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## The glassy state as the lawfully disarranged state. Vibration uncertainty and chaos-like movements.

Bořivoj Hlaváček<sup>a\*</sup>, Čestmír Drašar<sup>b</sup>, Andréa Kalendová<sup>a</sup>, Pavel Menc<sup>a</sup>,  
Jaroslav Šesták<sup>c</sup>, David Veselý<sup>a</sup>

<sup>a</sup>*Institute of Chemistry and Technology of Macromolecular Materials, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

<sup>b</sup>*Department of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic*

<sup>c</sup>*Research Centre New Technologies Region, University of West Bohemia, Universitní 8, 301 14 Plzeň, Czech Republic*

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### Abstract

The effect of a non-linear oscillator's vibrations (either in solids or in liquids) is the primary source of the amorphous state of the matter. The number of nonlinear oscillators (N.Os.) is considered to be very small at  $T_g$  (approximately 2.5 %), and rises with the increase in temperature, reaching approximately 100 % at the critical temperature  $T_c$ . In the main transition zone (covering the area between  $T_g$  and the crossover temperature  $T_{cr}$ ), there are high amplitudes of N.Os. restricted by the particle neighbors and also by the internal energy related to the shear modulus. The shear modulus disappears above the  $T_{cr}$ , where the matter exists either in the form of a liquid or in the form of a rubber-like state (which is not considered in this study). In the present study, the liquid is considered as a heterogeneous structure, formed on the one hand by domains, which are responsible for the linear viscoelastic behavior, and on the other hand with the stand alone N.Os., which act as the trembling motion sources of the optically observed aspect of Brownian motion. Under the  $T_{cr}$  and  $T_g$  temperatures, the secondary  $\beta$  and tertiary  $\gamma$  processes are studied as well.

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\* Corresponding author. Tel.: +420-466-037-192; fax: +42466036124.

E-mail address: [borivoj.hlavacek@upce.cz](mailto:borivoj.hlavacek@upce.cz).

## 1. Introduction

In the model presented below, the solid and liquid phases of amorphous bodies are characterized by two types of oscillators, which are distinguished by two types of mathematics:

1. The theory of deterministic chaos
2. The theory of linear viscoelasticity

The main part of the liquid or solid body's theory is formed and represented by models built using the concept of linear oscillators (L.Os.). These models are used for the calculation of specific quantities, starting from the determination of energy changes of individual particles. From mild deviations of linearity, Ch. Kittel and J. Frenkel [1, 2] were able to calculate the thermal expansion coefficient and high temperature specific heat ( $c_v$ ), respectively. Inside the material body, the L.Os. essentially show the tendency to mutually stick together and form blocks with a size that depends on the numbers of elements arranged into the linear element series. Thus, the L.O. connects itself into the structures of blocks, icebergs or domains [3, 4]. However, just opposite is true (in our presented theory) for the nonlinear oscillators (N.Os.). These oscillators act individually and are characterized by their chaotic and irregular motion [5, 6, 29-31] perturbing the motion of L.O. blocks. Thus, the second state of an oscillator (opposite to the L.O.) is an N.O., which exists in bodies as a stand-alone oscillator. These oscillators accompany and govern the onset or disappearance of certain phenomena (such as the glassy transition  $T_g$ , the crossover temperature  $T_{cr}$  and the boiling point phenomena  $T_b$ ) and provide us the overall picture of the phase transition behavior of liquid substances. The nonlinear oscillators are stand-alone objects, which crack down the blocks of connected L.Os. into the manifold of "floating" icebergs or domains. With these oscillators, comes the consideration of a new type of mechanics that is connected to deterministic chaos.

Thus, an N.O. must be considered in terms of nondeterministic elements [5, 6, 31], which imbue the properties of amorphous bodies with local structural irregularities and local non-equilibrium structural arrangements. The concentration of N.Os. increases with increasing temperature, starting from about two volumetric percent at the glassy temperature  $T_g$  [7] and reaching the form of "foamy-like structures" with a whole body of condensed liquid phase. The foamy-like structures finally characterize approximately one hundred volumetric percent of the N.Os. at the critical temperature  $T_c$  [12, 28]. Above the  $T_c$ , the condensed phase oscillations cease to exist [8]. The gas phase above  $T_c$  does not contain any traces of liquid phase vibration motion, and its molecular motions are defined in a different coordinate system (inside a whole vessel or a sample container).

The main contribution of this paper is the model of the division of a system into the following:

- 1) The individual N.Os., which cause the shivering motion of microparticles through their amplitude switch
- 2) The blocks of L.Os. grouped into viscoelastic series connections

Each type of oscillating species provides us specific information about the physical properties connected with the L.O. or N.O model. For example: The N.Os. are, through their amplitude switch, the movers and shakers in the liquid system. The groups of L.Os. are the carriers of the relaxation time response, and provide us the relaxation times series. The inherent properties of the L.Os. are their ability to associate and to be mutually connected into the blocks and, thus, create the icebergs or domains (which are characterized by an entire series of relaxation times [9- 11]).

## 2. The properties stemming from L.O. blocks formed by linearly connected elements. (The size and extent of viscoelasticity relaxation spectra determines the size of the domains).

The fundamental, experimentally determined linear viscoelastic functions (relaxation modulus, dynamical modulus, creep, compliance etc.) are comprehended in the relation to the central function of the

relaxation spectra, according to J.D.Ferry [10]. The relaxation spectra themselves are the functions of relaxation times, which can be considered either in discrete form [11], containing the specific relaxation times  $\tau_1, \tau_2, \dots, \tau_i, \dots, \tau_N$  (models of Maxwell and Voigt), or presented in the form of the relaxation time, as the continuous variable of  $\log \tau$  [9-11]. Thus, A. V. Tobolsky [9] proposed the main transition zone of the “prototype” of continuous relaxation spectra, which, since then, has been called the “Tobolsky’s wedge-like spectra”. The extent of such relaxation spectra in the main transition zone determines the amount of heterogeneity of the domains [12] as well as the extent of the linear viscoelastic series.

The general shape of the discrete relaxation spectra has been used for the non-linear viscoelastic model by P.J. Carreau [13-15] and was also applied to a general flow situation by P.J. Carreau, R.B. Bird and coworkers [12-15]. The alternative definitions of relaxation times, (for the whole sample) stems from the measured functions of the relaxation modulus  $G(t, T)$ , dynamical modulus  $G^*(\omega, T)$ , creep, or compliance, etc. The alternative definition of the integral relaxation times [15-18],  $\Theta_{int, 1}$  or  $\Theta_{int, 2}$ , can be a function of temperature or time/frequency variables and depends strongly on the cumulative number in the consecutive series “n” of the Voigt or Maxwell elements, which individually possess the constant relaxation times  $\tau_1, \dots, \tau_i, \dots, \tau_N$  [16-18].

$$\Theta_{int, 1} = \frac{G(t, T)}{\frac{dG(t, T)}{dt}} \quad (1)$$

$$\Theta_{int, 2} = \frac{G'(\omega, T)}{G''(\omega, T)\omega} \quad (2)$$

These collective relaxation times,  $\Theta_{int, 1}$  or  $\Theta_{int, 2}$  in the form of eqs. (1, 2), are functions of temperature  $T$ , time-frequency, and the cumulative number  $n$  in the consecutive series of  $N$  elements  $\tau_1, \dots, \tau_i, \dots, \tau_N$ , [17-18]. The temperature dependent relaxation time is used in the fundamental literature [7, 9, 10] dealing with the glassy state of amorphous bodies, with its transition either into the liquid or into the rubber-like form of states. Such defined integral relaxation times show a similar (but not coinciding) temperature dependence to that of the shear viscosity function, as used by J.P. Johari and M. Goldstein [19-21]. This comparison has been elegantly shown in the work of J. Wiederich, N. V. Surovcev and E. Rossler [32-35].

Using eqs. (1) and (2), we can distinguish three types of fundamental relaxation processes that depend on the parameter “n” in eq. (5). It can be stated that the so called “integral” relaxation processes grow with the number of elements “n” upon cooling. The number “n” reaches infinity (for the  $\alpha$  process only) as the relaxation time  $\tau_{max}$ , associated with the “n” of eq. (5), reaches infinity as well. In another words, the number “n” can reach infinity as the series of elements grows and eventually establishes the network structure of the solid body.

However, strictly for the given structure, the number of elements “n” does not grow upon cooling to infinity and instead stops (as a result of heterogeneity and variability of the amorphous phase) at a limited level. In such a case, the temperature dependence of the relaxation time is governed by only the viscosity of the environment, and it behaves strictly as Arrhenian. Such relaxation processes we can call the  $\beta$  or  $\gamma$  processes. In literature, such “frozen in processes” are referred to in connection to G.P.Johari-M.Goldstein [19-21] relaxations processes. To be correct, however, we must note that the  $\beta$  and  $\gamma$  processes have been described previously [22-24, 37] in polymer literature, mainly based on the ratio of the imaginary and real parts of dynamical module [10,36,37] studies. Note also that it is necessary to distinguish the steady state shear viscosity [10]  $\eta(\dot{\gamma})$  (where  $\dot{\gamma}$  is the gradient of velocity) and the real part  $\eta'(\omega, T)$  of the

dynamical viscosity, which relates the dynamical module and dynamical viscosity [10], even though both quantities  $\eta'(\omega, T)$  and  $\eta(\gamma, T)$  appear similar in their numerical values through the simple substitution  $\omega \cong \dot{\gamma}$  [36, ].

In our approach, it is the number of elements that are connected upon cooling that differentiates the process  $\alpha$  from the processes  $\beta$  and  $\gamma$ . As the number of elements for the processes  $\beta$  and  $\gamma$  stops growing upon cooling, the  $\beta$  and  $\gamma$  processes must behave as Arrhenian.

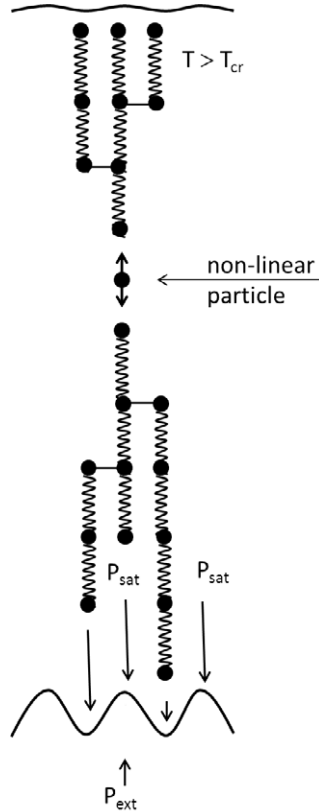


Fig. 1. A schematic model for the solid-like structure just above the  $T_g$  temperature, when the first particle starts to act as a non-linear oscillator and causes irregularity in the structure of linear elements. The splitting of blocks approximately halves the number “ $n$ ” in eq. (5) and interferes with the  $\alpha$  process sequence, which otherwise forms the infinite structural network.

### 3. The use of A.V. Tobolsky's wedge-like spectra for the determination of the number of linear oscillators connected in the series inside liquid domains. The relaxation spectra and the size of heterogeneity domains.

One of the methods of determination of the interconnectedness of L.Os. in icebergs or domains stems from the extent of relaxation spectra in the main transition zone. As an example, we present wedge-like spectra for the polymer of "polyisobutylene", which A.V. Tobolsky [9] provides as the most typical example of data for the characteristic dimension of the main transition zone.

A. V. Tobolsky quotes the following data:

$$\tau_{max} = 10^{-12,5} \text{ hours} = 3,6^{-9,5} \text{ sec} \quad (3)$$

$$\tau_{min} = 10^{-5,4} \text{ hours} = 3,6^{-2,4} \text{ sec} \quad (4)$$

$$\tau_{max} = n^2 \cdot \tau_{min} \quad (5)$$

where the number "n" in equation (5) reflects the number of serial elements in the linear viscoelastic spectra of the famous Rouse series [11]. For polymers, equation (5) also provides detailed molecular interpretation [9-11, 28]. For the low molecular weight substances data of J. Jackle [25- 27], R.Piccereli and T.A. Litowitz [25] present a similar extent of the relaxation time zone of  $\tau_{min}$  and  $\tau_{max}$ . The analogy for the main transition zone between the polymers and the low molecular weight substances regarding the basic viscoelastic functions in the main transition zone is obvious. Additionally, the basic idea of a consecutive series of relaxation times was also incorporated into the general description of material behavior possessing of a memory function by P.J. Carreau, R.B. Bird [13-15, 18] and coworkers. These authors provide a broad generalization of the rheological properties of polymers and the value of  $\tau_{max}$  they obtained from the expression.

$$\tau_{max} = n^{2\alpha} \cdot \tau_{min} \quad (6)$$

This formula brings the number "n" of Tobolsky's spectra to approximately 660 and is an estimate of the domain size related to the sum of the polarizabilities of the individual atoms forming the domain, leading to the approximate dimension of approximately 2 nm [12, 28].

### 4. The consequences of non-linear oscillator behavior

Our main idea stated in this paper is the division of a system in the area of glassy-liquid transitions into:

- 1) A "few" N.Os. on the one hand
- 2) The vast majority of L.Os. on the other hand (these are bonded into a viscoelastic series of elements)

Thus, the elements of the structural positional uncertainty and the structural chaos of an N.O. can be intermingled side by side with the L.O. deterministic elements of linear viscoelastic structures, which we call the internal domain structures. The maximal relaxation time of a linear series will impose limits on the N.O. lifetime because we assume that the motion of the N.Os. ends their life time when the blocks or icebergs of L.Os. are displaced as well [28]. We suggest that this process of the formation and extinction of N.Os. is common to Brownian motion that is observable under a microscope. Note that only a "few"

particles of N.Os. drive the flickering effects in the liquid state (above  $T_g$ ), which are caused by the discontinuities of the vibration amplitudes [28-31]. The action of the amplitude jumps, as visualized in the forms of pollens, etc., (flickering and shaky motions) observable under normal conditions. Interestingly, we can see the action of only a few N.O. particles as they undergo the amplitude discontinuities (Fig. 2). In the mathematical sense, the two- or three-fold possibilities for the multiple particle space trajectories bring the consequence of the irregular displacement of atoms or molecules in form of amorphous phase. The remaining particles (the L.Os.) are, through their mutual connections, participating in the relaxation process movements, which provide us the characteristic relaxation times and which obey the classical mathematical deterministic treatment.

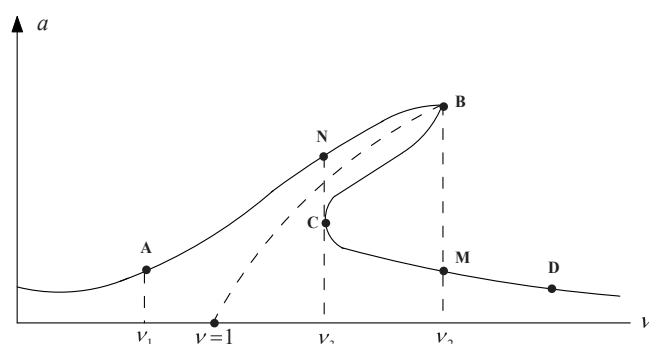


Fig. 2. The typical feature of nonlinear oscillators. The amplitude of the N.O. is shown with its amplitude “ $a$ ” duplicity or multiplicity (as the function of oscillator frequency  $\nu$ ).

## 5. The presentation of the amorphous phase as the lawfully chaotic phase, which reflects the sample history

The consequence of the existence of non-linear individual oscillators (by their origin and individual character of motion) consists of the problems of the elements of chaos and the elements of the uncertainty in the trajectories [5, 28-31]. Thus, we must consider the glassy and the glassy-liquid transition states as the disarranged states, which are out of thermodynamic equilibrium even at their origin. Upon cooling, the N.O. oscillator loses its momentum and finds itself closer to its focus of vibration. At the same time, however, the N.O. is surrounded by a block of L.Os., which influence or hinder its pathways to the minimal free energy position. Thus, the N.O. can be stuck in an energetically “inconvenient” position rather than its minimal free energy position. We must be aware that the glassy state was always previously formed from the molten state or from the other forms of a liquid state, i.e., that the state of abundant individual N.Os. has always “historically” preceded the formation of the glassy state. Therefore, with the glassy state, we must always consider it as lawfully irregular and chaotic in its origin. From a thermodynamic point of view, the glassy state represents the lawfully positional disorganized state and also as the state that cannot be identified with potential Helmholtz-Gibbs energy minima. We must take the glassy state as a state that, by cooling, has bypassed the formation of a crystal state. This bypassing of the

$T_m$  point was caused by the disturbing effects of N.Os. on the structures of the internal vibration movements inside of the liquid bulk. The N.O. motion disturbance was so intensive in the area of the  $T_m$  temperature that the crystal nucleus precursor did not have sufficient time to grow into a whole domain.

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