscous flow	Stress tensor ($\boldsymbol{P}$)	$-(1/T)\nabla \boldsymbol{u}$	Tensor

∇ represents the gradient of the appropriate function, i.e. it means the vector which components are derivatives of the space coordinates x, y and z, μ_i is the chemical potential of the ith component, U is the potential of the electric field.

and their gradients (we should note that the above mentioned classical equilibrium is characterised by the absence of both the macroscopic constraints, $X_a^{\mathrm{eq}} = 0$ and travelling fluxes $J_a^{\mathrm{eq}} = 0$).

In the linearity range of irreversible processes, the phenomenological Onsager coefficients, L_{ab} [19,21], are determined by the internal structure of the system, independently of the applied constraints (but dependent on the state variables $X(t) = T, P, \ldots$) yielding $J_a = \sum_b L_{ab} X_b$ where $L_{ab} = (\mathrm{d}J_a/\mathrm{d}X_b)_0$, fulfilling $\sigma = \sum_{ab} L_{ab} X_a X_b > 0$. An important issue of dynamic equations is the stationary solution which describes the state of the system that is independent of time. The answer to the question of how this state remains stable during the action of small fluctuations of physical values (fluctuations are usually damped with time), lies in the criteria of stability. Linearised stability asserts asymptotic stability around its reference state, e.g. $X_i = X_{i,\mathrm{ref}} + \mathrm{d}X_i$ (for $\mathrm{d}X_i/X_i \ll 1$) and expanded for small $\mathrm{d}X_b$ we obtain, in abstract notation, $\mathrm{d}\{\mathbf{d}\boldsymbol{x}\}/\mathrm{d}t = \boldsymbol{L}\,\mathbf{d}\boldsymbol{x}$, where $\boldsymbol{L}$ is a linear operator and the problem is solved by determining so called eigenfunctions and eigenvalues of $\boldsymbol{L}$ and the unseen characteristic parameters m. The reference state is asymptotically stable for most m but, for some m, the solution of such a thermodynamic branch is unstable and, for critical values of Ψ_{crit}, *bifurcation* appears, in other words, several quite different evolutions of the system are possible and that which is realised depends on Ψ in a non-analytical fashion (a special domain of non-linear mathematics).

5. Stereology aspects

In the special case of non-isothermal reaction kinetics, which regularly involves solid-state processes, the rate equations are often solved almost naively by analogy with apparently gradientless homogeneous reactions. Other oversimplified approximations (as mentioned above where reacting particles are often assumed to be regular circles or spheres regardless of their true morphology) are introduced that never match the results of traditional morphology measurements by, e.g. light or electron microscopy. This is worth of similar attention, being related to the above discussed case of disregarded temperature and concentration gradients. This simplification aspect is often neglected, although very important, because we have to keep in mind that all possible images (postulated geometrical models or real structures seen on a screen, or otherwise observed) are only two-dimensional representations of the real three-dimensional structures. For a more objective evaluation of the numerical characteristics of real geometrical bodies we, therefore, have to employ so called *steorology*, understood here as integral geometry.

Invariant measures of the internal configuration of a multiphase body (where individual phases $A, B, \ldots$ internally form three-dimensional structures must fulfil three basic criteria: invariance of *motion*, *additivity and monotony* which corresponds to a mathematical hypothesis based on the four Minkowski functionals [29] (quermass integrals or measures) abbreviated as W_i^3. These measures have, for each i, a definite practical meaning, i.e. volume of A, W_0^3, mean area (surface), W_1^3, length, W_2^3 and number of disjunctive features of A (e.g. number of opened against closed structural holes), W_3^3, needed for a global geometrical characterisation M. It follows that $M_i^3(A) = \sum c_i W_i^3(A)$ where each $W_i^3(A)$ is a homogeneous functional of the root $(3 - i)$ and $M_i^3(A)$ is then a monotonous functional ($c_i > 1$). For actual calculations, the two-dimensionally screened images

Table 2
Measure of the induced structure

Measure of structure (A)	Section by random probe L_i^3		
	Plane L_2^3	Line L_1^3	Point L_0^3
Volume (V_3)	A_2	L_1	P_o
Surface (S_2)	B_1	I_o	
Length (D_1)			

can be used bearing in mind, however, that these evaluations are only statistical. The solution is based on the utilisation of so-called symmetrical functions of curvature, $C^3_{i=1,2,3}$, providing the relations for mean curvature ($C_0^3 = 1$), Gaussian curvature ($C_1^3 = (k_1 + k_2)/2$) and fundamental curvature ($C_2^3 = 1/(k_1 k_2)$), where $k_1 = 1/\rho_{\min}$ and $k_2 = 1/\rho_{max}$ are the main curvatures for minimal and maximal radius of the oscillation circles in a given infinitesimal element of the measured phase surface ∂A. Objective proofs of stereological relations are difficult, but the resultant relations reveal surprising simplicity. A convenient universal relation is based on the so-called Kubota's recurrent formula [28] showing that $W_0^3(A) \Rightarrow V(A)$ (i.e. approaches the n-dimensional volume of A in the sample space E) which is the mean value of the W_{i-1}^{n-1} for all projections of the phase A onto the linear subspace with a lower dimension ($n - i$), providing more generalised values of constants $\sigma_{0,1,2,3} = 2$, 2π, 4π and $2\pi^2$. From measurements in a random section (planar or linear probes or random points) of the investigated structure, we can obtain concrete values of the quantities introduced in Table 2 and illustrated in Fig. 2.

It is clear that introduction of the actual state of the system, either real body structures or imposed gradients, is not easy. The introduction of legitimate non-equilibrium phenomena in the non-linear range leads to new regimes differing quantitatively from the "reference" stationary states of regular equilibrium or near-equilibrium descriptions.

6. Dissipative structures

The question that arises is, therefore, whether the move away from a standard configuration can lead to states displaying spatial or temporal order. We call these regimes dissipative structures to show that they can only exist in conjuction with their environment and if influence constraints are relaxed and the system is allowed to approach equilibrium, the entire organisation will collapse. They can form only in open systems far from equilibrium and dynamic equations have to be non-linear. The best example comes from fluid dynamics when a horizontal fluid layer is heated from below. When the temperature gradient remains small with respect to some characteristic values, heat passes through the fluid by conduction. As the heating is intensified, however, at a certain well-defined critical temperature the gradient pattern (regular due to convention) changes spontaneously, being organised in a cell-like fashion. This high degree of molecular/cell organisation becomes possible through transfer of

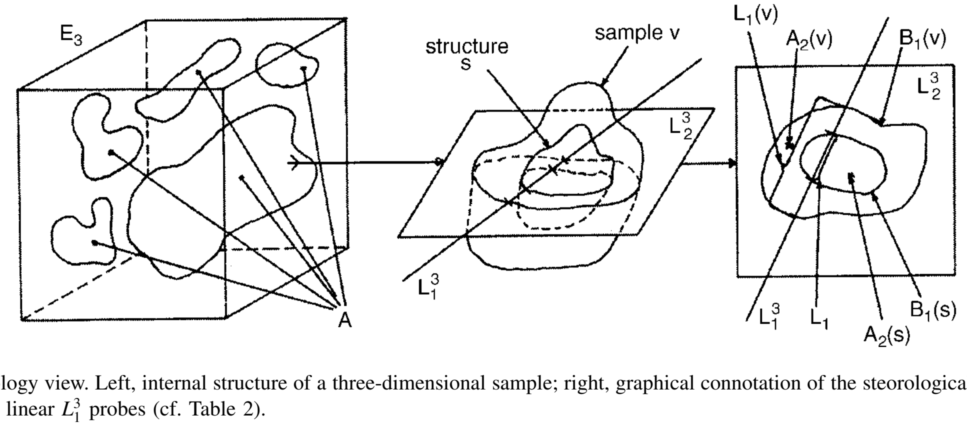

Fig. 2. Stereology view. Left, internal structure of a three-dimensional sample; right, graphical connotation of the steorological quantities for planar L_2^3 and linear L_1^3 probes (cf. Table 2).

energy from thermal motion to macroscopic convection currents. A similar situation can occur at a reaction interface under the cooperative action of thermal and concentration gradients, within yet unreacted layer of reactants (solidification). Other examples are the Belousov–Zhabotinsky reaction [39] or the variety of biophysical signals emitted by living cells to control a number of key processes.

Let us analyse the simplest cases of bifurcation. Higher-order non-linearities, by involving two or more variables in connection with spatially inhomogeneous systems, give rise to more complex phenomena. The best examples are systems controlled by simultaneous chemical reactions and mass diffusion. Their evaluation is given by Eq. (3), with the additional assumption that the diffusion flux $\boldsymbol{j}_i$ is approximated by Fick's law, a special form of the linear phenomenological laws given in Table 1, that is

$$\boldsymbol{j}_i = -D_i \nabla \rho_i \tag{8}$$

where ∇ is the above mentioned space derivative and D_i are the diffusion coefficients which are in the first approximation, assumed constant. The reactions rates, w_ρ, are (generally non-linear) functions of the concentrations (often in a cubic manner). This gives rise to the following evolution equation

$$\frac{\mathrm{d}\rho_\mathrm{i}}{\mathrm{d}t} = v_i\left(\sum_i \rho_i, \Psi\right) + D_i \nabla^2 \rho_i \tag{9}$$

where Ψ denotes again a set of parameters descriptive of the system (e.g. initial composition, cooling rate, undercooling, characteristic lengths, etc.). When $\Psi = \Psi_\mathrm{crit}$, the state of the system may change dramatically causing the symmetry breaking in space and time. From the mathematical point of view, the system becomes localised at the thermodynamic branch and the initially stable solution of the appropriate balance equation bifurcates. New stable solutions suddenly appear and may overlap. One possibility is time-symmetry breaking, associated with the merging of time-periodic solutions known as limit cycles whose period and amplitude are stable and independent of the initial conditions. Their importance lies in the fact that they can constitute models of rhythmic phenomena observed in nature, particularly biological or chemical clocks. Cascading bifurcations are also possible. This opens the way to a gradual increase of complexity by a mechanism of successive transitions, leading either to the loss of stability of a primary branch and the subsequent evolution to a secondary solution displaying asymmetry in space similar to stable rotating waves as observed in the classical Belousov–Zhabotinsky reaction [38,39]. Such transitions are sometimes accompanied by some remarkable trends, e.g. certain classes of reaction-diffusion systems under zero-flux boundary conditions, may exhibit no net entropy production change when the system switches from the thermodynamic branch to a dissipative structure. On the other hand, there is a systematic decrease in entropy in the vicinity of bifurcation points. Associated fields are the theory of chaos [40–43], fractals [44] and some aspects of the prediction of weather [35].

7. The chaotic case of dendritic growth

One of the most practical applications is the highly non-equilibrium crystallisation of highly supersaturated solutions or, as mentioned above, any solidification of rapidly quenched alloys. They exhibit a free dendritic growth, i.e. unconstrained development of curious shapes of crystals precipitating within concentration or temperature gradients (mostly in undercooled melt). This phenomenon has long been known in the technology of the crystal growth and is exemplified in the formation of cellular structures [27]. Explanation of this complex phenomena is usually done in terms of constitutional undercooling, ΔT, and its thermodynamic meaning is associated with the local equilibrium temperature of the melt solidification in an arbitrary point near the solidification front. It corresponds to a local concentration in the melt which is higher than that for the actual temperature in the same point. Consequently, the disturbance of the solidification front spontaneously increases and the phase interface become unstable, see Fig. 3.

The formation of a dendrite begins with the breakdown of an unstable planar solid/liquid interface, cf. Fig. 1. Perturbations are amplified until a marked difference in growth of the tips and depressions occurs. The temperature gradient must be deformed in the liquid at the tip increases, while that in the solid decreases. Therefore, more heat will flow into the tip and less will flow out of it. Meanwhile, the reverse

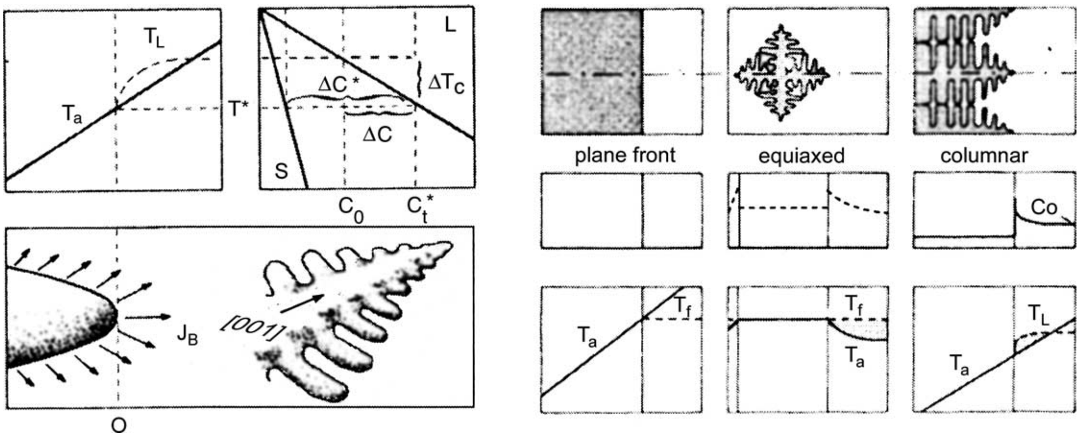

Fig. 3. The conditions of dendritic growth. The right diagrams illustrate the reacting front geometry (upper), temperature (bottom) and concentration (middle) fields resulting in dendrite growth. T_q is the temperature field in the system, T_f the equilibrium temperature of solidification, T^* the growth temperature, T_l the temperature of liquidus, C_0 the concentration in the liquid phase, ΔC^* the supersaturation (as a length of the tie-line at the temperature tip), G the temperature gradient and mG_c the gradient of liquidus (l). In pure substances with the plane ($C_0 = 0$ and $G > 0$) or equiaxed ($C_0 = 0$ and $G < 0$) front dendrites can grow in an undercooled melt only. The necessary condition of dendritic growth in binary systems is a constitutional undercooling, illustrated for both the columnar (dashed, $C_o > 0$ and $mG_c > G > 0$) and equiaxed ($C_0 > 0$ and $G < 0$) conditions. When a positive gradient of temperature ($G > 0$) is imposed (such as directional columnar solidification) the latent heat is transported together with unidirectional heat flux into the solid(s). When heat is extracted through the solid the solute diffusion will be the limiting factor only. ΔT_c, see phase diagram left, factually provides the degree of supersaturation, $\Delta C/\Delta C^*$, but its determination is also a function of other parameters and requires its evaluation by a set of differential equations. The simplest solution is obtained when the tip morphology is supposed to be hemispherical, instead, the real form of the dendrite tip is best represented by a paraboloid of revolution. Due to the anisotropy the dendrite will grow in the preferred crystallographic direction which is closets to the heat flow, J_B, whereas cells grow with their axes parallel to the heat flow direction without regard to the crystal orientation (e.g. marked [0 0 1]). In the opposite case of one component system the heat is rejected at the interface of a tip into the liquid phase. Consequently, the equiaxial dendrites emerge in solid phase.

situation occurs in the depressions forcing perturbations to be damped out. Moreover, the equilibrium temperature at the interface, determined mainly by composition, is changed as a consequence of the local interface curvature. Because the tip can also reject solute in the lateral direction, it will tend to grow more rapidly than a depression, which tends to accumulate the excess solute rejected by the tips. Therefore, the form of the perturbation is no longer (initially) sinusoidal but adopts the form of cells which are ellipsoid-like crystals growing anti-parallel to the net flux direction. If the growth conditions continue close to the limit of constitutional undercooling of the corresponding planar interface, tree-like formation occurs and the cells rapidly change to dendrites, which then exhibit secondary arms and crystallographically governed growth directions. If the heat extraction is isotropic, dendritic growth is equiaxial. For a single dendrite, a short parabolic tip region can be observed which often constitutes less than 1% of the length of the whole dendrite and perturbation appear on the initially smooth needle as in the case of the breakdown of the originally discussed planar interface. If the primary spacing is sufficiently great, these cell-like secondary branches will develop into dendrite-type branches and thus leads to the formation of tertiary and higher-order arms. When the tips of the branches encounter the diffusion field of the arms of neighbouring dendrite, they will stop growing and begin to ripen and thicken. Beside the normal temperature gradients discussed above, the radial temperature gradient can also be accounted through convention usually originating by the non-homogeneous distribution of the mass density throughout the fluid (Rayleigh–Bernard instability [29,34]) or by variation of the surface tension of free surfaces (Marangoni convection [29, 34]) for the densities differences between phases or by electromagnetic forces (electrophoresis). Numerical computations provided both a long-wave convective instability or short-wave bifurcations.

These diffusion processes are driven by gradients in the liquid which are in turn due to temperature on the interface. The interface temperature is related to the interface composition, the surface curvature and the departure of interface from local equilibrium. The last contributions are curvature undercooling, composition and kinetic undercoolings. The ratio of the change in concentration at the tip to the equilibrium concentration difference is known as supersaturation and represents the driving force for the diffusion. The form of the tip is affected by the distribution of the rejected heat or solute and interactions makes the development of an exact theory extremely complex, usually involving an exponential integral (known from nonisothermal evaluation procedures [4]). The methods of the perturbation analysis were introduced into crystal growth theory by Mullins and Sekerka [33] who expressed the deviations from the spherical form in terms of spatial functions $Y_{\mathrm{lm}}(\Theta,\varphi)$

$$R = r_0(t) + \delta(t) Y_{\mathrm{lm}}(\Theta,\varphi) \tag{10}$$

where r_0 is the radius of the unperturbed sphere, $\delta(t)$ the time-dependent amplitude of the perturbation and R is the distance of the perturbed surface from sphere centre. It was assumed that the principle of local thermodynamic equilibrium is satisfied. Relationships describing the rate of change of the perturbation amplitude were derived. This quantity determines the stability conditions of the growing interface: when $\mathrm{d}\delta/\mathrm{d}t > 0$, than the perturbations are amplified and the growth process is unstable.

More complex equations of perturbation balance of the discontinuity interface were derived within the framework of the linear approach. Generalised conditions for the heat transport at a curved interface have the form

$$\begin{aligned} & v_{\mathrm{N}}[(\rho c T)_{\mathrm{L}} - (\rho c T)_{\mathrm{S}}] \\ & \quad = D_{\mathrm{S}} \frac{\partial T_{\mathrm{S}}}{\partial n} - D_{\mathrm{L}} \frac{\partial T_{\mathrm{L}}}{\partial n} v_{\mathrm{N}}[Q + CM(f_{\mathrm{S}} - f)] \end{aligned} \tag{11}$$

where C_{M} is twice the mean curvature of the solidification front, v_{N} is the normal component of the growth rate, $(f_{\mathrm{S}} - f)$ is the difference between Gibbs and surface energy, $D_{\mathrm{L,S}}$ is the diffusion coefficients in the liquid (L) and solid (S) phases, $T_{\mathrm{L,S}}$ is appropriate temperatures on interface, ρ is density and c is heat capacity. All the derivatives are taken with respect to the direction normal to the interface. Since the surface energy can be expressed in terms of interface entropy, the last term on the right hand side of Eq. (11) destabilizes the system for negative values of the surface entropy (and vice versa).

The applications of linear and also non-linear morphological stability theory to diverse areas of crystal growth are developing rapidly. Any steady-state description of dendritic growth ignores the rather obvious fact that dendrites are inherently time-dependent structures. The dendritic side branches also appear to be oscillatory in time and space. These important morphological and dynamical properties of dendrites suggest that a dendrite might be better treated as a dynamical phase transformation displaying time-dependent behaviour. So, dendritic growth may represent an example of self-organising formation phenomena, which is a deeply researched subject within the broader field of nonlinear dynamics and dissipative phase formation [29,39]. The effect of temperature flow can affect the degree of ordering of certain directionally solidified eutectics to produce a characteristic growth of well-organised lamellae [27,28] and can be found in directionally grown composites, layered products of decompositions, etc.

8. Conclusion

It is clear that above-mentioned, *single-value characterisation* of non-equilibrium processes [11,40,44] is not fully agreeable and thus needs to undergo modifications to match another style of presentation adequate to the modern level of scientific treatments available. Some progress was achieved in the determination of activation energy E_{A} of reaction in theories, in which the temperature gradient, temperature dependence of E_{A} or competitive processes were assumed [45–47]. But it should be brought into concurrence with the description of fluxes, in particular, with the ever-participating heat flux that is involved in all thermophysical measurements that employ higher rates of temperature changes. During such a non-equilibrium (or even ‘‘thermodynamically near-equilibrium’’) processing the resulting overall reaction rate is determined not only by kinetic processes taking place at the phase interface (usually characterizable by some set of constants) but also by the nearby mass and energy transport. Both features combine their course of action in a complex manner, because the transport properties determine the conditions on the entire phase interface and, vice versa, the depletion of interfacial reactants controls the strength of the fluxes. The kinetics of phase transformations is thus influenced by the neighbouring temperature, stress, concentration and similar distribution gradients both across and along the reaction interface. Thus, it is necessary to bring all processes together in one model, which is capable of describing the evolution of the system as whole. Such a model of the total process needs to be described by a *set of functions* of time and space coordinates yet inconvenient in our, so far common, kinetic language.

As an example of such functions resulting from non-linear theories of diffusion or heat conduction we can mention the following relations [48,49]:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}\left[D_1(x)\frac{\partial \rho}{\partial x} + D_2(x)\left(\frac{\partial \rho}{\partial x}\right)^2\right] \tag{12}$$

$$\tau\frac{\partial^2 \rho}{\partial t^2} + \frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} \tag{13}$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}\left(\int_0^t \mathrm{d}t' \int_{-\infty}^{\infty} \mathrm{d}x'\, D(t-t', x-x')\frac{\partial \rho}{\partial x}\right) \tag{14}$$

Eq. (12) reflects the dependence of the fluxes on the quadrate of the density gradient (by coefficient D_2). During the derivation of the next Eq. (13), the relaxation of fluctuated fluxes to the value given by the Fick law was supposed. The relaxation time of this process is τ. The Eq. (14) introduces the generalised diffusion coefficient $D(t,x)$ which described non-local dependence of fluxes on the density gradients and on history of the density profiles. It would be also interesting to see this classical diffusion process in relation to quantum mechanics [39,50–52] which would be the subject of our next communication.

In the view of our thermoanalytical practice, the expected results in terms of functions instead of the traditional constants would, however, be quit unfamiliar but we need to get acquainted with them when facing the new prospects of the 21st century. It, in fact, would be better to match the real thermal state dynamics than to use the old representation in terms of customary and almost "religious" constants [1] mostly linked with the activation energy that never express the ease of reaction (desirably to be related to the reactivity "tolerance" and mechanism "annexation"). High values of activation energies are often misleading when determining the character of the process investigated, because high values do not mean difficult reactivity (e.g. spontaneous and rapid exothermic crystallisation) and low values do not imply easy reactivity (e.g. for habitually slow diffusional processes). The interpretation is exactly the other, example is the repeatedly studied case of the reversible $CaCO_3$ decomposition, which is strongly mass and heat flow dependent (CO_2 partial pressure and diffusion as well as its due concentration gradients created within the solid). The related classical kinetic analysis is thus generating the numberless figures of almost insignificant values of activation energies [3,4] strongly dependent on the experimental conditions applied.

From the experimental point of view it means that we must complete our thermal analysis by the methods describing more details about the resulting material. We often require to determine chemical composition of phases and their distribution in sample (by energy dispersive analysis of X-rays, or wave dispersive analysis of X-rays, by X-ray microanalysis or electron probe microanalysis). Important information is given by the geometrical relations between all phases present in the system as well as geometrical properties of any individual phase. In this respect the best results can be obtained by image processing and stereology of images obtained by electron microscopy or STM, AFM, etc. The structure and texture of resulting phase depend on conditions of phase transformation process, on its stability and the particular course. The analysis of relation between these conditions (actual temperature, cooling rates, volume and geometry of sample, variable external fields, etc.) and changes of resulting phase properties contribute to the real description of reaction kinetics. As an example of the dependence of solid phase transitions on the thermal conditions is the transformation amorphous—microcrystalline or polycrystalline silicon [55].

The flux approach discussed above was assumed to be important as early as during the 1974 NATAS/Mettler award lecture "Rational approach to the study of processes by thermal analysis" [44] and expanded upon our review [28] and book [29] by introducing a new discipline entitled "*kinetic phase diagrams*". The concept of heat allocation may also be recognised as an integrating element in the pathway of ordering not only matter, but also society [53,54] supporting our better understanding of both our environment and the science of nature in general.

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