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ON THE BOUNDARY CONDITIONS IN THE TOPOLOGICAL MODEL OF PURELY DISSIPATIVE COUPLING

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The relationship between the behaviour of a composite system and the boundary conditions imposed by the external energetic circuit from a laboratory reference system is established. The thermally activated character of the transformation processes visualized in the measuring systems is expressed topologically by superposition of the time and temperature dependences (of Arrhenius type) for the component which is found in transformation relative to the laboratory system. The temporal relativistic principle is extended to the thermally driven processes by using this superposition condition. The kinetic equations for three particular cases of purely dissipative coupling are deduced in this way: in the case when the two fluxes associated with the component are of opposite directions; the shift equation for the relaxation periods in amorphous morphology; and for the case of capacitive dependence as boundary condition.

The study of transformation processes in non-equilibrium systems by using topological models has recently led to the qualitative and quantitative explanation of some experimental results and might possibly help to outline certain working principles in topological thermodynamics [1–3]. The reexamination of numerous experimental results (some of them unexplained by classical non-equilibrium thermodynamics) in the light of this new theory will establish these principles. So far topological thermodynamics has been characterized by the following ideas:

(i) Non-equilibrium systems have a composite nature. In this way the capacitive elements were defined as topological components for thermally [1, 2] and viscous [3] driven processes.

(ii) A transformation process in a non-equilibrium system is topologically expressed by the time-dependence of the flux and potential variables. This principle of exclusive time-dependence seems to remove the spatial dependence for the mass and energy transport phenomena associated with the transformation process. This classical aspect is replaced by the time-dependence of a response function which characterizes the system behaviour to an external perturbation.

The two principles have been used to describe the transformation processes in systems with dissipative coupling between components [1, 2], and to define the inductive element by its temporal relativistic effect [3]. The internal energetic circuit, and the external one which imposes the boundary condition of the perturbation, are described topologically by constitutive equations. In this paper the system behaviour to external perturbation is explained by separation of the boundary condition in the response function proper for the measuring system which consists of the two circuits. The temporal relativistic principle is thus extended to explain the transformation processes in systems with dissipative coupling in which the accumulation fluxes are of opposite directions.

To explain the transformation processes, at least the thermally driven ones, a condition is imposed on the relaxation time associated with the transforming component, i.e. it must be of Arrhenius type. This condition of a thermally activated process is experienced practically for all energetic modes, which leads one to consider the time-temperature superposition as a new principle in topological thermodynamics. On the basis of this principle, two other important results for the case of purely dissipative coupling are found again, namely the temperature shift equation of the relaxation times for amorphous morphology, and the kinetic equation for the capacitive dependent experiment as boundary condition.

Boundary condition in the measuring systems

Internal and external energetic circuits in the measuring systems

We consider the internal circuit for a composite system with capacitive components C_1 and C_2 coupled by the dissipative element R_1 (Fig. 1). The constitutive equations for thermal and viscous modes coincide [1, 3], so that we may express the energetic circuits by the general flux $u(t)$ and potential $U(t)$ variables.

The coupling manner of this internal circuit to an external one establishes the behaviour of all the system to the boundary condition imposed by the external

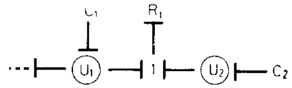

Fig. 1. The bond diagram of the internal circuit for two components coupled purely dissipative

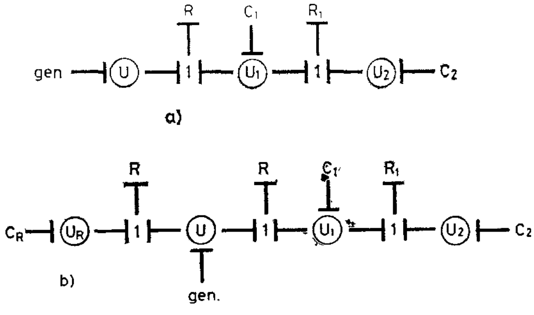

Fig. 2. Bond diagrams for single measuring system (a) and differential measuring system (b), respectively

circuit. Let us consider the cases for which the behaviour of this system experienced by a response function (associated with a measurable value) is proportional to the external perturbation which defines the boundary condition. These systems will be called measuring systems. The differential thermal analyses were previously [1] defined as measuring systems on account of the linearity condition between the response function $\theta(t)$ and the internal transforming flux $w(t)$.

In Fig. 2 are represented two cases of dissipative coupling of the internal circuit to the external boundary condition $U(t)$, frequently used in thermal analyses, defined as a single measuring system (SMS) and differential measuring system (DMS), respectively. For these systems the following response functions are measured:

$$\begin{aligned} &\text{SMS:} \quad U_1(t) \text{ or } \theta(t) = U(t) - U_1(t) \\ &\text{DMS:} \quad \theta_d(t) = U_R(t) - U_1(t)\,. \end{aligned} \tag{1}$$

To express the relationship between these response functions and the boundary condition, we will take into account the constitutive equations and the scaling expressions of the following type [1–3]:

$$\tilde{U}_2 = \tilde{U}_1/(1 + p\tau_2) \tag{2}$$

where the upper sign denotes the Laplace transform, $p = \omega + i\delta$ is a complex variable with reciprocal time dimensions, and $\tau_2 = \tilde{R}_1 C_2$ is the relaxation time associated with the process of accumulation of the flux u_2 and dissipated through R_1 [1].

Taking into account these facts, we may generally write

$$\tilde{\theta} = \tilde{U}\tilde{H} \tag{3}$$

where θ is the general response function associated with the considered measuring system, and H the distribution function of the relaxation times proper to this system. For the three above-mentioned measuring systems, function H becomes explained as in Table 1, where

$$\tau = \tilde{R}(C_1 + C_2/(1 + p\tau_2)) = \tilde{R}C_e = \tau_1 + \tau_2'/(1 + p\tau_2) \tag{4}$$

$$K = C_2/C_1, \quad \tau_2' = RC_2, \quad \tau_R = \tilde{R}C_R, \quad \tau_2 = \tilde{R}_1 C_2\,. \tag{5}$$

The measuring systems which directly measure the Laplace component of the response function will be called resonance systems. In these systems function H represents exactly the response function corresponding to a delta perturbation $U(t) = U_0\delta(t)$ [4]. Equation (3) may be interpreted as a separation of the boundary condition in the response function $\tilde{\theta}(p)$ from a function $\tilde{H}$ which represents an intrinsic characteristic of the measuring system.

Finally, we may assume that the internal flux u is accumulated by an equivalent topologic element denoted Z_i after the following constitutive equation

$$\tilde{u} = (1/\tilde{Z}_i)\tilde{U}\,. \tag{6}$$

Table 1

Associated functions to the three consi

Measuring system	Response function Θ	Distribution function, H
S M S	U_1	$1/(1+p\,\tau)$
	$U-U_1$	$p\,\tau/(1+p\tau)$
D M S	U_1-U_R	$Kp\,\tau_R/(1+p\tau_R)(1+p\tau_R)$

On the other hand, this flux u is dissipated in the measuring system through an equivalent dissipative element Z_e, so that

$$\tilde{\theta} = \tilde{Z}_e\tilde{u} \tag{7}$$

which defines the impedance of the measuring system. Taking into account Eqs (3), (6) and (7), we obtain a general relationship

$$\tilde{Z}_e = \tilde{H}\tilde{Z}_i \tag{8}$$

available for all measuring systems (see Table 1).

As an immediate consequence of these relations, we may observe that the internal circuit of the considered system (Fig. 1) accumulates the flux u through the impedance R in the SMS systems. For a linear system we may assume that the flux u consists of the contributions u_1 and u_2, corresponding to two branches of transformations of the internal circuit, so that

$$u = u_1 + u_2\,. \tag{9}$$

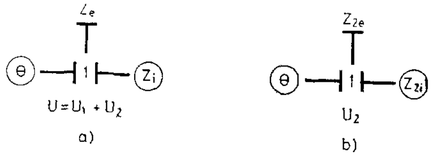

Fig. 3. The equivalent bond diagram of the measuring system corresponding to the total flux u (a), and the partial one u_2 (b), respectively

The measuring system may be represented aschematically taking into account the constitutive Eqs (6) and (7) as in Fig. 3a. If the response function θ (as general notation) measures directly the partial flux u_2, these equations become:

$$\tilde{u}_2 = (1/\tilde{Z}_{2i})\tilde{U} \tag{6$\cdot$}$$

$$\tilde{\theta} = \tilde{Z}_{2e}\tilde{u}_2 = (\tilde{Z}_{2e}/\tilde{Z}_{2i})\tilde{U} = \tilde{H}_2\tilde{U} \tag{7$\cdot$}$$

dered measuring systems (see the text)

Internal circuit $u = u_1 - u_2$		Internal circuit $u_2 = u - u_1$	
$\tilde{\boldsymbol{Z}}_i$	$\tilde{Z}_e$	$\tilde{Z}$	$\tilde{Z}_e$
$\tilde{R}/\tilde{H}$	$\tilde{R}$	$\tilde{R}/(\tilde{H}-\tilde{H}_1)$	$\tilde{R}/(1-\tilde{H}_1/\tilde{H})$
$\tilde{R}/(\tilde{H}-\tilde{H}_R)$	$\tilde{R}/(1-\tilde{H}_R/\tilde{H})$	$\tilde{R}/\tilde{H}$	$\tilde{R}$

and the measuring system is represented as in Fig. 3b.

Let us consider as an example a SMS system relative to flux u_2 associated with component C_2:

1. $\theta = U_1$

The starting point is the relation

$$\tilde{U} - \tilde{U}_1 = \tilde{R}(\tilde{u}_1 + \tilde{u}_2) \tag{10}$$

where

$$\tilde{u}_1 = pC_1\tilde{U}_1 = (pC_1/(1 + p\tau_1))\tilde{U}\,. \tag{11}$$

Taking into account (3) and (11), Eq. (10) becomes:

$$\tilde{\theta} = \tilde{U} - (p\tau_1/(1 + p\tau_1))\tilde{U} - \tilde{R}\tilde{u}_2 = \tilde{H}\tilde{U}$$

so that

$$\tilde{Z}_{2i} = \tilde{R}/(\tilde{H} - \tilde{H}_1) \tag{12}$$

where

$$\tilde{H}_1 = 1/(1 + p\tau_1) \tag{13}$$

represents the distribution function of the measuring system in the absence of the transforming branch corresponding to flux u_2.

2. $\theta = U - U_1$

Taking into account (3) and (11), Eq. (10) gives in this case:

$$\tilde{\theta} = (p\tau_1/(1 + p\tau_1)))\tilde{U} + \tilde{R}\tilde{u}_2 = \tilde{H}\tilde{U} \tag{14}$$

where

$$\tilde{H}_1 = p\tau_1/(1 + p\tau_1) \tag{15}$$

has a similar definition as in the above case. Relation (12) is found again.

A similar result is obtained for a DMS system relative to the total flux $u = u_1 + u_2$. In this case the distribution function is modified by a partial function

$$\tilde{H}_R = p\tau_R/(1 + p\tau_R) \tag{16}$$

which corresponds to the above definition adopted for the reference branch in the bond diagram (Fig. 2b.)

As a general rule we may write

$$\tilde{Z}_{1,2e,i} = \tilde{Z}_{e,i}/(1 - \tilde{H}_{2,1}/\tilde{H}). \tag{17}$$

Taking into account Eqs. (6) and (7), we obtain:

$$1/\tilde{Z}_{i,e} = (1/\tilde{Z}_{1i,e}) + (1/\tilde{Z}_{2i,e}) \tag{18}$$

and

$$\tilde{H} = \tilde{H}_1 + \tilde{H}_2. \tag{19}$$

The signs of H_1, H_2 in Eqs (17) and (19), and of $Z_{1i,e}$ and $Z_{2i,e}$ in Eq. (18) correspond to the signs of the fluxes u_1 and u_2, respectively, in relation (9).

The reversal property of a time-boundary condition in measuring systems

Let us consider a measuring system with two internal branches corresponding to the partiel fluxes $u_1 > 0$ and $u_2 < 0$, respectively. If we choose the sign of u_1 as a reference, we may write for the partial measuring system that

$$\tilde{Z}_{2i} \to - \tilde{Z}_{2i} \tag{20}$$

relative to U, θ and u_1. On the other hand, this system (Fig. 3b) exclusively measures the flux u_2, so that

$$u_2 > 0. \tag{21}$$

Taking into account (20) and (21), another condition results:

$$\tilde{U} \to - \tilde{U}. \tag{22}$$

Conditions (20) and (22) simultaneously exist in this local measuring system corresponding to the flux u_2 and define a local reference system (LocRS). A similar situation results for the case when $u_1 > 0$, and $u_2 > 0$, and also choosing the u_1 sign as a reference. This property of simultaneous changing in sign of the boundary condition U and internal accumulative element Z_{2i} in LocRS relative to the changing in sign of the partial flux u_2 in the total measuring system (denoted as the laboratory reference system – LabRS) will be called the reversal property of the time-boundary condition. If the local element is purely capacitive, so that

$$\tilde{Z}_{2i} = 1/(pC_2) \tag{23}$$

this property becomes directly:

$$\mathrm{LabRS}\,(u1' - u_2, U, t) \to \mathrm{LocRS}\,(u_2, -U, -t). \tag{24}$$

Let us take as an example the kinetic equation previously deduced for DMS calorimetric system (Fig. 2b) in thermal mode and verified for the crystallization process of polyethylene [2]:

$$\ln(t_m T) = -E/(\mathcal{R}T) + k \tag{25}$$

where t_m is the time period associated with the maximum flux u_2, T is the temperature of transformation, E is the activation energy of the process in the branch, $\mathfrak{R}$ is the gas constant, and k is a scaling constant. This system measures directly the transformation flux u_2, which is of the same sign as u_1 in the SMS system (Fig. 2a) for this process. If we now consider a process with u_2 of opposite sign relative to u_1, according to the reversal property (24) the kinetic equation (25) becomes

$$\ln (t_m T) = +E/(\mathfrak{R}T) + k. \tag{26}$$

This equation was verified for the process of thermal curing in an epoxy resin-curing agent system in which u_2 is exothermal and u_1 endothermal, respectively [5]. The temperature domain of validity for Eq. (26)

$$T \ll E/\mathfrak{R} \tag{27}$$

is the same as for Eq. (25). A classical kinetic model, applied to these curing processes in epoxy-composite systems and verified on a scanning calorimetric system [6], involves the same condition as (27), but these models [7] give the value of the activation energy as twice that resulting from the topologic model [5]. This fact may be explained in that in the topologic model only one component is considered in transformation, which would correspond in the classical kinetic model to the resulting activation energy divided by the reaction order [6]. On the other hand, the reversal property may be written as a consequence of the connection between E, T and t according to Arrhenius conditions or kinetic equations (25) and (26):

$$\text{LabRS}\,(T, t\colon -E) \rightarrow \text{LocRS}\,(-T, -t\colon E). \tag{24'}$$

Time-temperature superposition principle

The topologic kinetic model proposed [2] for thermally driven transformation processes in purely dissipative coupled composites uses the condition

$$\tau_2 = \tilde{R}_1 C_2 = \tau_{20} e^{-E/RT} \tag{28}$$

where τ_{20} is the value of τ_2 for $T \rightarrow 0$ K. Condition (28) is experienced practically for transformation processes occurring in all energetic modes, so that it may become a general principle in topological thermodynamics. Two representative experimental results are explained topologically below by using condition (28) as the time-temperature superposition principle.

Amorphous morphology

An amorphous material behaves as a composite system with purely dissipative coupling between two components, and two aspects may be distinguished: the behaviour of a quenched morphology and annealed morphology, respectively [8]. In thermal measuring system, a SMS for example, these two behaviours are represented as in Figs 4a and 4b, respectively. Quenched behaviour is released in an amorphous system by its quenching (rapid cooling) from a high temperature ($T > T_0$) to a low temperature ($T < T_0$) so that an immediate calorimetric scan in the SMS system reveals a pure stepwise change in the capacitive element of the internal circuit for a temperature T_0 (Fig. 4a) [9]. This fact may be interpreted by the appearance of a new capacitive element, the local temperature scale of which is shifted relative to the "inert" component by value T_0. The two components are considered purely dissipative coupled, and condition (28) becomes in this case

$$\tau_2 = \tau_{20}\, e^{-E/R(T-T_0)} \tag{29}$$

relative to LabRS.

If a quenched morphology is annealed before the calorimetric scan, an endothermal effect will be revealed (Fig. 4b) in addition to the capacitive changing [9]. At present, this phenomenon is explained by the relaxation process of the enthalpy, but many recent results lead to the conclusion that an order-disorder transformation process occurs. Topologically, this fact may be supported by a separation process during annealing via a viscous mode. The behaviour of this annealed morphology in amorphous systems will be the subject of a future study, because the viscous mode implies the inductive elements [3].

Let us consider again the relaxation time corresponding to the SMS system and defined by Eq. (4), and determined under experimental conditions of resonance. We propose to calculate the ratio

$$a_T = Re\tau(T)/Re\tau(T_0) \tag{30}$$

known as the shift factor for relaxation time for a temperature T relative to T_0 in the isothermal measurements on the amorphous system. Equation (30) will become

$$a_T = (1/(C_1 + C_2))(C_1 + C_2(1 + \omega\tau_2)/((1 + \omega\tau_2)^2 + \delta^2\tau_z^2) \tag{31}$$

taking into account Eq. (4) and the fact that $p = \omega + i\delta$.

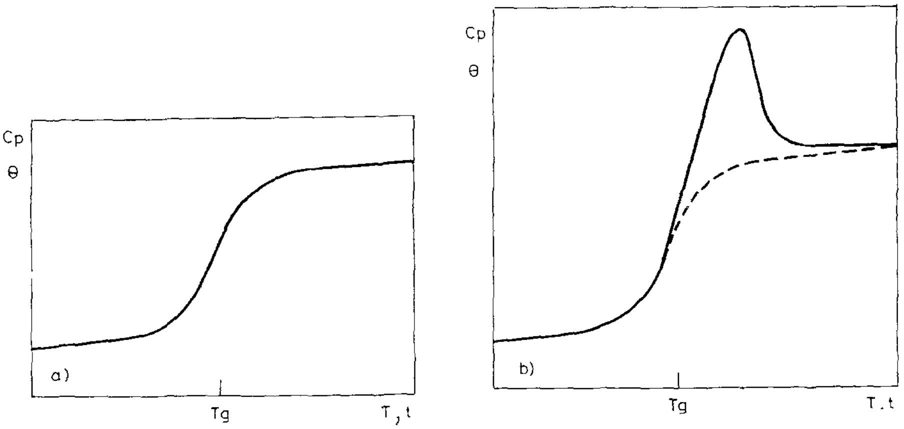

Fig. 4. The response function in a thermal analysis for the quenched amorphous morphology (a) and annealed amorphous morphology (b), respectively

We further refer to the amorphous systems with $E \simeq 40 \div 100$ kcal/mole (determined according to the classical consideration of the hole theory) and $T_0 \simeq 300 \div 400$ K [9], so that

$$\varepsilon \ll 1. \tag{32}$$

In this approximation Eq. (31) becomes

$$\ln a_T = A/(T - T_0) + B \tag{33}$$

where

$$A = E/\mathfrak{R}, \quad B = \ln(\omega\tau_0). \tag{34}$$

Taking into account the above considerations, it is important to note that the shift equation (33) may be experienced in isothermal measurements in the resonance systems in any energetic mode, and is similar to the phenomenological Williams–Landel–Ferry equation [10]:

$$\ln a_T = -A'(T - T_e)/((T - T_e) + B'). \tag{35}$$

Comparing Eqs (33) and (35), we have

$$T_e = T_0 + \varepsilon, \quad A' = -B, \quad \varepsilon = B' = +A/B. \tag{36}$$

The capacitive dependence as boundary condition

The general condition (28) suggests that we may correlate the behaviour of the internal circuit of the system under isothermal conditions and considering variable C_2 towards a saturation value for which the transformation flux becomes zero in the external circuit. In this measuring system (similar to that in Fig. 3b) the associated kinetic equation becomes (taking into account condition (28)):

$$\ln C_2 = -A_1/T + A_2 \tag{37}$$

where

$$A_1 = +E/\mathfrak{R}, \quad A_2 = \ln Re(\tau_{20}/\tilde{R}_1). \tag{38}$$

This equation has been established experimentally under very accurate conditions for a series of studies on solubility in the saturation of a large number of organic and inorganic compounds in inert liquids [11].

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Résumé — On a établi le rapport entre le comportement d'un système composite et les conditions aux limites imposées par le circuit d'énergie externe au système de référence du laboratoire. Le caractère thermiquement activé des processus de transformation visualisés dans les systèmes de mesure est exprimé topologiquement en superposant les relations d'interdépendances (de type Arrhenius) temps-température du composant qui se transforme vis-à-vis du système laboratoire. Le principe relativiste temporaire est étendu aux processus thermiquement commandés en se servant de cette condition de superposition. Les équations cinétiques pour trois cas particuliers de couplage purement dissipatifs sont établies de cette façon, à savoir dans le cas où les deux flux associés au composant sont de directions opposées, l'équation de déplacement pour les périodes de relaxation pour la morphologie amorphe ainsi que pour le cas de la dépendance capacitive en tant que condition aux limites.

Zusammenfassung — Der Zusammenhang zwischen dem Verhalten eines zusammengesetzten Systems und den durch den äusseren Energie-Stromkreis des Laboratoriums-Referenzsystems bedingten peripheren Bedingungen wurde festgestellt. Der in den Meßsystemen sichtbar gemachte thermisch aktivierte Charakter der Umwandlungsvorgänge wird topologisch für die Komponente, welche sich in der zum Labor-Referenzsystem gehörenden Umwandlung befindet, durch Überlagerung der Zeit- und Temperaturabhängigkeit (vom Arrhenius-Typ) ausgedrückt. Das temporäre Relativitätsprinzip wird auf thermisch gesteuerte Prozesse durch Einsatz dieser Überlagerungs-Bedingungen erweitert. Die kinetischen Gleichungen für drei besondere Fälle der rein dissipativen Schaltung werden auf diese Weise abgeleitet, d. h. für den Fall wo die beiden der Komponente zugeordneten Strömungen von entgegengesetzter Richtung sind, die Verschiebungsgleichung für die Relaxationsperioden in der amorphen Morphologie vorliegt und für den Fall der kapazitiven Abhängigkeit als peripherer Bedingung.

Резюме — Установлена взаимосвязь между поведением сложной системы и граничными условиями, накладываемыми внутренним энергетическим циклом из лабораторной стандартной системы. Термических активированный характер визуально протекающего превращения в измеряемой системе выражается топологически наложением временной и температурной зависимостей (аррениусовского типа) для компоненты, найденной при превращении относительно лабораторной системы. Этот релятивистский принцип, используя условие наломения, распространен на термически управляемые процессы. Таким путем выведены кинетические уравнения для трех частных случаев чисто рассеивающего совокупления, а именно: для случая, когда два потока, связанные с компонентой, являются противоположных направлений, для случая смещения уравнения для релаксационных периодов в аморфной морфологии и для случаи нагружающей зависимости как граничного условия.