MODELLING PHYSICAL AGING IN GLASSY POLYMERS: 1. AN OVERVIEW OF PHENOMENOLOGICAL MODELS

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A survey is presented of mathematical models for structural relaxation in glassy polymers. The first part of this review deals with phenomenological constitutive relations. The emphasis is on volume recovery in amorphous polymers after thermal treatment. Physical models for structural relaxation in disordered media will be the subject of the other part of this work.

1. Introduction

The paper is concerned with constitutive models for the kinetics of physical aging (structural relaxation) in glassy polymers. This subject has attracted considerable attention in the past four decades [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. This may be explained by the strong effects of structural recovery on

1. dimensional stability and residual stresses in polymers cooled after thermal treatment [19, 25, 26, 27, 28, 29, 30];
2. static (creep and relaxation) [7, 10, 31, 32, 33, 34, 36, 37, 38, 39, 40] and dynamic [1, 41, 42, 43, 44, 45, 46, 47, 48, 49] moduli;
3. yield stress and post-yield response [41, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64];
4. elongation to break [63, 65, 66, 67];
5. fracture toughness [52, 66];
6. impact strength [50, 51, 53, 68, 69, 70, 71];
7. rates of crack initiation and slow growth [72, 73];
8. density fluctuations [74];
9. specific entropy [3, 10, 48, 57, 61, 62, 75, 76, 77, 78, 79, 80];
10. dielectric relaxation [81, 82, 83, 84, 85];

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11. birefringence [86] and optical refractive index [19];
12. diffusivity [7];
13. rates of curing and crystallization [87, 88].

Structural relaxation is observed in amorphous and semicrystalline polymers. It may be demonstrated in a one-step thermal test, where a specimen equilibrated at some temperature Θ_0 is instantaneously heated or cooled at time $t = 0$ to another temperature Θ and is preserved at that temperature,

$$\Theta(t) = \begin{cases} \Theta_0, & t \leq 0, \\ \Theta, & t > 0. \end{cases} \tag{1}$$

Dilatometric (length and volume) experiments show that in thermal test (1) the specific volume v changes at $t = 0$ from its equilibrium value at Θ_0 to some new value $v(0)$. The quantity v slowly decreases with time and tends to its equilibrium value v_∞ corresponding to the new temperature Θ. The attribute "slowly" means here that the characteristic time for volume recovery essentially exceeds that for creep and relaxation in specimens equilibrated at the same temperature Θ.

To reveal structural relaxation in static mechanical tests, a specimen equilibrated at the temperature Θ_0 is suddenly heated (quenched) to a temperature Θ, annealed at the final temperature Θ for a time t_e, and loaded in a tensile (torsional) machine. It is demonstrated that short-term (with the test duration essentially less than the elapsed time t_e) relaxation (compliance) curves measured at different times t_e and plotted in double logarithmic coordinates can be superposed by horizontal (along the time axis) shifts. This assertion is confirmed fairly well by a series of graphs for various amorphous [7] and semicrystalline [89] polymers and various initial and final temperatures.

A thorough analysis shows, however, that horizontal shifts should be accompanied by vertical shifts, which indicates that not only relaxation times increase with t_e, but instantaneous elastic moduli as well. For examples we refer to data for polycarbonate [35], poly(ether imide) [35], polystyrene [32, 90], and an epoxy glass [36]. Constitutive equations accounting for changes in relaxation spectra and equilibrium elastic moduli of crystalline polymers were derived in [8, 14]. These relations were criticized in [91], where it was demonstrated that they disagreed with observations for amorphous polymers.

The thermal program (1) is also employed to study structural relaxation in dynamic tests with small strains. The only difference is that the storage and loss moduli are plotted in double logarithmic coordinates as functions of frequency, and curves obtained at various elapsed times t_e are superposed by shifts along the frequency axis [1]. Observations in low-frequency dynamical tests (10^{-1} to 10^1 Hz) result in the same qualitative conclusions as data obtained in static tests: relaxation (retardation) spectra practically do not change their shapes and they monotonically move to higher times with an increase in the elapsed time t_e. However, when the width of the frequency window increases these assertions become inadequate. For example, in order to superpose results in dynamic tests for polycarbonate and poly(methyl methacrylate), it is necessary not only to shift them along horizontal and vertical axes, but also to rotate experimental curves [42].

Results of high-frequency tests (up to 10^8 Hz) recalculated into creep curves reveal that the conventional conclusions are valid (to some extent) only for a part of the spectrum located in the α region (the relaxation time of the order of 1 s and higher). On the contrary, the elapsed time t_e practically does not affect relaxation times in the β region, but entails a substantial decrease in equilibrium elastic moduli. Experimental data for polypropylene and poly(vinyl acetate) presented in [37, 38] imply that structural relaxation of polymers causes an increase in the average relaxation time and spread of relaxation spectra. These conclusions are in agreement with experimental data for poly(vinyl acetate) in dielectric relaxation tests [82, 83] and for polystyrene in creep [32] and calorimetric [90] tests.

The present paper is confined to the analysis of mechanical response, and we do not dwell on calorimetric and dielectric tests. Experimental data for glassy polymers demonstrate that the growth of the annealing time t_e entails the following phenomena:

1. a decrease in the rate of volume recovery;
2. an increase in the current elastic moduli and a decrease in the average rate of creep and relaxation;
3. an increase in strength;
4. a decrease in the impact fracture energy;
5. a decrease in the elongation to break;
6. a decrease in fracture toughness;
7. an increase in the time to failure;
8. transition from ductile to brittle fracture.

Changes in the specific volume with time that follow upward and downward temperature jumps, as well as the accompanying phenomena listed above, are called structural relaxation, or structural recovery, or aging. Traditionally, the two former terms are associated with the time-dependent behavior of arbitrary supercooled liquids, whereas the latter is used for polymers.

The term "physical aging" is applied to the reversible behavior of glassy polymers (the latter implies that the temperatures Θ_0 and Θ should lie below the glass transition temperature Θ_g). The reversibility means that if (after loading) a specimen is (i) heated above the glass transition temperature, (ii) annealed at some temperature Θ_* to remove residual strains, (iii) slowly cooled at the initial temperature Θ_0 and equilibrated at this temperature, and (iv) the program of thermo-mechanical loading is repeated, then results of the new test coincide with data for the virgin sample. Physical aging is conventionally opposed to chemical aging [92], when irreversible transformations occur in unstable polymers. The latter changes are associated with chain scission in polymeric networks driven by thermal and mechanical factors.

Physical aging is conventionally studied at temperatures located between the β transition temperature Θ_β and the α transition temperature $\Theta_\alpha \approx \Theta_g$. It is worth noting that the quantities Θ_α and Θ_β provide only rough boundaries for the region of physical aging. Even for amorphous polymers like poly(methyl methacrylate) and poly(vinyl chloride), physical aging has been revealed below the β transition temperature using dynamic mechanical spectroscopy [93, 94]. For semicrystalline polymers, both lower and upper bounds become questionable. For example, typical series of creep curves for polyethylene that permit superposition by horizontal shifts [89, 95] correspond to the initial temperatures $\Theta_0 = 100$ and $\Theta_0 = 80$ °C and to the final temperatures $\Theta = -100$, $\Theta = -60$, $\Theta = -40$, $\Theta = 0$ and $\Theta = 40$, whereas the glass transition temperature for polyethylene is estimated as -30 °C [96].

Some authors use the term "physical aging" in a narrow sense. Donth [87] applies it to time-dependent phenomena observed far below Θ_g, where coupling between α and β modes occurs. On the contrary, Struik [7, 19] refers to time-varying response observed after rapid cooling from above the glass transition temperature, $\Theta_0 > \Theta_g$, to below it, $\Theta < \Theta_g$. In this work, however, we accept the traditional viewpoint and do not impose restrictions on Θ_0 and Θ.

There is no generally accepted theory of physical aging. According to a conventional concept (going back to F.E. Simon, 1930, see [87] for a historical survey), time-dependent phenomena observed in supercooled liquids and glasses reflect irreversible processes of approaching equilibria in systems losing their equilibrium states because of thermal treatment. This means that at any temperature Θ a material is entirely characterized by some ordering parameter ε which determines its "thermokinetic structure." At quenching (heating) from the initial temperature Θ_0 to some final temperature Θ, a medium equilibrated at Θ_0 instantaneously turns into a non-equilibrium state, where its structural parameter equals $\varepsilon(\Theta_0)$. Structural relaxation is treated as slow changes in ε from $\varepsilon(\Theta_0)$ to $\varepsilon(\Theta)$.

Another mechanism for structural relaxation in disordered media has been recently developed in [97, 98, 99], see also references therein. According to the Bouchaud approach, time-dependent phenomena in glasses are caused by a "weak" ergodicity break below the glass transition temperature Θ_g. This theory will be discussed in detail in the second part of this paper.

Mathematical models for structural relaxation may be divided into four groups according to what physical meaning they assign to the parameter ε.

The first group of models is based on the Tool concept of fictive temperature [100]. This temperature, Θ_f, is determined as an equilibrium temperature, corresponding to the current state of a specimen in the process of structural relaxation. At volume recovery, Θ_f is such a temperature that the equilibrium specific volume v_∞ corresponding to Θ_f coincides with the current specific volume $v(t)$. Two shortcomings of the Tool concept may be mentioned [87]:

1. there is no evidence that the current "thermokinetic structure" in the process of structural relaxation corresponds to any equilibrium structure at any temperature Θ_f;

2. fictive temperatures corresponding to different activities (volume recovery, changes in relaxation spectra, changes in the yield stress, etc.) can substantially differ from each other.

Despite these disadvantages, the concept of fictive temperature is widely used in the analysis of experimental data for inorganic and polymeric glasses, see [4, 5, 16, 78, 101, 102, 103], to mention a few.

The second group of models is based on the Doolittle concept of free volume [104]. According to it, a volume V ascribed to any long chain is split into two parts: occupied volume V_0 and free volume V_f. The quantities V_0 and V_f change with time independently of one another driven by thermo-mechanical stimuli. The free volume V_f is estimated as a few percent of the total volume (4.5% for polyethylene and 5.7% for polytetrafluoroethylene at the glass transition temperature [105]). The rate of structural relaxation in a polymeric medium is governed by the free volume fraction $f = V_f/V$. At relatively small thermal jumps, this ratio linearly increases with temperature,

$$f = f_r + \alpha_f(\Theta - \Theta_r), \tag{2}$$

where f_r is the free volume fraction at the reference temperature Θ_r, and α_f is the difference between the (equilibrium) coefficients of thermal expansion for the bulk material and that for the occupied volume. Combining Eq. (2) with the Doolittle formula, we arrive at the Williams-Landel-Ferry (WLF) equation for the thermal shift of relaxation spectra [106] when $f_r \neq 0$ and at the Vogel-Fulcher-Tammann (VFT) equation [87] when $f_r = 0$. The Doolittle model has been refined in a number of studies, see e.g. [107, 108, 109, 110]. The following shortcomings of the free volume concept are noted [111]:

1. the physical meaning of the free volume is ill-defined for general liquids;
2. there is no agreement regarding the definition of the free volume. For example, Doolittle refers to the free volume as a volume between long chains (treated as rigid elements), whereas Cohen and Turnbull define it as a part of the excess volume that may be changed with no increase in energy;
3. the free volume concept totally neglects thermal activation necessary for redistribution of free volume clusters [112];
4. observations demonstrate systematic discrepancies between experimental data for the thermal shift factor in the vicinity of the glass transition temperature and predictions of the free volume theory (the influence of temperature is overestimated by the model);
5. the free volume theory fails to predict the effect of pressure on relaxation spectra. In particular, under elevated pressure two specimens with the same specific volume, but different thermal histories exhibit different responses [74];
6. dependence of the glass transition temperature on stresses following from the concept of free volume contradicts experimental data.

The concept of free volume was utilized in the original version of the Kovacs model for volume recovery in polymers [1, 113, 114].

Constitutive models of the third group employ the concept of cooperative relaxation based on the Gibbs–DiMarcio "lattice" theory of polymeric media [115, 116]. The kinetics of structural relaxation is determined by the Adam–Gibbs formula [117], where the specific configurational entropy S_c is determined in terms of the specific heat capacity by the standard relation

$$S_c(\Theta_f) = S_c(\Theta_0) + \int_{\Theta_0}^{\Theta_f} \frac{\Delta c}{\theta} d\theta.$$

Here Δc is the difference between the specific heat for the equilibrium liquid and that for the glass and $S_c(\Theta_0)$ is the configurational entropy in the initial state. The Adam–Gibbs model was first applied to the analysis of structural relaxation in inorganic glasses [118]. That approach has been recently revised in [119, 120]. Several expressions for the function Δc are used in constitutive relations. A constant Δc was successfully applied in [121] to fit experimental data for tri-α-naphthyl benzene. A linear dependence of the parameter Δc on the reciprocal temperature was accepted in [122, 123] to match observations for polycarbonate, poly(methyl methacrylate), polystyrene, poly(vinyl acetate) and poly(vinyl chloride). More sophisticated expressions (as series in powers of the reciprocal temperature) were adopted in [124, 125] for inorganic glasses. It is widely accepted that the theory of cooperative relaxation provides a better basis for modelling structural relaxation compared to other concepts [87]. However, this rule of thumb is questioned by some authors, since the concept of cooperative relaxation is equivalent (to a large extent) to the free-volume theory [126].

The concept of cooperative relaxation has been severely criticized in [111, 127, 128]. The following shortcomings of the Adam–Gibbs approach are pointed:

1. the function Δc may serve as a measure of configurational entropy, provided that a glass has the same contribution to the specific entropy as an appropriate crystal at the same temperature. However, this assumption does not seem realistic, since anharmonic vibrations and secondary relaxations not present in the crystal strongly affect the entropy of the glass;
2. the Adam–Gibbs equation is based on the hypothesis that the energy barrier to be overcome is proportional to the size of a cooperatively rearranging region. Although this assertion may seem reasonable, it has not been directly compared to experimental data;
3. the "lattice" theory, which provides a basis for the Adam-Gibbs formula, is not internally consistent. Its correction [128] leads to the conclusion that the configurational entropy is positive at any positive temperature, which contradicts the Kauzmann effect;
4. the concept of cooperative relaxation implies the VFT formula for the thermal shift factor, which is in poor agreement with observations in the vicinity of the glass transition temperature.

The fourth group of models employ some potential energy as a variable governing structural relaxation [99, 111, 129, 130, 131, 132, 133, 134]. Since time-dependent processes in polymers are highly cooperative, these materials are thought of as ensembles of mutually-independent structural elements rearranging at random times. The elements are usually called "relaxing units," "flow units," "cooperatively rearranging regions," "cooperatively rearranging subsystems," "quasi-independent units," "molecular regions," "thermokinetic structures," "dynamically correlated domains" [133]. An assumption common to all "energy" models is that flow units spend most time near their potential minima, because high material viscosity prevents diffusive flow below the glass transition temperature. This implies that potential energies of rearranging regions (conventionally referred to as their energies) entirely determine the kinetics of rearrangement [133]. A detailed discussion of energy models for volume recovery will be postponed till the second part of the paper.

The main hypothesis of all models is that structural recovery may be adequately described by a single internal variable ε. From the theoretical standpoint, it is hard to believe that this is the case with polymers, because of the extremely complicated shape of the energy landscape [129] which entails several mechanisms determining non-equilibrium processes. This conclusion is in agreement with the assumption [87] that different processes observed in experiments are characterized by different spectra, whose changes are driven by thermal treatment in their own ways. A strong objection to the theories of structural relaxation with one internal parameter was raised in [135] based on the thermodynamics of irreversible processes. As has been shown in [136], some equality should be satisfied which connects compressibilities, expansivities, and heat capacities for any system with one internal variable in liquid and glass states. Experimental data for glassy polymers show that this equality fails to be valid, which means that at least two internal parameters should describe the thermokinetic structure of glassy polymers.

Combined tests (where deviations from the equilibrium state are determined using simultaneous dilatometric, calorimetric and mechanical measurements) reveal that after quench by tens of degrees, the rates of changes in retardation spectra and in the specific volume coincide for polycarbonate and poly(vinyl chloride) [7, 137]. Analogous results were obtained for relaxation spectra and for the volumetric response of an epoxy glass after thermal jumps with small amplitudes [138]. Similar rates of changes in dynamic moduli and in the specific volume were measured for poly(vinyl acetate) [1]. The rates of evolution for the tensile yield stress were found to be close to the rates of changes in the specific entropy for polycarbonate [57, 61]. Rates of changes in the elongation to break for three rubber-modified epoxy glasses were compared with rates of changes in the relaxation spectrum and with rates of evolution of the specific enthalpy in [65], where it was demonstrated that equilibration in all three processes required the same time interval.

Other experimental data, however, exhibit different characteristic times for changes in mechanical, dilatometric and calorimetric properties of glassy polymers after thermal jumps. Dynamic and dilatometric measurements demonstrate that in down-jump tests relaxation spectra of poly(vinyl acetate) proceed to evolve after the specific volume equilibrates [139]. Comparison of time scales for the relaxation spectrum and for the specific volume of an epoxy glass shows that evolution of the mechanical response in down-jump tests occurs faster than that for the specific volume, whereas in up-jump tests the reverse is true [138, 140]. Different time scales for volume recovery and for evolution of retardation spectra were found in [137] for polystyrene. Significant differences in the rates of changes in the yield stress, in the relaxation spectra, and in the specific volume of epoxy glasses were observed in [64]: the viscoelastic moduli equilibrated first, afterward, the yield stress reached its equilibrium value, and, finally, volume recovery ended. It was demonstrated in [141] that evolution of the specific enthalpy for polycarbonate occurred faster than that of the specific volume. A similar conclusion was drawn for polystyrene [90, 138] in contrast with [65], where an inverse result was obtained using observations for a rubbery-modified epoxy glass. Different rates of evolution for the specific volume and for density fluctuations are observed for poly(methyl methacrylate) after thermal down-jumps [74]. Comparison of activation energies measured in mechanical and dilatometric tests on poly(vinyl acetate) specimens shows that the apparent enthaply for volume recovery significantly exceeds that for relaxation [1, 83].

A serious blow to kinetic models with one internal parameter has been struck by Kovacs' measurements of the effective time (the so-called effective time paradox [6], see Section 2). It is demonstrated that the equilibrium effective time after an upward jump in a one-step thermal test substantially depends on the initial temperature Θ_0, which means that a single measure of departure from equilibrium is insufficient to predict the spectrum of internal times in a new equilibrium state.

The entire concept of a one-parameter thermokinetic structure has become questionable after a series of experiments on apparent rejuvenation of glassy polymers [142, 143, 144, 145]. It was demonstrated in static and dynamic tests that application of relatively large loads (in the sub-yield region) caused changes in the relaxation (retardation) spectra contrary to those observed in tests on annealed specimens. By analogy with physical aging, this effect was baptized "rejuvenation" (or, to avoid discussing whether observations of thermally and mechanically driven samples are governed by the same physical mechanism, "apparent rejuvenation"). The most impressive result was that application of large shear stresses substantially affected relaxation spectra and did not cause any changes in the specific volume [138, 140]. The conclusion was drawn that changes in viscoelastic moduli of glassy polymers should be decoupled from changes in the specific volume, since these phenomena were driven by different physical mechanisms [140]. This assertion has been recently questioned in [145] based on the assumption that sub-yield stresses can cause fracture of van der Waals bonds (the so-called athermal fracture), which does not require changes in the free volume fraction.

The problem remains unresolved whether some relations exist between relaxation (retardation) spectra of polymers in thermal equilibrium at some temperature Θ and the limiting spectra of structural recovery (e.g., volume or enthalpy) for specimens equilibrated at the temperature Θ after thermal treatment. It is conventionally assumed that the characteristic time for isothermal volume recovery substantially exceeds that for relaxation and creep. This rule of thumb is concerned, however, with average characteristic times and says nothing about the distributions of relaxation (retardation) times. A hypothesis that mechanical, volume and dielectric relaxations are determined by the same spectra has been suggested in [83] and validated by comparison of observations for poly(vinyl acetate) and glucose with results of numerical simulation. Albeit fair agreement is established between experimental and numerical results, physical reasons for the coincidence of spectra remain obscure.

Summing up these observations, we arrive at the conclusion that structural relaxation of polymers is a complicated thermo-mechanical process driven by physical mechanisms which are far from fully comprehended. In sequel, we concentrate our attention on modelling volume recovery as the most illustrative manifestation of physical aging. The exposition is organized as follows. Section 2 focuses on characteristic features of volume relaxation in tests with complicated thermal programs. Section 3 is concerned with phenomenological equations for volume recovery. Some concluding remarks are formulated in Section 4.

2. Features of volume recovery

We begin with a one-step test (1) and introduce the following measure of departure from equilibrium for a glassy polymer [1, 4, 6]:

$$\delta(t) = \frac{v(t) - v_\infty}{v_\infty}, \tag{3}$$

where $v(t)$ is the specific volume at time t and v_∞ is its equilibrium value at the final temperature Θ. Evolution of the specific volume demonstrates the following characteristic features:

1. asymmetry of the function $\delta(t)$ after positive and negative temperature jumps, which implies the nonlinearity of this function with respect to the initial departure from equilibrium [6];

2. non-exponentiality of the function $\delta(t)$, which means that the decay in the specific volume cannot be adequately described by a single exponential function. Following common practice, a truncated Prony series is employed [146],

$$\delta(t) = \delta_0 \sum_{m=1}^{M} \eta_m \exp\left(-\frac{t}{T_m}\right), \tag{4}$$

where M, δ_0, η_m, and T_m are adjustable parameters and

$$\sum_{m=1}^{M} \eta_m = 1, \tag{5}$$

or a stretched exponential Kohlrausch-Williams-Watt (KWW) function is used,

$$\delta(t) = \delta_0 \exp\Bigl[-\Bigl(\frac{t}{T_0}\Bigr)^{\beta}\Bigr], \tag{6}$$

where β, δ_0, and T_0 are material parameters, and $\beta \in (0,1)$ (usually, $\beta \approx 0.5$);

3. the logarithmic kinetics of volume recovery far from equilibrium, which means that at the initial stage of aging the parameter δ changes as a linear function of $\ln t$ [12]. This pattern is also exhibited by polycrystalline metals and metallic glasses [147], and it is usually referred to as the "normal aftereffect;"

4. the Kovacs paradox.

To discuss the latter phenomenon in detail, we introduce the so-called effective time

$$\frac{1}{\tau_{\rm eff}} = -\frac{1}{\delta}\frac{d\delta}{dt}.$$

For presentation (4) with $M = 1$, the quantity $\tau_{\rm eff}$ is time-independent, $\tau_{\rm eff} = T_1$. In other cases, $\tau_{\rm eff}$ is a function of δ which tends to some limiting value $\tau_{\rm eff}^0$ as $\delta \to 0$.

Experimental data for poly(vinyl acetate) [2, 6] show that the limiting effective time is independent of the initial temperature Θ_0, provided that a specimen is quenched from the initial temperature $\Theta_0 > \Theta$ to the temperature Θ. The most surprising result is that when a specimen is suddenly heated from the initial temperature $\Theta_0 < \Theta$ to the temperature Θ, the limiting (equilibrium) effective time $\tau_{\rm eff}^0$ substantially depends on the initial temperature, and the equilibrium effective times corresponding to the same thermal jump $|\Theta_0 - \Theta|$, but with opposite signs differ by a half a decade (the expansion gap) [6]. Observations for polystyrene [146] demonstrate that the equilibrium effective times corresponding to different initial temperatures do not coincide not only for upward jumps, but for downward jumps as well (the contraction gap [148]).

Constitutive models predicting these results have been developed in [4, 6, 13, 17, 18, 146, 149, 150, 151, 152, 153] using different physical mechanisms. However, the main problem remains regardless of whether the Kovacs paradox really exists. The correctness of Kovacs' conclusions was questioned by Struik [148], who argued that his data for small δ (the final stage of equilibration) "are very inaccurate... and should be rejected," whereas observations for sufficiently large ratios δ were fairly well predicted by conventional phenomenological relations.

In tests with several temperature jumps, when the temperature $\Theta(t)$ remains constant and equal to Θ_m at the interval (t_{m-1}, t_m) and suddenly changes its value at time t_m, two phenomena are observed which are conventionally referred to as "memory effects":

1. reversibility: if the temperature $\Theta(t)$ remains constant and equal to Θ_1 for $t \geq t_\diamond$, where $t_\diamond$ is a fixed time, then the specific volume $v(t)$ tends to its equilibrium value at the temperature Θ_1, independently of what thermal program was used in the interval $[0, t_\diamond]$ [7, 12, 137];

2. crossover effect: consider a two-step thermal program, when a specimen is quenched from the initial temperature Θ_0 to a temperature Θ_1 at time $t = 0$, preserved at the temperature Θ_1 in the interval $(0, t_1)$, suddenly heated to some temperature Θ_2 at time t_1, and preserved at the temperature Θ_2 for $t > t_1$. Suppose that the quantity Θ_2 is chosen in such a way that the specific volume $v(t_1)$ coincides with the equilibrium volume v_∞ at temperature Θ_2. If evolution of the specific volume were entirely determined by its current state, the function $v(t)$ would remain constant and equal to v_∞ at $t \geq t_1$. On the contrary, experimental data show that the specific volume increases, reaches its maximum, which essentially exceeds v_∞, and then drifts back toward v_∞ as $t \to \infty$ [6, 12, 146].

In isotachyc tests (where the rate of temperature changes is constant [154]), the memory effects are revealed when a specimen is cooled from above the glass transition temperature Θ_g to some temperature $\Theta < \Theta_g$, annealed at the temperature Θ for a time t_e, and heated to the initial temperature Θ_0 with the same rate. Observations show that in the interval (Θ, Θ_0), the specific volume at heating $v(t)$ is essentially less than the specific volume at cooling, and the difference grows with an increase in the elapsed time t_e. An even more interesting behavior is demonstrated by the material expansibility

$$\tilde{\alpha} = \frac{dv}{d\Theta}.$$

At cooling, this function monotonically decreases, while at heating it increases, reaches its maximum at some temperature $\vartheta \in (\Theta, \Theta_0)$, and rapidly decreases to the equilibrium value $\tilde{\alpha}_0$ corresponding to the initial temperature Θ_0. The intensity of the peak on the graph $\tilde{\alpha}(\Theta)$ and its position ϑ substantially depend on the elapsed time and grow with t_e [6, 114, 137, 146, 154, 155].

The memory effects are conventionally associated with the presence of several kinds of relaxing regions (components of free volume) with different characteristic times (multi-parametric models). The longer relaxation time a component has, the slower its volume recovery occurs (following common practice, we do not dwell on what is the physical meaning of these "components") [83]. The parameter δ is treated as a sum of measures for departure from equilibria for appropriate components, which means that it does not serve as a measure of departure from equilibrium for some thermokinetic structure, but provides only some "average" characteristics for the non-equilibrium ensemble. At any time after quenching to the temperature Θ_1, the faster-moving components are closer to, while the slower-moving units are farther from their equilibria than the entire ensemble. When the temperature $\Theta(t)$ suddenly increases from Θ_1 to Θ_2, the fastest components become over-densified, and their volume begins to grow, whereas the slower-moving components proceed with their densification. This results in a temporary increase in the specific volume (caused by an increase in volume of the fastest components) until the parameter δ reaches its maximum. The increase is followed by densification of the specimen (when the fast components reach their equilibrium, and the kinetics of volume recovery is determined by slow-moving components, which have not practically recovered at the temperature Θ_1).

Structural relaxation is traditionally studied on stress-free specimens (the influence of atmospheric pressure is negligible). Unlike thermal effects, which have been already described in a number of works, only a few papers may be mentioned that deal with the influence of mechanical stresses on physical aging. Specimens of cellulose acetate butyrate were aged in [34] being stress-free and being loaded by tensile stresses (in the range of linear viscoelasticity). Practically no difference has been discerned between relaxation spectra of loaded and unloaded samples. Volume recovery kinetics was studied in [138] for an epoxy glass after upward and downward thermal jumps on specimens loaded in a torsional dilatometer. It was shown that the rates of structural relaxation for unloaded specimens and for specimens loaded by 3% and 5% strains were very close to each other. The effect of pressure on the equilibrium specific volume has been experimentally studied in several works. It was demonstrated for poly(vinyl acetate) [9] and polypropylene [156] that (i) an increase in pressure implies a decrease of the specific volume v_∞ and a substantial growth of the glass transition temperature Θ_g, and (ii) pressure affects the specific volume the stronger, the higher is the current temperature Θ. Polymeric specimens slowly cooled under high pressure reveal the densification effect: removal of pressure after cooling causes an increase in their specific volume. This response is in contradiction to the behavior of specimens quenched under atmospheric pressure which demonstrate time-dependent densification [19].

3. Phenomenological models for volume recovery

This section deals with phenomenological constitutive models which describe evolution of the specific volume without providing transparent physical mechanisms for structural relaxation.

3.1. The Kovacs model

The simplest model (the so-called one-parameter KAHR equation) is based on the assumption that the rate of approaching equilibrium is proportional to the measure of departure from the equilibrium state. For nonisothermal recovery, this assertion implies that

$$\frac{d\delta}{dt} = -q\Delta\alpha - \frac{\delta}{T}, \qquad \delta(0) = \delta_0, \tag{7}$$

where $q = d\Theta/dt$ is the rate of temperature changes, the characteristic time of aging T is a function of ε and Θ, and $\Delta\alpha = \alpha_l - \alpha_g$ is the difference between the coefficient of thermal expansion for the supercooled liquid, α_l, and that for the glass, α_g. The parameters $\Delta\alpha$ and α_f in Eqs. (2) and (7) do not necessarily coincide; for example, $\Delta\alpha = 4.4 \times 10^{-4}$ 1/K and $\alpha_f = 5.3 \times 10^{-4}$ 1/K for poly(vinyl acetate) [17].

The time T is expressed in terms of the "reference" time T_r (the time of aging in thermal equilibrium at the reference temperature Θ_r) by the formula

$$T = T_r a(\Theta, \varepsilon), \tag{8}$$

where a is a shift factor. There are three approaches to the description of the function a. The first is based on the free volume concept [113, 114]. The Doolittle equation [104] for the function a reads

$$\ln a = b\Big(\frac{1}{f} - \frac{1}{f_r}\Big), \tag{9}$$

where f_r is the equilibrium free volume fraction at the reference temperature Θ_r and b is an adjustable parameter. Assuming structural relaxation to reflect changes in the free volume only (which means that the occupied volume is time-independent), we find from Eqs. (2) and (3) that for small $\delta \ll 1$ and small changes in temperature $|\Theta - \Theta_r|/\Theta_r \ll 1$,

$$f = f_r + \alpha_f(\Theta - \Theta_r) + \delta.$$

Substitution of this expression into Eq. (9) results in the one-parametric Kovacs model, Eqs. (7), (8) and

$$\ln a = -\lambda(\Theta - \Theta_r) - \kappa\delta, \tag{10}$$

where λ and κ are adjustable parameters.

Constitutive equations (7), (8) and (10) fail to correctly predict volume recovery of polystyrene at heating [114]. To refine this model, the only relaxation time T is replaced by a distribution of relaxation times. For this purpose, the free volume V_f is split into M components corresponding to M Simon's ordering parameters [6, 114, 146, 150, 155],

$$\delta = \sum_{m=1}^{M} \delta_m. \tag{11}$$

Assuming the parameters δ_m to obey the linear kinetic equation (7) with appropriate $\Delta\alpha_m$ and T_m and preserving formula (10) for the shift factor a, we arrive at the multi-parameter Kovacs model [6]. This model adequately predicts volume recovery in poly(vinyl acetate) [6, 113, 150] and polystyrene [150, 157]. Tests for determining material constants λ and κ are discussed in [158].

The second approach employs the Tool concept of fictive temperature [100]. The Adam–Gibbs formula [117] for the shift factor reads

$$\ln a = \frac{\Delta\mu\, S_*}{k_B \Theta S_c(\Theta_f)}, \tag{12}$$

where $\Delta\mu$ is the energy of a potential barrier hindering rearrangement, S_* is the critical entropy, and k_B is Boltzmann's constant. Combining Eqs. (7), (8) and (12) and assuming that [4]

$$\delta = \Delta\alpha(\Theta_f - \Theta), \tag{13}$$

we obtain the constitutive model introduced in [114]. This model (with a peculiar expression for the specific heat Δc) was applied to fit experimental data in enthalpy relaxation tests for an inorganic glass [125, 159] and to predict volume recovery in a metallic glass [160].

Another way to link the free volume theory with the concept of cooperative relaxation was proposed in [161], where a polymeric material was treated as an ensemble of free volume clusters, and the Flory–Huggins formula was used for the configuration entropy:

$$S_c = K\Big[f \ln f + (1-f)\ln(1-f)\Big], \tag{14}$$

where K is an adjustable parameter. The model (7), (8), (12) and (14) was applied in [161] to match experimental data in calorimetric tests for poly(vinyl acetate). The use of Eq. (14) is, however, questionable, since it determines the combinatorial (not configurational) contribution to the specific entropy.

An interesting connection between the concept of cooperative relaxation and "energy" theories of glass-forming liquids has been established in [162], where structural relaxation is associated with changes in the strength of walls for rearrangement regions. A bulk material is modeled as an ensemble of flow units linked by cohesive forces on their boundaries. The initial homogeneous state of the medium (when cohesive forces coincide for all relaxing units) is destroyed with time due to the rearrangement process, and regions arise that are weakly connected with their surroundings. Based on the tear–repair mechanism of relaxation, it has been found that the shift factor a is expressed in terms of the configurational entropy by an analog of the Adam–Gibbs formula (12) with the $\frac{2}{3}$ exponent

$$\ln a = \frac{\Delta\mu}{k_B\Theta}\Big[\frac{S_*}{S_c(\Theta_f)}\Big]^{\frac{2}{3}}. \tag{15}$$

To our knowledge, no attempts have been made to validate Eq. (15) by comparison with experimental data for glassy polymers.

The third approach is based on the Arrhenius law for the shift factor a [101, 102]

$$\ln a = \frac{H}{k_B}\left(\frac{1}{\Theta} - \frac{1}{\Theta_r}\right), \tag{16}$$

where H is an apparent activation enthalpy. Splitting the reciprocal temperature into two terms,

$$\Theta^{-1} = \kappa\Theta^{-1} + (1-\kappa)\Theta^{-1},$$

where $\kappa \in (0,1)$ is an adjustable parameter, and replacing the real temperature Θ in the second term by the fictive temperature Θ_f, we arrive at the Narayanaswamy formula

$$\ln a = \frac{H}{k_B}\left(\frac{\kappa}{\Theta} + \frac{1-\kappa}{\Theta_f} - \frac{1}{\Theta_r}\right). \tag{17}$$

Equation (17) was used to fit experimental data in calorimetric tests for several polymers in [103, 122, 123]. The following shortcomings of the Narayanaswamy approach may be mentioned [122]:

1. in equilibrium Eq. (17) turns into the Arrhenius equation (16), which poorly predicts experimental data in the vicinity of the glass transition temperature Θ_g [163];
2. the parameter κ has no physical meaning;
3. observations show that the quantities H and κ are not constant, but systematically change with temperature Θ and the elapsed time t_e.

To assign some physical meaning to the constant κ, Macedo and Litovitz [112] assumed that structural relaxation in polymers is governed by two internal processes. One is thermally activated, and its rates are determined by the current temperature in accordance with the Eyring theory of absolute reaction rates [164]. The other process is athermal, and its kinetics is characterized by some measure of departure from equilibrium. The parameter κ serves as a measure of "weights" for thermal and structural mechanisms of volume recovery when the Arrhenius kinetics is accepted for the thermally activated process. "Hybrid" constitutive relations that (formally) combine thermal and structural mechanisms are listed in [83, 123]. For examples we refer to a hybrid of the Arrhenius and Doolittle equations [31]

$$\ln a = b\Big(\frac{1}{f} - \frac{1}{f_r}\Big) + \frac{H}{k_B}\Big(\frac{1}{\Theta} - \frac{1}{\Theta_r}\Big), \tag{18}$$

and to hybrids of the VFT and Arrhenius relationships

$$\ln a = \frac{H}{k_B}\Big[\frac{A}{\Theta_f - \Theta} + \Big(\frac{1}{\Theta} - \frac{1}{\Theta_r}\Big)\Big], \qquad \ln a = \frac{H}{k_B}\Big[\frac{A}{\Theta_f - \Theta} + \Big(\frac{1}{\Theta} - \frac{1}{\Theta_f}\Big)\Big].$$

The following shortcomings of the Kovacs model are mentioned [17]:

1. constitutive equations (7), (8) and (10) are based on the free volume concept which is (i) merely phenomenological and (ii) irrelevant on the time scale of primary segmental motion;
2. multi-parameter versions of the model use sums of M contributions δ_m which are not physically identified. Since Eq. (11) does not provide any hint regarding the way for determining the initial conditions $\delta_m(0)$, these quantities should be treated as adjustable parameters, which results in a huge number of constants to be found;
3. parameters in Eqs. (12) and (17) determined by fitting experimental data take physically unacceptable values;
4. constitutive relations fail to correctly predict the behavior of $\tau_{\rm eff}$ expansion curves near the equilibrium state for any reasonable set of parameters.

3.2. The Matsuoka model

The constitutive model is based on the hypothesis that the relaxation spectrum in thermal equilibrium at the reference temperature Θ_r coincides with the limiting spectrum for volume recovery in polymers equilibrated at the temperature Θ_r after thermal treatment [83].

The relaxation measure $Q(t)$ in equilibrium at the temperature Θ_r may be expanded into a truncated Prony series with M terms,

$$Q(t) = -\sum_{m=1}^{M} \eta_m \Big[1 - \exp\Big(-\frac{t}{T_{rm}} \Big) \Big],$$

where T_{rm} is the mth equilibrium relaxation time and η_m is the mth equilibrium intensity of relaxation. The parameters η_m obey condition (5). The Kovacs splitting of free volume into M components (11) is replaced by the equality

$$\delta = \sum_{m=1}^{M} \eta_m \delta_m, \tag{19}$$

where δ_m is determined by Eq. (3) for the mth component of free volume. It is postulated that the parameters δ_m satisfy governing equations (7), where the actual recovery time T_m is expressed in terms of the reference relaxation time T_{rm} by Eq. (8). The initial conditions for Eq. (7) read

$$\delta_m(0) = \delta_0,$$

where δ_0 is the initial departure from equilibrium. This equality allows the number of adjustable parameters to be substantially reduced compared to the Kovacs model. The shift factor a in Eq. (8) is given by one of Eqs. (10), (12) and (17). The model (7), (8), and (19) with the hybrid formula (18) for the function a adequately describes volume and dielectric relaxation in poly(vinyl acetate), polystyrene and glucose. In particular, it allows memory effects and the expansion gap to be correctly simulated [83]. The following shortcomings of the model may be mentioned:

1. no physical mechanisms are revealed which ensure that equilibrium mechanical relaxation and non-equilibrium volume recovery have the same spectra;
2. the parameters δ_m in Eq. (19) have no physical meaning;

3. experimental data for glassy polymers in the vicinity of the glass transition temperature Θ_g show that apparent activation enthalpies for equilibrium mechanical relaxation are essentially less than the activation enthalpies for volume recovery [1]. This implies that even if mechanical and dilatometric spectra coincide at one temperature, they should differ at another temperature.

3.3. The Moynihan model

Equations (7) and (8) mean that some internal clock may be introduced in a polymeric material similar to that employed in viscoelasticity of thermorheologically simple media [22]. The internal time ξ coincides with the real time t when the material is in thermodynamic equilibrium at the reference temperature Θ_r, and its is given by the formula

$$\xi(t) = \int_0^t \frac{d\tau}{a}$$

for an arbitrary (non-equilibrium) process.

Based on experimental data, it is proposed in [4] that evolution of the parameter δ is determined by the KWW function (6), where the real time t is replaced by the internal time ξ,

$$\delta(t) = \delta_0 \exp\Big\{-\Big[\frac{1}{T_r}\int_0^t \frac{d\tau}{a(\Theta(\tau), \varepsilon(\tau))}\Big]^\beta\Big\}. \tag{20}$$

Equations (13) and (20) result in the nonlinear integral equation

$$\Theta_f(t) - \Theta = (\Theta_0 - \Theta)\exp\Big\{-\Big[\frac{1}{T_r}\int_0^t \frac{d\tau}{a(\Theta(\tau), \Theta_f(\tau))}\Big]^\beta\Big\}, \tag{21}$$

provided that the fictive temperature Θ_f is chosen as a measure for departure from equilibrium. Constitutive equations (13) and (21) demonstrate acceptable agreement with observations in calorimetric tests for several polymers [11, 122, 123].

For a one-step thermal program, Eq. (21) is reduced to an ordinary differential equation. Its natural generalization is a nonlinear differential equation [165]

$$\frac{d\Theta_f}{dt} = \mathcal{F}(\Theta, \Theta_f), \qquad \Theta_f(0) = \Theta_0, \tag{22}$$

where the function $\mathcal{F}$ is determined by fitting experimental data. This function was approximated by a truncated Taylor series in the difference $\Theta_f - \Theta$ in [27], and it was presented as a product of an exponential function and a truncated Taylor series in the difference of temperatures in [26].

Another way to fit experimental data was proposed in [102], where a quasi-linear integral equation for the fictive temperature was introduced

$$\Theta_f(t) - \Theta(t) = \int_0^{\xi(t)} M(\xi - \eta)\frac{d\Theta}{d\eta}(\eta)d\eta. \tag{23}$$

The kernel of the Volterra operator $M(t)$ was presented in the form of a truncated Prony series in [166] and in the form of a stretched exponential function in [167]. Properties of Eqs. (22) and (23) were discussed in detail in [22].

The following disadvantages of the Moynihan model are mentioned [17]:

1. the KWW expression (6) for the function $\delta(t)$ is taken as an assumption and not derived from any kinetic theory for glasses;

2. the parameter β in Eqs. (20) and (21) has no physical meaning. Observations show that it is not a constant, but a function of the elapsed time t_e [32];
3. the model cannot predict the expansion gap for $\tau_{\rm eff}$.

3.4. The coupling model

Recent results in the structural dynamics of Hamiltonian systems with high numbers of degrees of freedom demonstrate that changes in macroscopic quantities (mean values of functionals over all microscopic variables) are governed by relatively simple formulas (despite the complicate dynamics for individual state variables). In particular, it is shown that for "typical" systems (the attribute means that cases not revealing generic features are neglected [17]) isothermal macro-kinetic processes obey the quasi-linear rate equation similar to Eq. (7),

$$\frac{d\varepsilon}{dt} = -\frac{\varepsilon}{T_\diamond}, \tag{24}$$

where ε stands for a measure of departure from equilibrium, and the parameter $T_\diamond$ depends explicitly on time,

$$T_\diamond = T\varphi(t). \tag{25}$$

Here T is the characteristic time for structural relaxation in a non-aged material (which depends on temperature and ordering parameters in the same way as in the Kovacs model), and the function $\varphi(t)$ satisfies the asymptotics

$$\varphi(t) = \begin{cases} 1, & \text{small} \quad t; \\ t^{1-\beta}, & \text{large} \quad t. \end{cases} \tag{26}$$

The parameter β is located in the interval $(0, 1)$, whereas "small" and "large" times mean that the ratio t/t_0 is small or large compared to unity, where t_0 is of the order of 10^{-9} to 10^{-10} s.

The decay (26) is explained as follows: at the initial stage of recovery, the rates of kinetic processes are determined by the initial short-range order that provides the characteristic time T for structural relaxation. Subsequent "adjustment of primitive species" ("newspeak" for rearrangement of flow units) imbedded into a "complex environment" (a bulk material) decelerates the relaxation process, because of the growth in the spatial scale for micro-order. The parameter β characterizes both the strength for coupling between relaxing units and the degree of complexity for the environment. This quantity is treated as an increasing function of temperature and decreasing function of the elapsed time t_e [32].

Basic technical assumptions of the model for volume relaxation are that (i) expression (26) for the function φ at large times may be used for any $t \geq 0$, and (ii) the ratio δ provides the measure of departure from equilibrium. These hypotheses together with Eqs. (24) and (25) result in the differential equation

$$\frac{d\delta}{dt} = -\frac{\delta}{Tt^{\beta-1}}, \qquad \delta(0) = \delta_0. \tag{27}$$

Integration of Eq. (27) with constant parameters T and β implies the KWW formula (6) with $T_0 = (\beta T)^{\frac{1}{\beta}}$. For a constant parameter β and an arbitrary shift function a in Eq. (8), integration of Eq. (27) implies the Moynihan formula (20). When both T and β are functions of δ and Θ, Eq. (27) may be integrated numerically.

According to [18], the coupling model (8), (24) and (25) is second to none among constitutive relations that predict an expansion gap on the $\tau_{\rm eff}(\delta)$ diagram for poly(vinyl acetate).

The following shortcomings of the coupling model may be mentioned:

1. the asymptotics (26) seems plausible for large-scale Hamiltonian systems, but no explicit conditions (both on a system and on a functional) are provided which ensure that Eq. (26) holds;

2. the use of Eq. (27) instead of the asymptotical formula (26) is questionable, and it requires additional argumentation;

3. no physical model is derived for the dependence $\beta(\Theta, t_e)$, which plays the kee role in successful fitting of experimental data for $\tau_{\rm eff}(\delta)$.

3.5. The Bauwens-Crowet model

Constitutive relations similar to the Kovacs equations have been derived and verified on polycarbonate specimens in a series of papers [43, 57, 61, 62, 141]. The fictive temperature Θ_f is used as the main internal variable, and it is postulated that in a one-step thermal test (1) this function obeys the kinetic equation

$$\frac{d\Theta_f}{dt} = -\frac{\Theta_f - \Theta}{T}, \qquad \Theta_f(0) = \Theta_0. \tag{28}$$

Equation (28) coincides with the Kovacs relation (7), provided that the parameter δ is determined by Eq. (13). Formula (28) can also be deduced from the Davies–Jones theory [135], which makes it more plausible than Eq. (7).

The characteristic time of structural relaxation T obeys Eq. (8), where the shift factor a is determined by an analog of the WLF formula

$$\ln a = \frac{c_1(\Theta_f - \Theta_0)}{c_2 + (\Theta_f - \Theta_0)}, \tag{29}$$

where c_1 and c_2 are "universal" constants [106].

Constitutive relations (8), (28) and (29) ensure acceptable agrement with experimental data in calorimetric tests on polycarbonate specimens [57, 61, 62]. These equations combined with an Eyring-type relationship in nonlinear viscoelasticity provide a good fit of observations in dynamic tests on stretched samples [43]. The model (8), (28) and (29) together with a simple formula for the yield stress permits the effect of annealing on the yield of polycarbonate to be correctly predicted [57, 61, 62].

The following shortcomings of this model may be mentioned:

1. Equation (28) has been deduced from the Clausius–Duhem inequality in [135], but no specific expression for the function T has been developed. This means that the shift factor a in Eq. (8) should be treated as an arbitrary function of temperatures Θ and Θ_f, and any specific form of this function should be substantiated and verified by observations;

2. the use of the WLF law (29) seems questionable, since this equality is satisfied above the glass transition only [106]. The authors' remark [57] that they use a nonstandard variable in this equation (the difference $\Theta_f - \Theta_0$ instead of Θ) provides no justification for their approach.

3.6. The Egami model

Unlike previous models aimed at describing all stages of structural recovery of glasses, the Egami equation [168] serves to predict the $\ln t$ kinetics at the initial stage of volume recovery only. It is assumed that (i) changes in the specific volume after a thermal jump are thermally activated, (ii) the rate of this thermally activated process is determined by the Eyring formula [164], and (iii) the energy of activation is proportional to the departure from equilibrium. These hypotheses imply the constitutive equation

$$\frac{d\delta}{dt} = -A\exp\Bigl(-\frac{H\delta}{k_B\Theta}\Bigr), \qquad \delta(0)=\delta_0, \tag{30}$$

where A is the equilibrium rate of volume recovery and H is an analog of the apparent enthalpy. The quantities A and H are treated as adjustable parameters. The solution of Eq. (30) for a one-step thermal program (1) reads

$$\delta(t) = \delta_0 + \frac{k_B\Theta}{H}\ln\Bigl[1-\frac{AHt}{k_B\Theta}\exp\Bigl(-\frac{H\delta_0}{k_B\Theta}\Bigr)\Bigr].$$

Formally, this formula does not imply the logarithmic kinetics. However, choosing appropriate values of adjustable parameters A, H and δ_0, observations can be fitted with an acceptable level of accuracy.

The following shortcomings of the constitutive model (30) may be noted [12]:

1. it is not obvious why the activation energy should be proportional to a measure of departure from equilibrium;
2. Equation (30) correctly describes only the initial stage of the volume recovery curves, but it fails to predict the final stage, where the most intriguing phenomena are observed (see Section 2).

4. Concluding remarks

Characteristic features of structural relaxation (physical aging) in amorphous polymers are discussed in detail. The emphasis is laid on volume recovery and accompanying phenomena. Phenomenological models for the kinetics of volume relaxation are exposed, and their advantages and shortcomings are discussed. Physical models for evolution of the specific volume with time (which provide transparent physical mechanisms for structural relaxation) will be the subject of the other part of this work.

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