JOURNAL OF MATERIALS SCIENCE 28 (1993) 901–908

Rheology of non-Newtonian glass-forming melts

Part II *Kinetics of relaxation and retardation*

I. GUTZOW, A. DOBREVA
Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria
J. SCHMELZER
Sektion Physik, Universität Rostock, Universitätsplatz 3, Rostock 2500, Germany

A general formalism describing the kinetics of relaxation and retardation in glass-forming materials is developed. By introducing the real flow behaviour of a particular system into an extended analogue of Maxwell's equation, a set of non-linear relaxational and retardational dependences, applicable to liquids with different structures, is obtained. The Kohlrausch stretched-exponent formula and similar dependences with time-dependent relaxation times are also derived. A comparison with established empirical relations and existing experimental data gives satisfactory coincidence.

1. Introduction

From a more general point of view, the relaxation of strains in glasses or the retarded reaction of glass-forming melts under an external disturbance can be treated either as an evolution of the frozen-in system towards equilibrium (relaxation as a process of glass stabilization [1–6]) or as a response of a dissipative system to a time-limited external influence. Thus the rheology of glass-forming melts which determines the kinetics of the two most significant processes in undercooled melts (their vitrification [6] and crystallization [7, 8]) also gives an illustration of the behaviour of dissipative systems in general.

It was mentioned in Part I of the present investigation [9] that Maxwell's equation in its classical formulation cannot describe the kinetics of relaxation in glass-forming melts [1, 10]. In order to overcome the deficiencies of this classical formulation two other approaches have been advanced – the use of a set of linear Maxwellian-type equations with different relaxation times [6, 11, 12], or the employment of empirical non-linear formulae with time-dependent relaxation times [6, 13–16]. These approaches contain a logistic inconsistency: it is known, as it is demonstrated also in Part I [9], that the flow of real glass-forming systems under stress is, in fact, non-linear non-Newtonian, whereas in the above formulations only linear Newtonian flow is anticipated.

This is why we suggest here an alternative formalism: to introduce in an appropriate way the real non-linear flow kinetics into a generalized analogue of Maxwell's equation, and thus to derive the non-linear kinetics of relaxation. This approach, which was indicated for the first time by Eyring [17], gives an additional and very serious advantage: knowing the flow of the system (e.g. from the experiment) a definite relaxational behaviour should be expected. In this way the relaxation kinetics is not predetermined by any assumptions (e.g. by the hypothesis of the existence of a spectrum of relaxation times) but follows in a natural way from the mechanism of flow.

In deriving the classical relaxational and retardational equations of the phenomenological rheology, Maxwell and Kelvin have used linear combinations of mechanical elements (e.g. of Hookean-like springs and Newtonian-like dash pots). At present, the linear combination of the elements in these equatioins can be derived in the framework of the thermodynamics of irreversible processes [18] where it can be considered as a consequence following from the dynamic equation of state [19]. Accepting this thermodynamic result and accounting for the non-Newtonian flow behaviour of real glass-forming melts (i.e. introducing a non-linear element in this way), non-linear relaxational dependences and time-dependent relaxation times are obtained.

We define below an apparent time of relaxation in analogy to the widespread procedure of introducing an apparent viscosity. This approach is similar to the thermodynamic method of employing activity coefficients for describing non-ideal behaviour of a real system. Thus our task is reduced to the mathematical problem of solving a number of differential equations in which different flow–stress dependences following from the same theoretical flow model are introduced into an extended Maxwellian equation.

As a basic theoretical flow model, the Prandtl–Eyring potential barrier approach is used.

2. Basic flow–stress dependences

The analysis, performed in Part I [9], has shown that a very general dependence connecting the shear rate of flow, $\dot{\gamma}$, and the shear stress, S is

$$\dot{\gamma} = \frac{A}{\eta_0}\sinh(aS)\exp(-\Gamma_0\dot{\gamma}) \qquad (1)$$

Equation 1 was derived in Part I [9] by extending the concept of the Prandtl–Eyring potential barrier model to include dilatant effects. Here η_0 = constant is the Newtonian viscosity of the melt, the parameter $a = 1/A$ is determined by the so-called viscous volume of the structural units taking part in the flow process and Γ_0 is a factor reflecting the complexity of molecules and especially their ability to form entanglements upon flow.

A thorough discussion on the problems of molecular flow, on the derivation of Equation 1, as well as on the physical nature of a, A and Γ_0, is given in Part 1 [9].

For melts, which exhibit no dilatant effects, $\Gamma_0 = 0$ and Equation 1 gives the classical Prandtl–Eyring formula [20–23]

$$\dot{\gamma} = \frac{A}{\eta_0}\sinh(aS) \tag{2}$$

describing the flow of pseudoplastic (or even plastic [24]) liquids. Using the well-known approximation of the sinh (x) and exp (x) functions, all existing empirical formulae proposed for $\dot{\gamma}(S)$ dependences can be easily obtained (see Part I [9]). In this connection the de Waele–Ostwald equation is of special interest [25, 26]

$$\dot{\gamma} = A_2\frac{S^n}{\eta_0} \tag{3}$$

where A_2 and n are empirical constants. At $n > 1$, Equation 3 accounts for pseudoplasticity and at $n < 1$ dilatant behaviour follows. The advantage of Equation 3 is in its obvious simplicity. However, as shown in Part I, it is applicable with n = constant only for relatively narrow S intervals.

Three other important $\dot{\gamma}(S)$ approximations can be obtained from Equation 1 as limiting cases [9].

(i) For $\Gamma_0\dot{\gamma} \ll 1$, Equation 1 transforms into

$$\dot{\gamma} \approx \left[\frac{A}{\eta_0\Gamma_0^*}\sinh(aS)\right]^{1/2} \tag{4}$$

where Γ_0^* is an appropriately chosen constant.

(ii) For $\Gamma_0\dot{\gamma} \gg 1$ the following relations

$$\dot{\gamma} \approx \frac{1}{\Gamma_0}\left(\ln\frac{A}{\eta_0} + \ln aS\right) \tag{5a}$$

$$\dot{\gamma} \approx \frac{1}{\Gamma_0}\left(\ln\frac{A}{\eta_0} + \frac{1}{2}aS\right) \tag{5b}$$

are obtained for $aS \ll 1$ and for $aS \gg 1$, respectively. At $aS < 1$, Equation 4 gives Darcy's formula, i.e. Equation 3 with $n = 1/2$.

For $aS \to 0$, Equations 1–3 lead directly to Newton's law

$$\dot{\gamma} = \frac{S}{\eta_0} \tag{6}$$

Equation 1 and the approximations derived from it describe with sufficient accuracy any type of flow: pseudoplastic (or plastic), dilatant as well as the transition from dilatant to pseudoplastic (see [9]).

3. Stress dependence of the apparent viscosity

In order to retain the linearity of the flow–stress dependences even for non-Newtonian flow, an apparent value of the viscosity $\eta(S) = \eta_{\text{app}}$ can be introduced by the relation

$$\dot{\gamma} = \frac{S}{\eta_{\text{app}}} \tag{7}$$

Equation 7 gives all benefits known from the thermodynamic treatment of real systems in which the simple form of laws derived for ideal solutions, ideal gases, etc., is preserved by the introduction of thermodynamic activity coefficients depending on concentration, pressure, etc. In this way the use of linear dependences is guaranteed even when the system under consideration is far from ideal.

In the $\dot{\gamma}(S)$ dependences considered above the apparent viscosity can always be expressed in the form

$$\eta_{\text{app}} = \frac{\eta_0}{\psi(S)} \tag{8}$$

where $\psi(S)$ is a dimensionless function of S. For pseudoplastic liquids, $\psi(S)$ is either

$$\psi(S) = \frac{\sinh aS}{aS} \tag{9}$$

(cf. Equation 2) or it can be considered as being obtained from Equation 9 using some of the approximations mentioned for the sinh(x) function. Thus for Equation 3, $\psi(S)$ is given by

$$\psi(S) = A_2S^{n-1} \tag{10a}$$

According to Equations 9 and 10 (for $n > 1$) a decreasing $\eta_{\text{app}}(S)$ dependence is always obtained (pseudoplastic liquids). Some typical cases are

$$\psi(S) = A_2S \tag{10b}$$

for $n = 2$, or

$$\psi(S) = A_2S^{1/2} \tag{10c}$$

for the semi-cubic parabola case ($n = 3/2$). This n value, as discussed in Part I, corresponds to the flow of most glass-forming melts when it is described in terms of the de Waele–Ostwald equation. However, with $n < 1$ (as it is in Darcy's equation), an increasing $\eta_{\text{app}}(S)$ function with

$$\psi(S) = \frac{A_2}{S^{1/2}} \tag{10d}$$

is expected (dilatant liquids). The simple analysis of the generalized $\dot{\gamma}(S)$ dependence given with Equation 1 indicates that dilatant behaviour generally follows at $aS < 1$ and $\Gamma_0\dot{\gamma} < 1$, i.e. at relatively small shear-stress values and for relatively complex molecules, where

$$\psi(S) \approx \left(\frac{\eta_0\sinh aS}{\Gamma_0^* aS^2}\right)^{1/2} \tag{11a}$$

At $\Gamma_0\dot{\gamma} > 1$ we must expect either

$$\psi(S) = \frac{\text{const.} + \eta_0\ln aS}{S} \tag{11b}$$

from Equation 5a, or

$$\psi(S) = \left(\frac{\eta_0}{\Gamma_0}\ln\frac{A}{\eta_0}\right)S^{-1} + \frac{\eta_0}{2\Gamma_0}a \tag{11c}$$

from Equation 5b. Equation 11a–c predict dilatant behaviour of η_{app} at smaller aS values and a quasi-Newtonian behaviour (i.e. $\eta_{\mathrm{app}} \approx$ constant) at high aS values.

4. Apparent relaxation time

It is also useful to introduce an apparent time of relaxation (or apparent time of retardation) in analogy to the procedure adopted with Equations 6, 7. Assuming Newtonian flow for which Maxwell's classical dependence

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{S}{\tau_0} \tag{12}$$

holds we define for ideal systems a Maxwellian time of relaxation

$$\tau_0 = \frac{\eta_0}{g_0} \tag{13}$$

where g_0 is the respective shear modulus of the body under consideration.

Analogous to Equation 8, an apparent relaxation time, τ_{app}, characterizing real systems, can be introduced

$$\begin{aligned} \tau_{\mathrm{app}} &= \frac{\eta_{\mathrm{app}}}{g_0} \\ &= \frac{\eta_0}{g_0 \psi(S)} \end{aligned} \tag{14}$$

assuming that g_0 remains constant at the S values under consideration.

Thus, accounting for Equation 14, Equation 12 can be transformed into

$$\begin{aligned} \frac{\mathrm{d}S}{\mathrm{d}t} &= -\frac{S}{\tau_{\mathrm{app}}} \\ &= -\frac{S\psi(S)}{\tau_0} \end{aligned} \tag{15}$$

where τ_0 is defined using Equation 13. For liquids with Newtonian flow, $\psi(S)$ in Equation 8 is equal to unity and the well-known solution of Equation 12 follows (at the boundary condition $S = S_0$ for $t \to 0$)

$$S = S_0 \exp\left(-\frac{t}{\tau_0}\right) \tag{16}$$

known as Maxwell's relaxational law.

For non-Newtonian liquids, however, Equation 15 indicates that the integral $\int \mathrm{d}S/(S\psi(S))$ must be solved for the cases of different $\psi(S)$ functions (Equations 9–11) already discussed.

5. Non-linear kinetics of relaxation

In order to analyse the kinetics of relaxation for systems with a given type of non-Newtonian flow, we must introduce through Equation 14 the respective $\psi(S)$ function given with Equations 9–11, into Equation 15.

Thus for Prandtl–Eyring liquids (see Equation 9) with the boundary condition already mentioned, the following relaxational equation is obtained

$$\ln\left[\mathrm{tgh}\left(\frac{aS}{2}\right)\right] = \ln\left[\mathrm{tgh}\left(\frac{aS_0}{2}\right)\right] - \frac{t}{\tau_0} \tag{17}$$

This formula was derived, in fact, years ago by Tobolsky and Eyring [27].

The general solution of the relaxation kinetics, when instead of Equation 9 the de Waele–Ostwald approximation (Equation 10) is used, reads

$$S = S_0\left[1 + (n-1)S_0^{n-1}\frac{A_2}{\tau_0}t\right]^{-1/(n-1)} \tag{18}$$

This solution gives rise to a number of important particular cases. At $n = 2$ from Equation 18 follows the well-known Adams–Williamson empirical annealing formula discussed in detail by Morey [1]. It is usually written in the form

$$\frac{1}{S} - \frac{1}{S_0} = A_2\frac{t}{\tau_0} \tag{18a}$$

Taking into account that for small aS values (as found in Part I [9]), n in equation 3 is about 3/2, we should suggest that for pseudoplastic liquids a better relaxational dependence in terms of Equation 18a should read

$$\frac{1}{S^{1/2}} - \frac{1}{S_0^{1/2}} = \frac{1}{2}A_2\frac{t}{\tau_0} \tag{18b}$$

For higher aS values, corresponding to the $n = 5/2$ approximation of Equation 18 a more appropriate dependence would be

$$\frac{1}{S^{3/2}} - \frac{1}{S_0^{3/2}} = \frac{3}{2}A_2\frac{t}{\tau_0} \tag{18c}$$

In the case of dilatant liquids for $n = 1/2$ (i.e. for Darcy's formula) we have

$$S^{1/2} - S_0^{1/2} = -\frac{1}{2}A_2\frac{t}{\tau_0} \tag{18d}$$

In deriving the problems of the kinetics of relaxation in general, i.e. accounting for dilatant effects we must consider a number of mathematical problems.

The integration of Equation 15 with the $\psi(S)$ function having the form given with Equation 11a (i.e. at $\Gamma_0\dot{\gamma} < 1$) leads to [28]

$$F\left\{\phi[f(aS)], \frac{1}{2^{1/2}}\right\} = F\left\{\phi[f(aS_0)], \frac{1}{2^{1/2}}\right\} - P_0\frac{t}{\tau_0} \tag{19}$$

where $P_0 = (\eta_0\Gamma_0^{\#})^{1/2}$ and $F\{\phi[f(aS)], 1/2^{1/2}\}$ denotes the first order elliptic integral function [28–30] with a modulus $k = 1/2^{1/2}$ and an amplitude, ϕ, determined by

$$\phi = \arccos f \tag{20a}$$

where

$$f = \frac{1 - \sinh aS}{1 + \sinh aS} \tag{20b}$$

As shown in Fig. 1, where tabulated values of the mentioned elliptic integral function have been used [30, 31], a linear $F\{\phi, 1/2^{1/2}\}$ versus ϕ dependence

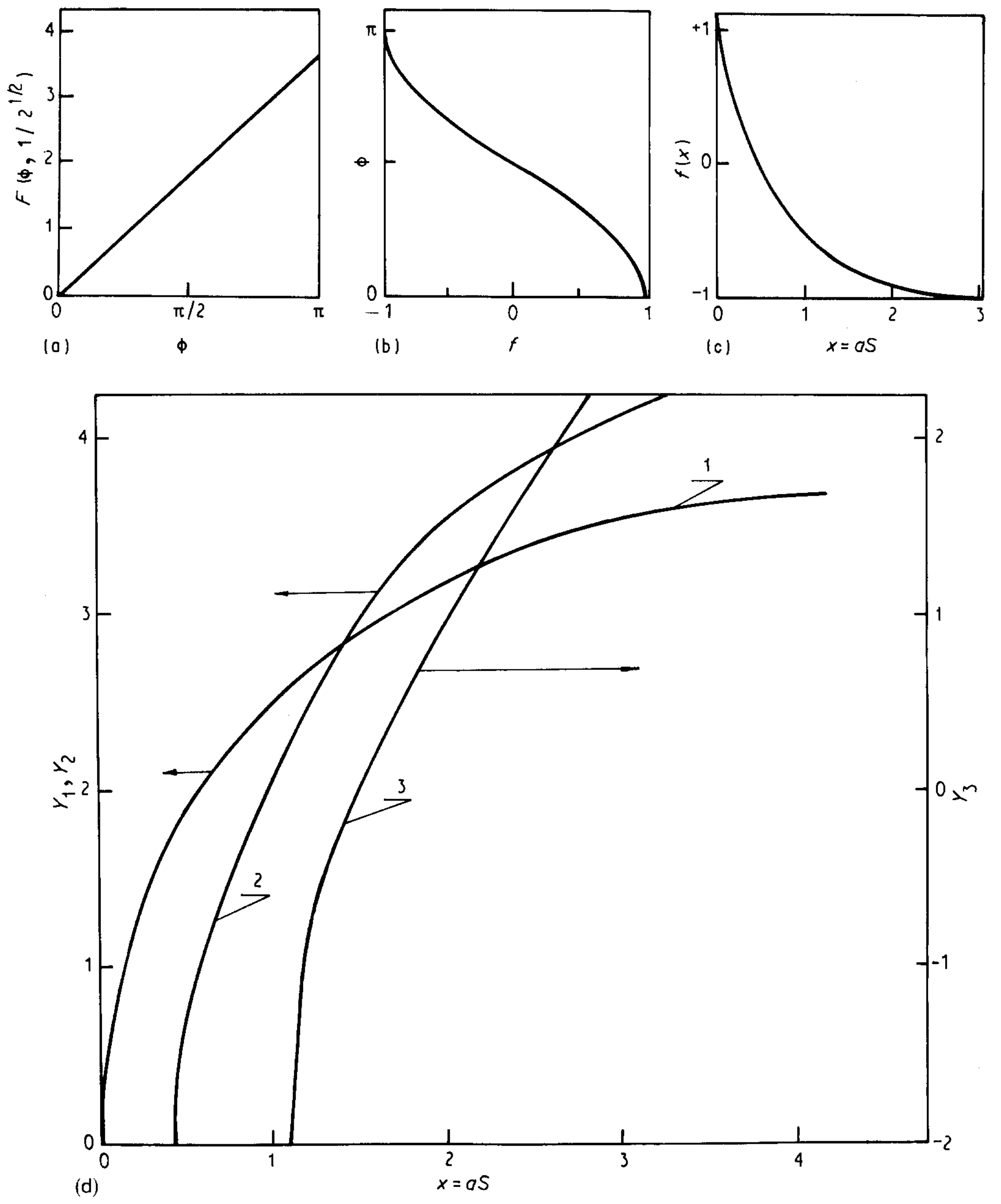

Figure 1 The solution of the kinetics of relaxation in the general dilatant–pseudoplastic case: (a) the $F(\phi, 1/2^{1/2})$ versus ϕ relation (Equation 20c), (b) the arccos f versus f dependence (Equation 20a), (c) f versus aS function (Equation 20b), (d) the three possible solutions: (1) Y_1, $F\{\phi[f(aS)], 1/2^{1/2}\}$ versus aS (Equation 19) (left-hand side coordinate); (2) Y_2, the approximate solution of Equation 20 (left-hand side coordinate); (3) Y_3, the li(aS) function (Equation 21) (right-hand side coordinate).

exists and thus

$$F\{\phi[f(aS)], \frac{1}{2^{1/2}}\} \approx q\phi \qquad (20c)$$

where $q = 1.2$ (Fig. 1a). Accounting for the course of the arccos(f) and the $f(aS)$ functions (Equations 20a, b and Fig. 1b, c) and for Equation 20, the $F\{\phi[f(aS)], 1/2^{1/2}\}$ versus aS dependence given in Fig. 1d follows.

It is difficult to recommend a simple approximation to Equation 19 in terms of elementary functions. The expansion of the arccos(f) and the $f(aS)$ functions using Taylor's formula (accounting for the first terms in the respective series) gives, with the mentioned q value

$$F\{\phi[f(aS)], \frac{1}{2^{1/2}}\} \approx q\left[\frac{\pi}{2} + 2\ln(aS)\right] \qquad (20d)$$

However, Equation 20d is a poor approximation of Equation (19) as can be also seen from Fig. 1d (curve 2). So the $F\{\phi[f(aS), 1/2^{1/2}\}$ values from Fig. 1d (curve 1) must be used in quantitative calculations of the relaxation of systems exhibiting a combination of dilatant and pseudoplastic flow at relatively small dilatant interaction (i.e. at $\Gamma_0\dot{\gamma} \ll 1$).

The other limiting case of combined pseudoplastic and dilatant behaviour (i.e. $\Gamma_0\dot{\gamma} \gg 1$) should be in general, a rare event. Equation 11b introduced into equations 14 and 15 gives, after integration, a formula which includes another non-elementary function: the integral logarithm li(x) [29, 31]

$$\mathrm{li}\left[\frac{(aS)^n}{\eta_0\Gamma_0}\right] = \mathrm{li}\left[\frac{(aS_0)^n}{\eta_0\Gamma_0}\right] - \frac{t}{\tau_0} \qquad (21)$$

The resulting dependence is depicted in Fig. 1d (curve 3).

In order to compare and to illustrate the solutions for the kinetics of relaxation of a liquid with Newtonian flow (i.e. Maxwell's equation (Equation 16)) with those following for pseudoplastic liquids (i.e. the Tobolsky–Eyring formula, Equation 17) with our solutions for the empirical $\dot{\gamma}(S)$ functions (i.e. Equations 18a–d) and with the generalized model for a pseudoplastic and dilatant non-Newtonian behaviour (Equations 19 and 21) it is convenient to write all these functions in an exponential form. Thus we obtain

$$\exp\left(F\left\{\phi[f(aS)], \frac{1}{2^{1/2}}\right\}\right) = \exp\left(F\left\{\phi[f(aS_0)], \frac{1}{2^{1/2}}\right\}\right)\exp\left[-P_0\frac{t}{\tau_0}\right] \quad (22a)$$

from Equation 19

$$\exp\{\mathrm{li}[(aS)^n]\} = \exp[\mathrm{li}(aS)^n]\exp\left(-P_0\frac{t}{\tau_0}\right) \quad (22b)$$

from Equation 21

$$\mathrm{tgh}\left(\frac{aS}{2}\right) = \mathrm{tgh}\left(\frac{aS_0}{2}\right)\exp\left(-\frac{t}{\tau_0}\right) \quad (22c)$$

from Equation 17

$$\exp[2(aS)^{1/2}] = \exp[2(aS_0)^{1/2}]\exp\left(-\frac{t}{\tau_0}\right) \quad (22d)$$

from Darcy's equation, and

$$\exp\left(-\frac{1}{S}\right) = \exp\left(-\frac{1}{S_0}\right)\exp\left(-A_2\frac{t}{\tau_0}\right) \quad (22e)$$

from the Adams–Williamson equation. Considering also the classical Maxwell result (Equation 16) it is evident that for all types of flow behaviour the kinetics of relaxation can be written in the general form

$$Y(aS) = Y(aS_0)\exp\left(-\frac{t}{\tau_0}\right) \quad (23)$$

where Y denotes one of the aS functions considered above. In the simplest case of a Newtonian liquid the Y function degenerates to aS itself. These dependences are illustrated in Fig. 2.

It is important to note that in generalizing the discussed solutions (Equation 16–19 and 21) they can be written also in the form

$$\chi(aS) = \chi(aS_0) - \frac{t}{\tau_0} \quad (24)$$

where χ denotes different aS functions always having a logarithmic-type course. This applies also to the $\mathrm{li}(x)$ function in Equation 22b which can be approximated in the form (see [29, 31]

$$\mathrm{li}(x) = \varepsilon_0 + \ln(-\ln x) + \sum_{j=1}^{\infty}\frac{(\ln x)^j}{j \cdot j!} \quad (25)$$

where $\varepsilon_0 = 0.577$ is Euler's constant. Thus for $aS < 1$, an appropriate approximation of the $\mathrm{li}(aS)$ function (Equation 21) takes the form

$$\mathrm{li}(aS) \approx 0.6 + \ln\left[\ln aS + aS + \left(\frac{aS}{2}\right)^2\right] \quad (26)$$

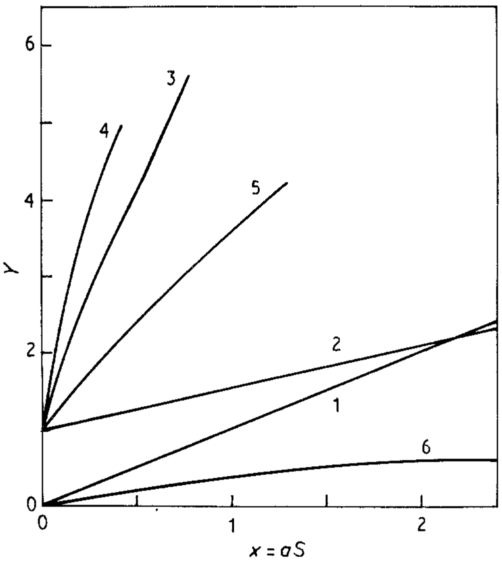

Figure 2 Exponential representation of the kinetics of relaxation. 1, Maxwell's solution for relaxation of Newtonian liquids (Equation 16); 2, Tobolsky–Eyring formula (Equation 22c) for pseudoplastic non-Newtonian behaviour; 3,4, generalized pseudoplastic and dilatant behaviour according to the generalized model at $\Gamma_0\dot{\gamma} \ll 1$ (curve 3) (Equation 22a) and for $\Gamma_0\dot{\gamma} \gg 1$ (curve 4) (Equation 22b); 5, the exponential form of the Adams–Williamson equation (Equation 22e).

Finally, it should be mentioned that according to Maxwell's differential equation (Equation 12), the rate of stress relaxation is proportional to the stress itself. This linear dependence is the simplest possible assumption. From the present discussion (and especially from Equations 9–11, it is evident that the more accurate approximation for the relaxation in a pseudoplastic liquid should not read

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{A_2}{\tau_0}S^2 \quad (27)$$

which corresponds to the Adams–Williamson annealing formula (Equation 18a) (see also [1]), but

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{A_2}{\tau_0}\left(1 + \tfrac{1}{6}S^2\right)S \quad (28)$$

or

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{A_2}{\tau_0}S^{n-1}S \quad (29)$$

with $n = 3/2$ to $5/2$. The above equations follow from the approximate representations of Equation 2 (cf. Equations 10a–e). This remark should be taken into account in discussing further attempts for optimal relaxational formulae.

In this respect, it is of particular interest to note that Equation 18c appears to be the optimal approximation in describing the kinetics of birefringence relaxation in technical glasses (Fig. 3). For the experimental data given in this figure, neither Maxwell's equation (Equation 16) nor the Adams–Williamson empirical formula (Equation 18a) proved to be applicable over the whole range of aS values. Similar results are also obtained for other experimental data, e.g. for the relaxational experiments reported by Narayanaswamy [32, 33], analysed in terms of equations 18a–d.

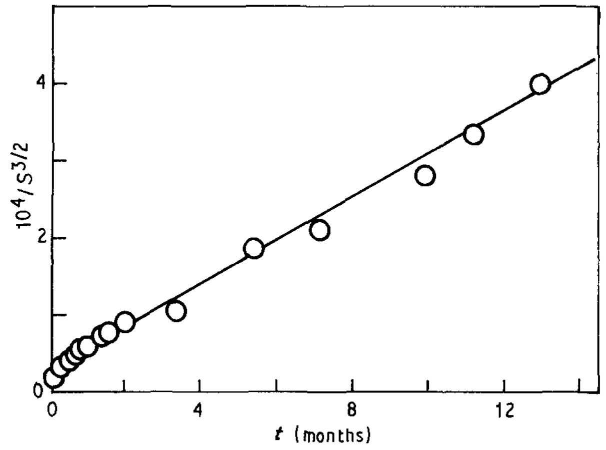

Figure 3 Application of Equation 18 with $n = 5/2$ to the particular problems of glass-annealing kinetics. Experimental data for annealing of optical birefringence in Pyrex glass as reported by Morey [1].

6. Kohlrausch's equation and time-dependent relaxation times

In considering the flow kinetics of liquids under constant stress, it is assumed that the $\psi(S)$ function in Equation 8 has a time-independent constant value. In the kinetics of relaxation, however, $\psi(S)$ in Equation 14 is, in fact, a time-dependent function changing from $\psi(S) = \psi(S_0)$ (at $t \to 0$) to $\psi(S) = \psi(0)$ (at $t \to \infty$). Thus our modified Maxwellian equation (Equation 15) can also be written in the equivalent form

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{1}{\tau_0}\psi(t)S \tag{30}$$

where $\psi(t) \equiv \psi(S)$ is a time-dependent function. The exact form of the $\psi(t)$ dependence for a given $\psi(S)$ function. Thus, accounting for Equation 10a and for tion following from the solution of the respective Maxwellian equation into the corresponding $\psi(S)$ function. Thus, accounting for Equation 10a and for the solution of the de Waele–Ostwald case (Equations 18a–d) the result is

$$\psi(t) = \frac{A_2 S_0^{n-1}}{[1 + (n-1)S_0^{n-1}A_2(t/\tau_0)]} \tag{31}$$

while the Tobolsky–Eyring formula (Equation 17) determines the $S(t)$ function as

$$S(t) = \frac{2}{a}\operatorname{arctgh}\left[\operatorname{tgh}\left(\frac{aS_0}{2}\right)\exp\left(-\frac{t}{\tau_0}\right)\right] \tag{32}$$

The above $S(t)$ dependence introduced into Equation 9 gives

$$\psi(t) = \frac{\sinh\{2\operatorname{arctgh}[\operatorname{tgh}(aS_0/2)\exp(-t/\tau_0)]\}}{2\operatorname{arctgh}[\operatorname{tgh}(aS_0/2)\exp(-t/\tau_0)]} \tag{33}$$

This dependence (assuming tgh $(S/2) \approx 1$) has been used in constructing the respective $\psi(t)$ functions shown in Fig. 4b.

In an analogous way, we can determine the $\psi(t)$ function for the general dilatant–pseudoplastic case (at $\Gamma\dot{\gamma} \ll 1$) according to Equation 19 with the reverse function of the elliptic integral, i.e. by introducing into Equation 11a the expression

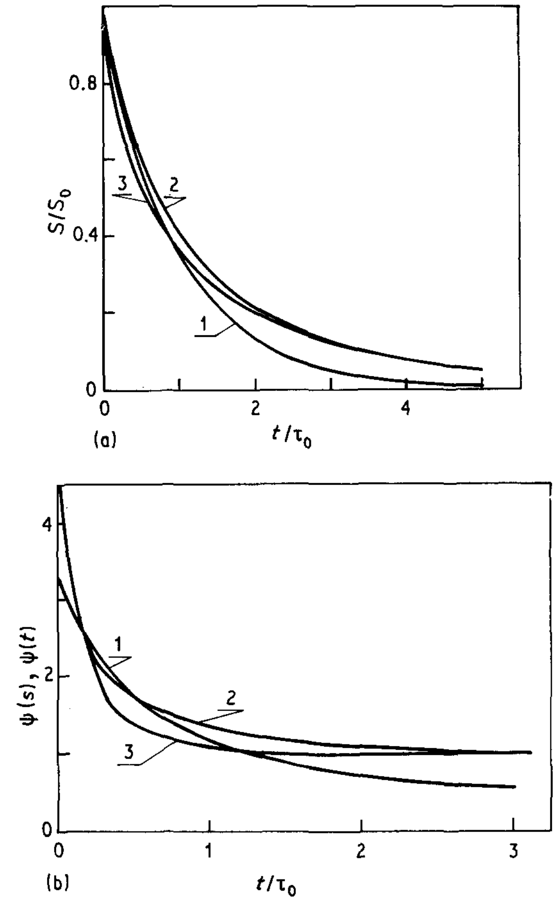

Figure 4 Illustration of the similarities and differences between the relaxational and $\psi(t)$ functions. (a) Relaxational dependences. 1, Maxwell's relaxational law (Equation 16); 2, relaxational dependence according to Equation 18 with $n = 1.3$; 3, Kohlrausch's fractional exponent relaxational formula (Equation 36) with $b = 0.67$. (b) $\psi(t)$ dependences. 1, $\psi(t)$ function according to Equation 31 with $A_2 = 1.2$, $S_0 = 10$ and $n = 1.5$; 2, $\psi(t)$ function corresponding to Kohlrausch's differential equation (Equation 35) with $m = 1.33$, $A_k = 1.2$ and $S_0 = 10$; 3, $\psi(t)$ dependences corresponding to the Tobolsky–Eyring formula (Equation 33).

$$S(t) = \operatorname{am}\left(F\left\{\phi[f(aS)], \frac{1}{2^{1/2}}\right\}\right) \tag{34}$$

where am(u) denotes the amplitude function of the elliptic integral $F(\phi, k)$ function [29, 30].

The same procedure can be also applied to Equation 21 in order to determine $S(t)$ in the dilatant case $\Gamma\dot{\gamma} \gg 1$ by means of the reverse li(x) function [29, 31] and thus to determine the $\psi(t)$ function corresponding to Equation 11b.

In 1876, Kohlrausch [13] suggested a differential equation for relaxational processes which in our notations can be written as

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}t} &= -\frac{A_k}{\tau_0 t^p}S \\ &= -\frac{1}{\tau(t)}S \end{aligned} \tag{35}$$

It is seen that this equation is more general than Maxwell's original formula (Equation 12) in assuming a time-dependent relaxation time $\tau(t) = \tau_0 t^p/A_k$. The solution of Equation 35, which reads

$$S = S_0 \exp\left[-\left(\frac{t}{\tau_k}\right)^b\right] \qquad (36)$$

is the already mentioned fractional (or "stretched") exponent function. Here $\tau_k = (\tau_0 b/A_k)^{1/6}$ and $b = 1 - p$. According to the evidence collected by Mazurin [6] for the relaxation in glass-forming melts $b \approx 0.5$–0.75; for polymers, lower b values ($b = 0.3$–0.35) have been reported [16].

Equations 35 and 36 have been proposed and used for many years as purely empirical formulae. Mazurin [6] suggested that the fractional exponent function has to be applied in relaxational processes in which the structure of the system changes during stress relaxation. More recent attempts to give a general theoretical background to Kohlrausch's equation may be found in the literature [34, 35].

From the foregoing discussion it is obvious that Equation 35 can be simply considered as an approximation to Equation 31 in which the expression $[1 + (n-1)S_0^{n-1}A_2(t/\tau_0)]$ is replaced by At^{n-1}. In terms of such a representation it turns out that $p \approx n - 1$ and $b = 2\text{-}n$, where n denotes the de Waele–Ostwald coefficient (cf. Equations 3, 10 and 18) in the respective flow stress or relaxational equation of a given system and p and b are the coefficients of both Equations 35 and 36 proposed by Kohlrausch.

It should be noted, that at $t \to 0$ the Kohlrausch $\psi(t)$ function leads to $\psi(t) \to \infty$ instead of $\psi(t) \sim S_0^{n-1}$ as required by Equation 31. However, Fig. 4 shows that Kohlrausch's $\psi(t)$ function is, in fact, a very good approximation to the $\psi(t)$ course predicted by the general solution of the pseudoplastic flow case, i.e. by the $\psi(S)$ function (Equation 33), corresponding to the Tobolsky–Eyring formula. In this sense, Kohlrausch's time-dependent relaxational formula is a remarkable approximation to the kinetics of relaxation of any pseudoplastic liquid. The above considerations give a simple method for determining the type of flow, i.e. the respective de Waele–Ostwald equation of flow from the b value in Equation 36. The b values mentioned give an indication that all glass-forming melts described by Mazurin [6] are pseudoplastic liquids with $n = 1.25$–1.5, as was, in fact, found in Part I [9].

A better approximation to Equation 31 gives a differential equation proposed by Jenckel [15, 36] according to which

$$\frac{dS}{dt} = -\frac{A}{1 + at^m}S \qquad (37)$$

At present it is difficult to say to what extent the Kohlrausch formulae (Equations 35 and 36) also approximate Equation 34, i.e. the relaxation with combined pseudoplastic and dilatant effects or the relaxation in purely dilatant liquids where $b > 1$ should be expected (i.e. $b = 3/2$ for Darcy's equation).

7. Kinetics of retardation

In the same way as we have considered the kinetics of relaxation, we can also treat the kinetics of retarded reactions in a glass-forming melt under constant stress $S = S_0$. Starting with the classical Kelvin–Voigt equation (applicable, in fact, only to Newtonian liquids) the kinetics of retarded change of some extensive property, ω, of the system [37] (volume, index of refraction, etc.) is determined by

$$\frac{d\omega}{dt} = \frac{S}{g_0}\left(1 - \frac{1}{\tau_0}\omega\right) \qquad (38)$$

where the retardation time, τ_0, is again given by Equation 13.

Denoting $\omega_\infty = S/g_0$ (i.e. ω_∞ is the value of $w(t)$ at $t \to \infty$) we obtain (with the necessary boundary condition $\omega = 0$ at $t \to 0$) the classical solution of the Kelvin–Voigt equation

$$\omega(t) = \omega_\infty\left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right] \qquad (39)$$

Considering this solution, Equation 38 can be written in the form

$$\frac{d[\omega(t)]}{dt} = \tau_0 \exp\left(-\frac{t}{\tau_0}\right) \qquad (40)$$

Introducing again with Equation 14 an apparent time of relaxation τ_{app} (here time of retardation), we can analyse the kinetics of retarded reaction in non-Newtonian liquids by writing in analogy to Equation 40

$$\frac{d[\omega(t)]}{dt} = \frac{d(\tau_{app})}{dt}\exp\left(-\frac{t}{\tau_{app}}\right) \qquad (41)$$

In order to determine the time dependence of τ_{app}, we can use the formalism of the $\psi(t)$ functions, employed in the preceding section.

Thus we obtain with Equation 41 the kinetics of the retarded reaction of a pseudoplastic non-Newtonian liquid following the Prandtl–Eyring mechanism of flow in the form

$$\mathrm{tgh}\left(\frac{aS_0[\omega(t) - \omega_0]}{2\omega_0}\right) = \mathrm{tgh}\left(\frac{aS_0}{2}\right)\exp\left(-\frac{t}{\tau_0}\right) \qquad (42)$$

This dependence has to be used instead of Equation 39 when Equation 2 and not Newton's law describes the flow of our systems. In this way a complete set of equations can be derived giving a new formulation of the kinetics of retarded reaction of a dissipative system. The corresponding formalism is discussed in greater details in a forthcoming publication [38].

8. Discussion

It transpires that by using $\dot{\gamma}(S)$ dependences describing the real non-Newtonian flow of glass-forming melts, a set of non-linear relaxational equations can be obtained. Comparison with existing empirical formulae and experimental data shows, in fact, that it is possible to derive a self-consistent and sufficiently accurate description of the experimentally observed non-linear relaxation kinetics. Knowing the type of flow behaviour of the glass-forming system, it is possible to predict the type of its relaxation and even to calculate the parameters governing this process. Thus, when n in the de Waele–Ostwald equation (Equation 3) is 3/2, a distinct value of the empirical dS/dt relation follows, and equations similar to the Adams–Williamson formula find their physical justification. The value of the parameter b in Kohlrausch's formula also can be directly calculated in this way.

In our derivation we have used the classical Prandtl–Eyring potential barrier model. Its application to experimental data raises a number of questions when quantitative agreement with the structure of the liquid is required. Other models, describing with sufficient accuracy the $\dot{\gamma}(S)$ dependences, also could be used. Our preference for the Prandtl-Eyring formalism stems from the conviction that a derivation made in the framework of such a general approach as the Absolute Rate Theory has to be basically correct, at least in a qualitative way. This was proved by our analysis performed in Part I [9].

In treating the response of a dissipative system exhibiting different types of molecular flow, we introduce non-linear flow into the linear Maxwell's equation in the same way as activity coefficients are introduced into the thermodynamics of non-ideal systems. In the same time, we preserve the value of the elastic modulus, g_0, in Equation 14, constant. This means that we assume non-linear non-Newtonian flow kinetics but the elastic elements in the system remain linear, as in Maxwell's original derivation.

In the classical analysis of Maxwell and Kelvin a linear combination of linearly functioning mechanical elements has been assumed. In modern phenomenological rheology, different mechanical models of non-linearly functioning elements connected in linear combinations are frequently used for describing non-linear relaxation and retardation kinetics. An example in this sense gives Sobotka's monograph [38] where problems similar to ours are considered for another case: for metallic materials under high stress with non-linear elastic behaviour but with linear flow characteristics.

In a forthcoming paper [39] we derive the formalism described here by using the above method of argumentation: we introduce non-linearly functioning mechanical viscous elements (Newtonian-like dashpots) into a linear combination with classical elastic mechanical elements (Hookean-like springs). The connection between these two approaches – the one derived in the framework of the thermodynamics of irreversible processes and the other following from the phenomenological rheology – can be easily established. A discussion in this respect can be found in a paper recently published [7].

References

1. G. MOREY, "Properties of Glass" (Reinhold, New York, 1954) p. 169.
2. R. O. DAVIES and G. O. JONES, *Adv. Phys.* **2** (1953) 366.
3. E. KANAI and T. SATOH, *J. Phys. Chem. (Jpn)* **9** (1954) 417.
4. *Idem, ibid.* **10** (1955) 1002.
5. G. ROPKE, in "Statisctische Mehanik fur das Nichtgleichgewicht" (Deutscher Verlag, Berlin, 1987) p. 91.
6. O. V. MAZURIN, in "Vitrification" (Nauka, Leningrad, 1986) in Russian.
7. R. PASCOVA, I. GUTZOW and J. SCHMELZER, *J. Mater. Sci.* **25** (1990) 921.
8. J. SCHMELZER, I. GUTZOW and R. PASCOVA, *J. Cryst. Growth* **104** (1990) 505.
9. I. GUTZOW, A. DOBREVA and J. SCHMELZER, *J. Mater. Sci.* **28** (1993) 890.
10. M. B. BEAVER, in "Encyclopedia of Material Science and Engineering", Vol. 4, "Mechanical Properties of Polymers" (Pergamon Press, Oxford, 1986) p. 2916.
11. A. KOVACS, J. AKLONIS, J. HUTCHINSON and A. RAMOS, *J. Polym Sci.* **17** (1979) 1097.
12. L. TRELOAR, in "The Physics of Rubber Elasticity " (Clarendon Press, Oxford, 1949).
13. F. KOHLRAUSCH, *Pogg. Ann. Phys. Chem.* **6** (1876) 337.
14. S. M. REKHSON and O. V. MAZURIN, *J. Amer. Ceram. Soc.* **57** (1974) 327.
15. E. JENCKEL, *Z. Electrochem. Angew. Phys. Chem.* **43** (1937) 796.
16. J. RIBELLES, A. R. GREUS and R. D. CALLEJA, *Polymer* **31** (1990) 223.
17. A. TOBOLSKY, P. POWELL and H.EYRING, in "Chemistry of High Molecules", Vol. 2, edited by V. A. Kargin (Inostr. Lit., Moscow, 1948) p. 206, in Russian.
18. J. MEIXNER, *Kolloid Z.* **134** (1953) 3.
19. R. HAASE, in "Thermodynamik der Irreversiblen Prozesse" (Steinkopf, Darmstadt, 1963).
20. S. MIDDLEMAN, in "The Flow of High Polymers. Continuum and Molecular Rheology" (Academic Press, New York, 1962) Ch. 4.
21. S. GLASSTONE, K. LAIDLER and H. EYRING, in "The Theory of Rate Process" (McGraw-Hill, London, 1941) pp. 480, 513.
22. L. PRANDTL, *ZAMM* **8** (1928) 85.
23. A. FRAUDENTHAL, in "Elastisches Verhalten von Werkstoffen" (Technik, Berlin, 1955) pp. 109, 191.
24. T. REE and H. EYRING, in "Rheology: Theory and Applications", Vol. 2, edited by F. R. Eirich (Academic Press, New York, 1960) p. 83.
25. W. OSTWALD, *Kolloid Z.* **47** (1929) 176.
26. *Idem, ibid.* **36** (1925) 99.
27. A. TOBOLSKY and H. EYRING, *J. Chem. Phys.* **11** (1943) 229.
28. I. S. GRADSTEIN and I. M. RYJIK, in "Tables of Integrals, Summs, Series and Products", 4th Edn (Nauka, Moscow, 1962) in Russian.
29. M. ABRAMOVITZ and I. A. STEGUN, in "Handbook of Mathematical Functions", Applied Mathematics Series (NBS, Washington, 1964).
30. E. JANKE, F. EMDE and L. LÖSCH, in "Tafeln höherer Funktionen", 6th Edn (Teubner, Stutgart, 1960).
31. S. LEBEDEV, in "Special Functions and their Applications" (Izd. Rhys. Mat. Lit. Leningrad, 1963) p. 55 in Russian.
32. O. S. NARAYANASWAMY, *J. Amer. Ser. Soc.* **61** (1978) 146.
33. *Idem, ibid.* **64** (1981) 109.
34. F. H. STILLINGER, *Phys. Rev.* **B41** (1990) 2409.
35. T. S. CHOW, *Macromolecules* **22** (1989) 701.
36. E. JENCKEL, in "Die Physik der Hochpolymeren", Vol. 3, edited by A. A. Stuart (Berlin, 1955) p. 620.
37. G. GOLDBOLCH and G. REHAGE, *Rheol. Acta* **6** (1967) 30.
38. ZD. SOBOTKA, in "Rheology of Materials and Engineering Structures" (Academia, Prague, 1984).
39. J. SCHMELZER, I. GUTZOW and A. DOBREVA, in preparation.

Received 18 December 1991
and accepted 25 June 1992