

On the Theory of Relaxation in the Glass Transition Region

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To begin with, relaxation equations will be generally examined within the framework of the thermodynamics of irreversible processes. The relaxation in the glass transition region specifically proves to be a non-linear process which resembles an accelerated or retarded autocatalytic reaction. Therefore it is physically not very useful to split the relaxation in the glass transition region into a sum of linear relaxation mechanisms. The linear response theory and the concept of normal modes lose their validity.

1. Introduction

The transition to an equilibrium state of a system first perturbed and then left alone is generally designated as relaxation. The characteristic physical quantities y of the system then often obey a linear differential equation of the form

$$\dot{y}(t) = -\frac{1}{\tau} (y - y_e), \quad (1)$$

where $\dot{y} \equiv dy/dt$ is the total derivative of y relative to time t , $\tau = \text{const.} > 0$ the so-called relaxation time and y_e the equilibrium value of the quantity y in the final state of the system. The solution of this equation is an exponential function

$$y(t) = [y(0) - y_e] e^{-t/\tau} + y_e \quad (2)$$

Exponential functions are totally monotonous functions for whose n th time derivatives $y^{(n)}$

$$\begin{aligned} (-1)^n y^{(n)} &\geq 0 & \text{if } y(0) > y_e; \\ (-1)^n y^{(n)} &\leq 0 & \text{if } y(0) < y_e \end{aligned} \quad (3)$$

is valid.

On the other hand, in the glass transition region, i.e. in the finite temperature region in which a liquid transforms into the vitreous state at a sufficiently slow cooling rate, the relaxation usually does not obey an exponential function (e.g. see [1–3]). Since the work of Hopkinson [4] one has attempted to explain monotonous non-exponential relaxation processes with the assumption that several molecular mechanisms (degrees of freedom) are present which simultaneously relax according to (2), but which have different relaxation times τ_i . One can always find reasons for a distribution of relaxation times, e.g. in the non-uniformity of the bonding situations in a silicate

glass, in the conformational isomerism of polymers, or in the always present fluctuations of the mass density. However, as long as one is not able to explicitly define the individual molecular mechanisms, not able to determine their relaxation times, and in particular, not able to prove the linearity of the problem, such attempts of explanation remain purely formal. The success of these “explanations” is solely based on the Bernstein theorem [5], according to which every arbitrary totally monotonous function $y(t)$ can be represented by a sum of exponential functions

$$y(t) = y_e + \sum_i c_i e^{-t/\tau_i} \quad (4)$$

(whereby in the case of a dense relaxation time spectrum the summation sign must be replaced by an integral).

A single molecular degree of freedom, on the other hand, can definitely also undergo a non-exponential relaxation, e.g. the scaling-invariant hyperbolic relaxation

$$y(t) \sim t^{-\gamma}, \quad \gamma > 0. \quad (5)$$

The hyperbolic relaxation can be approximated very well by a sum of the form (4), and, with the help of a dense relaxation time spectrum, can even be accurately simulated. However, the physical content of such an approximation is extremely questionable (see Mandelbrot’s sarcastic comment on this topic [6], pages 417, 418). Moreover, one should take into account that a complex molecular process involving several molecular degrees of freedom can also possibly be described by an individual macroscopic variable in the macroscopic-phenomenological theory.

In any case, relaxation processes are irreversible processes. It is, therefore, obvious to use the thermodynamics of irreversible processes (see e.g. [7–9]) in describing

ing these processes. In the following, this will be done for the relaxation processes in the glass transition region.

2. General Relations

Let us consider a homogeneous isotropic single-component fluid of constant mass. A single macroscopic internal variable ζ is assigned to the molecular internal degrees of freedom relevant in non-equilibrium. Gibbs' fundamental equation in the S-representation is then

$$s = s(u, v, \zeta) \quad (6a)$$

or in differential form

$$ds = \left(\frac{\partial s}{\partial u} \right)_{v, \zeta} du + \left(\frac{\partial s}{\partial v} \right)_{u, \zeta} dv + \left(\frac{\partial s}{\partial \zeta} \right)_{u, v} d\zeta \quad (6b)$$

with

$$\left(\frac{\partial s}{\partial u} \right)_{v, \zeta} \equiv \frac{1}{T}, \quad \left(\frac{\partial s}{\partial v} \right)_{u, \zeta} \equiv \frac{p}{T}, \quad \left(\frac{\partial s}{\partial \zeta} \right)_{u, v} \equiv \frac{a}{T}, \quad (6c)$$

where s is the specific entropy, u the specific internal energy, v the specific volume, T the temperature, p the hydrostatic pressure, and a the so-called affinity. In the framework of the thermodynamics of irreversible processes, the temporal change $\dot{s}$ of the entropy during an irreversible non-equilibrium process (*e.g.*, the relaxation) is given by

$$\dot{s} = \frac{1}{T} \dot{u} + \frac{p}{T} \dot{v} + \frac{a}{T} \dot{\zeta} \quad (7)$$

In a homogeneous isotropic fluid system of constant mass, the first law has the form

$$\dot{u} = \dot{q} - p\dot{v}, \quad (8)$$

where $\dot{q} > 0$ is the heat the system absorbs per unit time and mass from the exterior. Insertion of (8) into (7) leads to

$$\dot{s} = \frac{1}{T} \dot{q} + \frac{a}{T} \dot{\zeta}. \quad (9)$$

According to the second law of thermodynamics, the temporal change of the entropy can be split into two components [8]

$$\dot{s} = \frac{d_a s}{dt} + \frac{d_i s}{dt}. \quad (10)$$

Here, $d_a s/dt$ describes the entropy which the system exchanges with its surroundings and $d_i s/dt \geq 0$ the entropy created in the interior of the system per unit time and mass. If the temperature defined by (6c) is the temperature T^* of the surroundings of the system, one obtains

$$\frac{d_a s}{dt} = \frac{1}{T} \dot{q}; \quad \frac{d_i s}{dt} = \frac{a}{T} \dot{\zeta}. \quad (11)$$

The coincidence of T and T^* , however, is by no means essential in non-equilibrium [10] and is also not to be expected in the glass transition region [11]. With $T \neq T^*$, there is

$$\frac{d_a s}{dt} = \frac{1}{T^*} \dot{q}, \quad (12a)$$

i.e., with (9) and (10)

$$\frac{d_i s}{dt} = \left(\frac{1}{T} - \frac{1}{T^*} \right) \dot{q} + \frac{a}{T} \dot{\zeta}. \quad (12b)$$

The additional term which occurs here in the entropy production as compared to (11) corresponds to the irreversible part of the heat exchange between two homogeneous phases which are not in thermal equilibrium [8]. However, T^* is the temperature at which the heat exchange between system and surroundings occurs. Hence, T^* not only describes a property of the surroundings but also a property of the system. T^* has to be interpreted as a dynamic temperature and T as a static temperature of the system. If we disregard possible interferences, T and T^* are connected in the S-representation *via*

$$\frac{1}{T^*} = \frac{1}{T} + L_u \dot{u}$$

(L_u : phenomenological coefficient) [10].

Equations (8)–(12) are generally valid for homogeneous isotropic fluid systems of constant mass. Therefore we can directly proceed from these equations to the G-representation, in which the specific free enthalpy

$$g = g(T, p, \zeta) = h(T, p, \zeta) - Ts(T, p, \zeta) \quad (13)$$

as a function of the, usually experimentally given, independent variables T, p, ζ takes over the role of the Gibbs potential (h is the specific enthalpy of the system). In the G-representation, the affinity is given by

$$a = - \left(\frac{\partial g}{\partial \zeta} \right)_{T, p} = T\sigma_{Tp} - \eta_{Tp}, \quad (14)$$

whereby

$$\sigma_{Tp} \equiv \left(\frac{\partial s}{\partial \zeta} \right)_{T, p}; \quad \eta_{Tp} \equiv \left(\frac{\partial h}{\partial \zeta} \right)_{T, p} \quad (15)$$

describe the partial specific entropy, and the partial specific enthalpy with respect to the relevant internal variable.

In the following, we will not differentiate between the hydrostatic pressure p and the hydrodynamic pressure p^* and assume $p = p^* = \text{const}$. Equation (8) then leads to

$$\dot{q} = \dot{h}. \quad (16)$$

For the temporal change of the entropy at constant pressure one obtains in the G-representation

$$\dot{s} = \left(\frac{\partial s}{\partial T} \right)_{p, \zeta} \dot{T} + \left(\frac{\partial s}{\partial \zeta} \right)_{T, p} \dot{\zeta}.$$

Here,

$$T \left(\frac{\partial s}{\partial T} \right)_{p, \zeta} = c_{p, \zeta} \quad (17)$$

is the specific heat capacity measured in the arrested equilibrium ($\dot{\zeta} = 0$). Hence, we have

$$\dot{s} = \frac{c_{p, \zeta}}{T} \dot{T} + \sigma_{Tp} \dot{\zeta}. \quad (18)$$

With this and with (14) and (16), (9) results in

$$\dot{q} = \dot{h} = c_{p, \zeta} \dot{T} + \eta_{Tp} \dot{\zeta}. \quad (19)$$

Insertion of (19) into (12b) yields for the entropy production in the case $T \neq T^*$:

$$\frac{d_i s}{dt} = c_{p, \zeta} \left(\frac{1}{T} - \frac{1}{T^*} \right) \dot{T} + \frac{1}{T} \left[a + \eta_{Tp} \left(1 - \frac{T}{T^*} \right) \right] \dot{\zeta}. \quad (20)$$

One of the fundamental hypotheses of the thermodynamics of irreversible processes is that the product $T(d_i s/dt)$ always appears as a bilinear form of the fluxes and forces present [8]. Therefore we can conclude from (11) that a dynamic law of the form

$$\dot{\zeta} = La \quad (21)$$

exists in the case $T = T^*$. For the case $T \neq T^*$, if we disregard possible interferences, (20) leads to the dynamic laws (phenomenological equations)

$$\dot{T} = L_T c_{p, \zeta} \frac{T^* - T}{T^*}, \quad (22)$$

$$\dot{\zeta} = La^* \quad (23a)$$

with

$$a^* = a + \eta_{Tp} \frac{T^* - T}{T^*}. \quad (23b)$$

In the framework of the linear theory, the so-called phenomenological or kinetic coefficients L , L_T must always be regarded as positive constants [8, 12]. However, this is not possible when we describe the glass transition [9, 11]. The vitreous state is an (arrested) equilibrium state frozen with respect to the relevant internal degrees of freedom, which is characterized by the condition $\dot{\zeta} = 0$. However, $\dot{\zeta}$ does not disappear because of $a = 0$ or $a^* = 0$ (so-called internal equilibrium, see Section 3), but because of $L \rightarrow 0$. At least, L has to be regarded as a variable function $L(T, p, \zeta)$ when describing the glass transition.

3. Relaxation Equations

For the temporal change of the affinity $a(T, p, \zeta)$, we generally have in the G-representation

$$\dot{a} = \left(\frac{\partial a}{\partial T} \right)_{p, \zeta} \dot{T} + \left(\frac{\partial a}{\partial p} \right)_{T, \zeta} \dot{p} + \left(\frac{\partial a}{\partial \zeta} \right)_{T, p} \dot{\zeta}. \quad (24)$$

For the coefficient of the third term on the right-hand side we introduce the abbreviation

$$\begin{aligned} - \left(\frac{\partial a}{\partial \zeta} \right)_{T, p} &= \left(\frac{\partial^2 g}{\partial \zeta^2} \right)_{T, p} \\ &= \left(\frac{\partial \eta_{Tp}}{\partial \zeta} \right)_{T, p} - T \left(\frac{\partial \sigma_{Tp}}{\partial \zeta} \right)_{T, p} \equiv \gamma_{Tp}. \end{aligned} \quad (25)$$

Under the condition $T, p = \text{const}$, we then obtain

$$\dot{a} = -\gamma_{Tp} \dot{\zeta} = -L\gamma_{Tp} a,$$

see (21). The product $L\gamma_{Tp}$ necessarily has the dimension of reciprocal time. Therefore, one can also write

$$\dot{a} = -\frac{1}{\tau_{Tp}} a \quad (26a)$$

This is a non-linear relaxation equation, as the relaxation time

$$\tau_{Tp}(T, p, \zeta) \equiv \frac{1}{L\gamma_{Tp}} \quad (26b)$$

depends via $\zeta(t)$ on the present state of the system. Hence, the relaxation of a is generally non-exponential. Moreover, the relaxation time τ_{Tp} is composed of two factors: a kinetic factor $1/L$ and a thermodynamic factor $1/\gamma_{Tp}$.

The equilibrium with respect to the internal variable ζ , the so-called internal equilibrium, is described by $a = 0$, $da = 0$, and $T = T^*$. Although ζ remains variable

in the internal equilibrium, ζ becomes a dependent variable according to (14)

$$\zeta = \zeta_e(T, p), \quad (27)$$

(We indicate the quantities referred to an internal equilibrium state with “e”). If the internal equilibrium state is stable or metastable, one obtains further

$$\gamma_{Tp}^e > 0. \quad (28)$$

If one is not too far from a given internal equilibrium state “e”, the equation of state $a = a(T, p, \zeta)$ can be expanded in a Taylor series about this state, and the series can be terminated after the linear terms:

$$a = \left(\frac{\partial a}{\partial T} \right)_{p, \zeta_e} (T - T_e) + \left(\frac{\partial a}{\partial p} \right)_{T, \zeta_e} (p - p_e) + \left(\frac{\partial a}{\partial \zeta} \right)_{T, p}^e (\zeta - \zeta_e). \quad (29)$$

If the temperature and pressure are kept constant with $T = T_e$ and $p = p_e$, one obtains with (25)

$$a = -\gamma_{Tp}^e (\zeta - \zeta_e).$$

Insertion of this expression into the dynamic law (21) yields with (26b) the relaxation equation

$$\dot{\zeta} = -\frac{1}{\tau_{Tp}^e} (\zeta - \zeta_e). \quad (30a)$$

This is a linear differential equation which is identical with (1), since due to (27)

$$\tau_{Tp}^e(T, p) \equiv 1/L\gamma_{Tp}^e > 0 \quad (30b)$$

only depends on T, p , whereas T and p are kept constant. If the reference state “e” is a stable or metastable internal equilibrium state, $\tau_{Tp}^e > 0$ is always valid because of $\gamma_{Tp}^e > 0$ and $L > 0$.

In the same way, one can also linearize the mechanical equation of state $v = v(T, p, \zeta)$:

$$v = v_e + \left(\frac{\partial v}{\partial T} \right)_{p, \zeta_e} (T - T_e) + \left(\frac{\partial v}{\partial p} \right)_{T, \zeta_e} (p - p_e) + \left(\frac{\partial v}{\partial \zeta} \right)_{T, p}^e (\zeta - \zeta_e). \quad (31)$$

With the abbreviation

$$\varphi_{Tp} \equiv \left(\frac{\partial v}{\partial \zeta} \right)_{T, p} \quad (32)$$

one obtains under the conditions $T = T_e = \text{const}$, $p = p_e = \text{const}$

$$v - v_e = \varphi_{Tp}^e (\zeta - \zeta_e) \quad (33)$$

and

$$\dot{v} = \varphi_{Tp}^e \dot{\zeta},$$

i.e. with (30)

$$\dot{v} = -\frac{1}{\tau_{Tp}^e} \varphi_{Tp}^e (\zeta - \zeta_e)$$

or with (33)

$$\dot{v} = -\frac{1}{\tau_{Tp}^e} (v - v_e). \quad (34)$$

$\tau_{Tp}^e > 0$ is often designated as the Debye relaxation time. It is also composed of a kinetic factor and a thermodynamic factor [see (30b)]. The derivation of (30) and (34) shows that every non-linear relaxation process resulting from (21) and (26) must become an exponentially decreasing or increasing linear process in its final stage approaching internal equilibrium. Therefore, the hyperbolic relaxation (5) only agrees with the dynamic law (21) if $\tau_{Tp}^e = +\infty$ is valid in the final state. According to (30b), this is only possible if the final state with $\gamma_{Tp}^e = 0$ is a neutral equilibrium state or, with $L \rightarrow 0$, a frozen (arrested) equilibrium state.

In thermodynamics, as long as one does not differentiate between the static and the dynamic temperatures, relaxation equations can generally only be derived under the condition $T = \text{const}$, $p = \text{const}$. Linear relaxation equations of the types (1), (30), and (34) also require the restriction to linear equations of state and to constant phenomenological coefficients. The Gibbs fundamental equation of the system must be representable in a quadratic form

$$g = g_e + g_1(\zeta - \zeta_e) + g_2(\zeta - \zeta_e)^2. \quad (35)$$

In the literature, T and thus $\tau_{Tp}^e(T, p)$ are often regarded as variables in equations of the types (30) and (34). Such a procedure is beyond the framework of thermodynamics.

In the following, we will differentiate between T and T^* . If the dynamic temperature of the system (the temperature of the surroundings of the system) is suddenly brought to another constant value, the static temperature definitely stays variable and, according to (22), relaxes to the equilibrium value $T_e = T^*$. In this case, the affinity a^* determines the dynamics of the process for which, according to (14) and (23b), we can also write

$$a^* = T(T^* \sigma_{Tp} - \eta_{Tp})/T^*. \quad (36)$$

Under the condition $T^* = \text{const}$, $p = p^* = \text{const}$, one obtains

$$\dot{a}^* = \left(\frac{\partial a^*}{\partial T} \right)_{p, \zeta} \dot{T} + \left(\frac{\partial a^*}{\partial \zeta} \right)_{T, p} \dot{\zeta}. \quad (37a)$$

Here, we have

$$\left(\frac{\partial a^*}{\partial T} \right)_{p, \zeta} = \frac{a^*}{T} + \frac{T}{T^*} \cdot \left[T^* \left(\frac{\partial \sigma_{Tp}}{\partial T} \right)_{p, \zeta} - \left(\frac{\partial \eta_{Tp}}{\partial T} \right)_{p, \zeta} \right], \quad (37b)$$

$$\begin{aligned} \left(\frac{\partial a^*}{\partial \zeta} \right)_{T, p} &= \frac{T}{T^*} \left[T^* \left(\frac{\partial \sigma_{Tp}}{\partial \zeta} \right)_{T, p} - \left(\frac{\partial \eta_{Tp}}{\partial \zeta} \right)_{T, p} \right] \\ &= -\gamma_{Tp} + \left(\frac{\partial \eta_{Tp}}{\partial \zeta} \right)_{T, p} \left(1 - \frac{T}{T^*} \right). \end{aligned} \quad (37c)$$

For the hypothetical case that $T \neq T^*$ also remains constant with T^* , (37) in place of (26) yields the relaxation equation

$$\dot{a}^* = -\frac{1}{\tau_{Tp}^*} a^* \quad (38a)$$

with

$$\frac{1}{\tau_{Tp}^*} \equiv \frac{1}{\tau_{Tp}} - L \left(\frac{\partial \eta_{Tp}}{\partial \zeta} \right)_{T, p} \frac{T^* - T}{T^*}. \quad (38b)$$

With variable T , however, no relaxation equation can generally be derived from (37) and no relaxation time be defined. A relaxation equation only exists if [as we will assume in Section 4, see (55), (56)] σ_{Tp} and η_{Tp} do not depend on the temperature. (37) then leads to

$$\dot{a}^* = -\frac{1}{\tau_p^*} a^* \quad \text{with} \quad \frac{1}{\tau_p^*} \equiv \frac{1}{\tau_{Tp}^*} - \frac{\dot{T}}{T}. \quad (39)$$

The relaxation time τ_p^* not only depends on the variables T , ζ but also on the rate $\dot{T}$.

When describing relaxation processes under the condition $T^* = \text{const}$, it is useful to introduce the so-called fictive temperature T_f according to Tool [13, 14]

$$T_f \equiv \eta_{Tp} / \sigma_{Tp}. \quad (40)$$

According to (14), this is the temperature which the system in a non-equilibrium state (T, ζ) would have if it were in an internal equilibrium state with $a = a^* = 0$.

With (40) one can also write instead of (14)

$$a = \sigma_{Tp} (T - T_f) \quad (41)$$

and instead of (23b) or (36)

$$a^* = T \sigma_{Tp} (T^* - T_f) / T^*. \quad (42)$$

If the quantities η_{Tp} and σ_{Tp} do not depend on the temperature, (40) yields for the temporal change of the fictive temperature

$$\dot{T}_f = \gamma_{Tp}^f \dot{\zeta} / \sigma_{Tp}, \quad (43a)$$

whereby, according to (25),

$$\gamma_{Tp}^f \equiv \left(\frac{\partial \eta_{Tp}}{\partial \zeta} \right)_{T, p} - T_f \left(\frac{\partial \sigma_{Tp}}{\partial \zeta} \right)_{T, p} \quad (43b)$$

is defined. Insertion of (23) and (42) into (43) yields for the fictive temperature the non-linear relaxation equation

$$\dot{T}_f = -\frac{T}{\tau_{Tp}^f} \frac{T_f - T^*}{T^*} \quad (44a)$$

with

$$\tau_{Tp}^f (T, p, \zeta) \equiv 1 / L \gamma_{Tp}^f, \quad (44b)$$

corresponding to (26b).

Moreover, the observation that T relaxes to its equilibrium value $T = T_e = T^* = T_f$ and ζ to its equilibrium value $\zeta_e(T_e)$ does not suffice when describing a relaxation process. Rather, the response functions of the system (e.g., the coefficient of thermal expansion, the heat capacity, or the compressibility) also have to converge towards their equilibrium values. For example, the thermal expansivity of the considered homogeneous isotropic fluid system [9, 11] is given by

$$\alpha = \alpha_\zeta + \Delta\alpha. \quad (45a)$$

$$\alpha_\zeta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_{p, \zeta} \quad (45b)$$

is the expansivity of the arrested equilibrium and $\Delta\alpha$ the contribution of the relevant internal degree of freedom to the coefficient of thermal expansion. The contribution of the internal degree of freedom during an irreversible relaxation is given by

$$\Delta\alpha = \frac{1}{v} \varphi_{Tp} \frac{\dot{\zeta}}{\dot{T}}, \quad (46)$$

whereas in the internal equilibrium by

$$\Delta\alpha = \Delta^e\alpha = \frac{1}{v} \frac{\varphi_{Tp}^e \sigma_{Tp}^e}{\gamma_{Tp}^e}. \quad (47)$$

Hence, the limiting value

$$\lim_{t \rightarrow \infty} \frac{\dot{\zeta}}{T} = \frac{\sigma_{Tp}^e}{\gamma_{Tp}^e} \quad (48)$$

must be reached upon relaxation. Insertion of (22), (23a), and (42) leads to

$$\lim_{t \rightarrow \infty} \frac{\dot{\zeta}}{T} = \frac{L(\infty) T_e \sigma_{Tp}^e}{L_T(\infty) c_{p,\zeta}} \lim_{t \rightarrow \infty} \frac{T^* - T_f}{T^* - T}, \quad (49)$$

and if (43) is valid to

$$\lim_{t \rightarrow \infty} \frac{T^* - T_f}{T^* - T} = \frac{0}{0} = \lim_{t \rightarrow \infty} \frac{\dot{T}_f}{T} = \frac{\gamma_{Tp}^e}{\sigma_{Tp}^e} \lim_{t \rightarrow \infty} \frac{\dot{\zeta}}{T}. \quad (50)$$

This means that the limiting value of L_T must necessarily amount to

$$L_T(\infty) = \frac{T_e}{\tau_{Tp}^e c_{p,\zeta}}. \quad (51)$$

In addition

$$\lim_{t \rightarrow \infty} \frac{T^* - T_f}{T^* - T} = 1, \quad (52a)$$

and because of

$$\frac{T^* - T_f}{T^* - T} = 1 - \frac{T - T_f}{T - T^*}$$

finally

$$\lim_{t \rightarrow \infty} \frac{T - T_f}{T - T^*} = 0 \quad (52b)$$

must be valid. Hence, T must necessarily converge faster towards T_f than towards T^* .

4. Relaxation in the Glass Transition Region

The main problems when describing the relaxation in the glass transition region in the framework of the thermodynamics of irreversible processes are: 1) the explicit formulation of a Gibbs fundamental Equation (13) for the melt and 2) a suitable formulation for the phenomenological coefficients L and L_T in the equations (22) and (23).

If, according to Eyring [15, 16], one considers the melt as a mixture of vacancies and material particles, one obtains the simple (but certainly only approximately valid) Gibbs's fundamental equation [9, 11]

$$g = g_0 + RT \left[\frac{\varphi}{1-\varphi} \ln \varphi + \ln(1-\varphi) \right] + h_c \frac{\varphi}{1-\varphi + \lambda\varphi}. \quad (53)$$

Here and in the following, all the extensive quantities are referred to one mole of material particles. g_0 is the standard value of the chemical potential of the material particles, R the gas constant, $\varphi = v_2/v_1$, v_2 is the partial molar volume of the material particles, v_1 the partial molar volume of the vacancies, h_c the energy required to generate one mole of vacancies in the vacancy-free melt, λ a geometric factor which takes into account the different sizes and shapes of the mixing partners, and φ the volume fraction of the vacancies (the relative free volume). As the internal variable which determines the glass transition we choose the factor ζ . With its help the mole number N_1 of the massless vacancies can be determined via $N_1 = \zeta N_2$ from the mole number of N_2 of the material particles. Between ζ and φ we have the relations

$$\zeta = \frac{\varphi}{1-\varphi}; \quad d\zeta = \frac{\varphi}{(1-\varphi)^2} d\varphi. \quad (54)$$

For the quantities (15) and (32), determining the dynamics of the relaxation, (53) and (54) lead to

$$\eta_{Tp} = h_c \left(\frac{1-\varphi}{1-\varphi + \lambda\varphi} \right)^2, \quad (55)$$

$$\sigma_{Tp} = R \left[\ln \varphi + \frac{1}{\varphi} (\varphi - 1) (1 - \varphi) \right], \quad (56)$$

$$\varphi_{Tp} = v_1 = \frac{1-\varphi}{\varphi} v. \quad (57)$$

In the following we will approximately assume that the factors h_c , φ and λ do not depend on the temperature. η_{Tp} and σ_{Tp} thus also become independent of the temperature, so that (39) and (43) hold in the following. The structure of (55–57) shows clearly that the relaxation in the glass transition region must generally be a non-linear phenomenon.

The functional dependence of the phenomenological coefficients on the independent variables can not be derived in the framework of the macroscopic-phenomeno-

logical theory. Here, one rather depends on *ad hoc* formulations. The coefficient L in (21) or (23) has the dimension fluidity/volume. Therefore, association of L with the fluidity or the coefficient of self-diffusion of the melt suggests itself when describing the processes in the glass transition region. In [11], we proceeded from the Vogel-Fulcher-Tammann-Hesse equation

$$\ln \eta = \ln \eta' + \frac{c_V}{T - T_\infty}, \quad (58)$$

where η is the viscosity of the melt, $1/\eta$ the fluidity and T_∞ the so-called Vogel-temperature. This equation seems to be logically incomplete in that we also consider the free volume in addition to the temperature as an independent variable in the thermodynamic equations (53)–(57). The viscosity, however, is then only considered as a function of the temperature. According to Doolittle [17]

$$\ln \eta = \ln \eta'' + \frac{c_D}{\varphi} \quad (59)$$

should be valid. In the literature, (58) and (59) are often coupled with each other by postulating the relation

$$\varphi - \varphi_0 = \alpha_\varphi (T - T_0)$$

[1, 18, 19]. α_φ is a kind of expansivity of the free volume. However, such a coupling is not possible. In equilibrium the relation between φ and T is given by (27) and (54). In non-equilibrium, T and φ are mutually independent variables. In the following we will, therefore, proceed from a combined expression

$$\ln \eta = \ln \eta' + \frac{c_V}{T - T_\infty} + \frac{c_D}{\varphi}. \quad (60)$$

This corresponds, for example, to the formulation by Litovitz and Macedo [20] (see also [1]). We thus split L into three factors:

$$L = L_0 L_V L_D \quad (61a)$$

with

$$L_V \equiv \exp \left[c_V \left(\frac{1}{T_0^* - T_\infty} - \frac{1}{T^* - T_\infty} \right) \right] \quad (61b)$$

and

$$L_D \equiv \exp \left[c_D \left(\frac{1}{\varphi_0^e} - \frac{1}{\varphi} \right) \right]. \quad (61c)$$

L_0 is the value of L in an arbitrary fiducial state $Z[T_0^*, \varphi_0^e(T_0^*)]$. One postulates with (61) that the melt complete-

ly freezes at the Vogel temperature. Apart from that, $L \geq 0$ is always valid.

The coefficient L_T in (22) could first be associated with the coefficient of thermal diffusivity of the system. However, (22) does not describe the thermal equilibration between two phases but the equilibration between the static and the dynamic temperatures of the system. If the system, which is in an internal equilibrium state with $T_0 = T_e^0 = T_f^0 = T_0^*$ and $\varphi_e(T_0)$, is suddenly brought to the temperature T^* , the relaxation of the static temperature to the equilibrium value $T_e = T^*$ is described by (22). Correspondingly, L_T depends in this final state on the Debye relaxation time $\tau_p^e(T_e, \varphi_e(T_e))$, cf. (51). This then raises the question how (51) can be expanded in order to obtain a general expression $L_T(T, \varphi)$.

One could first assume $L_T = T/\tau c_{p,\zeta}$, whereby τ would have to be identified with one of the relaxation times defined above. Such a formulation, however, is not sufficient to generally guarantee the convergence (52). (51) holds independently of (52). In order to produce the convergence (52), L_T must necessarily also depend on T_f . The simplest approach to achieve this is

$$L_T = \frac{T}{\tau c_{p,\zeta}} \left(1 + \frac{T - T_f}{T - T^*} \right). \quad (62)$$

With this expression the contribution of the term involving $\dot{T}$ can become negative in the entropy production (20). This is acceptable in the case of non-linear phenomenological equations as long as only the total entropy production of the process remains positive [8, 21]. Since a^* is the driving force of the relaxation processes we have considered, it further seems logical to choose the relaxation time τ_p^* instead of τ in (62) (see further down). If we insert τ_p^* into (62), insert the given L_T into (22) and resolve the thus obtained equation according to $\dot{T}$, we obtain the equation

$$\dot{T} = - \frac{T}{\tau_p^*} \frac{2T - T_f - T^*}{2(T^* - T) + T_f} \quad (63)$$

as a description of the relaxation of T .

The temporal change of the volume is given with (32), (57), and (45b) by

$$\dot{v} = v \left(\alpha_\zeta \dot{T} + \frac{1 - \varphi}{\varrho} \dot{\zeta} \right), \quad (64a)$$

or with (54) by

$$(\ln v) \cdot = \alpha_\zeta \dot{T} + \frac{1}{1 - \varphi} \dot{\varphi}. \quad (64b)$$

The first term on the right-hand side describes the volume change resulting from thermal expansion of the material structure, the second term the volume change resulting from the change in free volume. The volume v is defined as volume per mole of material particles. The structure of our equations, however, allows also to specify v in $\text{cm}^3 \text{ g}^{-1}$. If we regard α_ζ as being approximately a constant, (64) can easily be integrated. Because of

$$\alpha_\zeta \dot{T} = (\ln v_2)'$$

one obtains with $\alpha_\zeta = \text{const.}$

$$v = \frac{v_2^A}{1 - \varphi} \exp[\alpha_\zeta (T - T_A)], \quad (65)$$

whereby $v_2^A \equiv v_2(T_A)$ refers to an arbitrary fiducial state. One should mention that instead of (64), one can also write

$$\dot{v} = v \alpha \dot{T}. \quad (66)$$

However, this is a purely formal equation, since, according to (45) and (46), α depends on the ratio ξ/T .

In order to do calculations for some figures, we proceed from the Eqs. (23), (36), (38b), (63), and (65) with (40), (55–57). We choose values for the constants of these equations which approximately apply for polystyrene namely

$$h_c = 10 \text{ kJ mol}^{-1}; \quad \varrho = 10; \quad \lambda = 3 \quad (67a)$$

according to [22],

$$\begin{aligned} T_\infty &= 340 \text{ K}; \quad c_V = 400 \text{ K}; \\ v &= 0.98 \text{ cm}^3 \text{ g}^{-1} \text{ at } T_A = 380 \text{ K} \end{aligned} \quad (67b)$$

according to [23], and

$$\alpha_\zeta = 0.00021 \text{ K}^{-1} \quad (67c)$$

according to [24]. Furthermore, we assume

$$\begin{aligned} L_0 &= 0.01 \text{ mol J}^{-1} \text{ s}^{-1} \text{ at } T_0 = T_0^* = 400 \text{ K} \\ \text{and } c_D &= 0.3 \end{aligned} \quad (67d)$$

($R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$). The given value of v leads to $v_2^A = 0.9516 \text{ cm}^3 \text{ g}^{-1}$. With these values, the fictive temperature T_f freezes at 372 K at a cooling rate of $\dot{T}^* = 1 \text{ K min}^{-1}$ (see [11]). This is a good measure for the so-called glass temperature otherwise described using T_g .

Figure 1A/B shows the relaxation of the volume ratio $(v - v_e)/v_e$ when the system in an internal equilibrium state is suddenly cooled down from $T^* = 380 \text{ K}$ to $T^* = 370 \text{ K}$ (Fig. 1, top) or heated from $T^* = 360 \text{ K}$ to

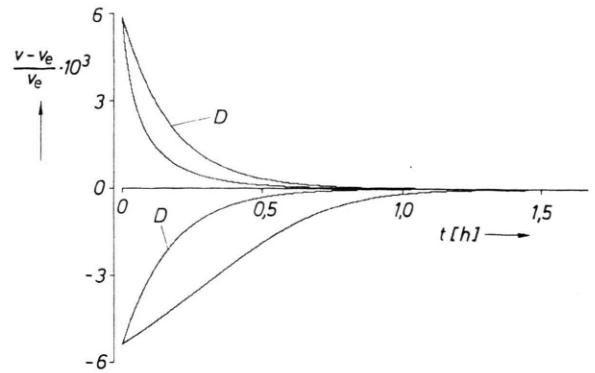


Fig. 1 A. Relaxation of the specific volume v after quenching the system from $T^* = 380 \text{ K}$ to $T^* = 370 \text{ K}$ (top) and suddenly heating from $T^* = 360 \text{ K}$ up to $T^* = 370 \text{ K}$ (bottom). In both cases, the initial state was an internal equilibrium state. v_e : specific equilibrium volume at $T_e = 370 \text{ K}$. The curves marked with D correspond to the Debye relaxation according to (34) with the relaxation time τ_{Tp}^e of the internal equilibrium at $T_e = 370 \text{ K}$.

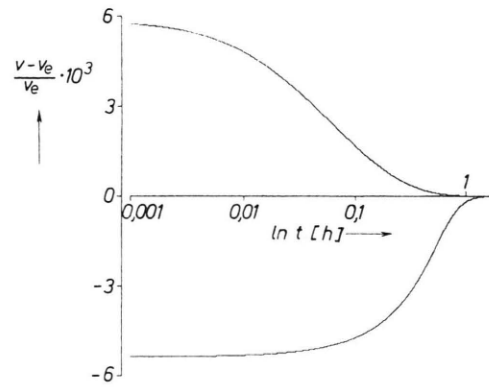


Fig. 1 B. As non-Debye relaxation in Fig. 1 A, but with a logarithmic time scale.

$T^* = 370 \text{ K}$ (Fig. 1, bottom). If the relaxation were to obey the linear equation (34), both relaxation curves would have to lie symmetrically to the axis $v = v_e(370)$, as both processes would then only be determined by the relaxation time $\tau_{Tp}^e(370)$ of the final state (in Fig. 1A these curves are marked with D; the small difference regarding the symmetry is due to the fact that the initial values of v are not completely symmetrical). According to our equations (and this corresponds to the experimental findings, see e.g. [1]), the relaxation considerably deviates from this exponential relaxation. When cooled, the system first relaxes faster, but then becomes slower. This essentially (but by no means exactly) corresponds to hyperbolic relaxation or to relaxation according to Kohl-

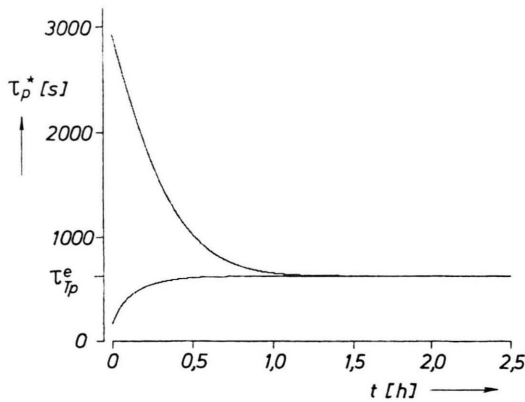


Fig. 2. Relaxation time τ_p^* according to (39b) during the relaxation processes shown in Figure 1. Top: after sudden heating; bottom: after sudden cooling. τ_{Tp}^e : relaxation time of the internal equilibrium at $T_e = 370$ K (see Table 1).

Table 1. Relative free volume $\varphi_e(T_e)$ and Debye relaxation time $\tau_{Tp}^e(T_e)$ in the internal equilibrium with (67) for different temperatures T_e .

T_e [K]	φ_e	τ_{Tp}^e [s]
400	0.0380778...	0.0284122...
380	0.0290318...	6.0958604...
375	0.0271454...	47.413328...
370	0.0253799...	626.29494...
362	0.0227802...	266668.7...
360	0.0221699...	2279210.4...
355	0.0207083...	4268491817.4...

rausch and Williams, Watts (see *e.g.* [9]). When heated, the system first relaxes more slowly, but then more rapidly, which leads to a slight convex curvature of the relaxation curve at the beginning of the process. In Fig. 1 B, we chose a logarithmic time scale in order to allow a better comparison with the representations common in the literature (see *e.g.* Figs. 7 and 8 in [1]).

The explanation for this non-linear behaviour is simple: Upon cooling, the relative free volume φ is first larger than in the final state (see Table 1), so that the relaxation can occur more rapidly. In the further course of the process, the free volume becomes ever smaller, so that the process becomes slower and slower. Upon heating, on the other hand, the free volume is at first small, then gradually increases to the final value, so that the relaxation has a distinctly autocatalytic character. In the same way, these situations are reflected in the relaxation time τ_p^* (Figure 2). The non-linearity of the problem expresses itself by the fact that the relaxation time considerably

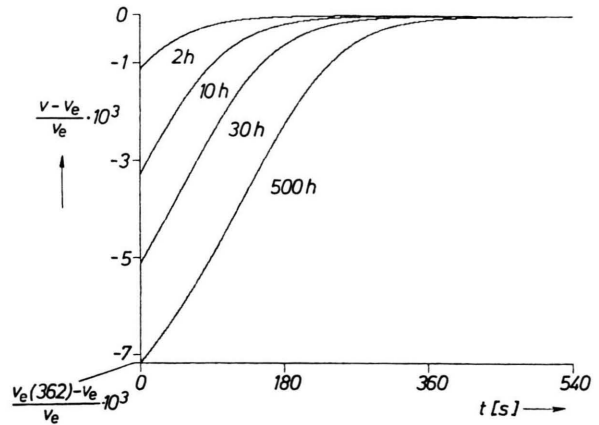


Fig. 3. The system in internal equilibrium was quenched from $T^* = 375$ K to $T^* = 362$ K. The starting relaxation was interrupted after the times (hours) indicated at the curves, and the temperature brought to $T^* = 375$ K. The figure shows the relaxation of the specific volume v back to the initial state. v_e : specific equilibrium volume at $T_e = 375$ K.

changes in the first part of the process. It should be noted that the relaxation time τ_p^* , even though the initial state is an internal equilibrium state, corresponds to the Debye relaxation time τ_{Tp}^e only at the end of the process (see Table 1). Apart from that, τ_p^* deviates only slightly from the relaxation times τ_{Tp}^e (26b) and τ_{Tp}^* (38b). Therefore one obtains, at least qualitatively, the same behaviour (Fig. 1–4) if one inserts either τ_{Tp}^e or τ_{Tp}^* instead of τ_p^* into (62) [regarding Fig. 5, however, there is a fundamental difference, see further below].

Figure 3 is based on the following experiment (see Kovacs [1], Fig. 9): The system, which is in internal equilibrium at $T = T^* = 375$ K, is suddenly cooled down to $T^* = 362$ K, whereas the starting relaxation is interrupted at different times t_n , and the system brought back to $T^* = 375$ K. The initial state of the second relaxation starting at t_n is then a non-equilibrium state. The second relaxation back to the original initial state [$(T = 375$ K; $\varphi_e(T))$] is shown in Fig. 3. At a small distance from the initial state, the relaxation seems to obey a linear equation, *i.e.*, to develop exponentially. The non-linearity only seems to become more and more pronounced with increasing distance from the initial state [1]. However, this is not the case. A measure for the deviation from the linearity is the ratio $\dot{v}/(v - v_e)$ which, according to (34), is equal to $-1/\tau_{Tp}^e = \text{const.}$ in the linear case. In Fig. 4, this ratio is given as a function of time for the cases shown in Figure 3. The relaxation is in principle non-linear. Independent of the distance to

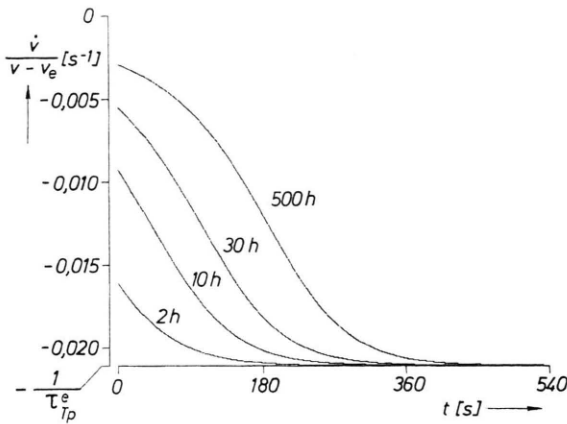


Fig. 4. Ratio $v/(v - v_e)$ according to (64) as a function of time t during the relaxation processes shown in Figure 3. v_e : specific equilibrium volume at $T_e = 375$ K; τ_{Tp}^e : relaxation time of the internal equilibrium at $T_e = 375$ K (see Table 1).

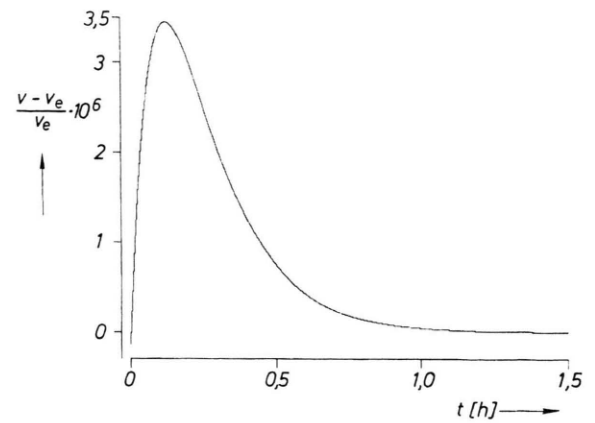


Fig. 5. Non-monotonous relaxation of the specific volume v . The system was quenched from $T^* = 380$ K to $T^* = 355$ K and the starting relaxation interrupted once the equilibrium value v_e of the volume at $T_e = 370$ K was exceeded. The system was then brought to $T^* = 370$ K. The relaxation starting at this point is shown in the figure.

the initial state, the processes only reach approximate linearity towards the end.

Of special interest are cases in which the relaxation in the glass transition region occurs non-monotonously (see e.g. Fig. 24 in [1]). For example, if one cools a sample from a temperature T_0 to a temperature T_1 , interrupts the starting relaxation process once the sample has reached a volume v , which approximately corresponds to the equilibrium volume $v_e(T)$ at the temperature $T_1 < T < T_0$, and then brings the sample to T , one would expect that hardly anything happens because the volume has already almost reached its equilibrium value. As a matter of fact however, the volume increases above its equilibrium value, passes through a maximum and only then returns to the equilibrium value. Judged on the basis of (34), such a behaviour seems to be absurd, even if τ_{Tp}^e is regarded as a variable. "Ce comportement révèle indiscutablement la multiplicité des configurations des verres, et elle correspond à une distribution des temps de retard qui caractérise le réarrangement de ces configurations" [1].

Nevertheless, when judging this strange behaviour, one should not proceed from (34), as this equation only strictly holds for the linear relaxation under the condition $T, p = \text{const.}$ According to (66), v with $\dot{T} \neq 0$ can pass through an extreme value if $\alpha = 0$, i.e. if according to (45), (46), and (43)

$$\alpha_\xi = -\frac{1}{v} \phi_{Tp} \frac{\dot{\xi}}{\dot{T}} = -\frac{1}{v} \frac{\phi_{Tp} \sigma_{Tp}}{\gamma_{Tp}^T} \frac{\dot{T}_f}{\dot{T}} \quad (68a)$$

or, according to (64),

$$\alpha_\xi = -\frac{1}{1 - \phi} \frac{\dot{\phi}}{\dot{T}}. \quad (68b)$$

Because of $\alpha_\xi > 0$, this is only possible if

$$\text{sgn}(\dot{\xi}) = \text{sgn}(\dot{\phi}) = \text{sgn}(\dot{T}_f) = -\text{sgn}(\dot{T}).$$

This is possible, however, if ξ or T_f relax at another rate than T (which is to be expected according to our equations). If the relaxation is interrupted and the system changed to a temperature T^* which is not too different from T and T_f , it can occur that T and T_f lie on different sides (above or below) of T^* at the beginning of the re-starting relaxation, so that $\text{sgn}(\dot{T}_f) = -\text{sgn}(\dot{T})$ is valid during the further course of the process.

Figure 5 shows an example: The system in internal equilibrium was suddenly changed from the temperature $T_0^* = 380$ K to the temperature $T_1^* = 355$ K. The starting relaxation was interrupted as soon as the non-equilibrium volume v exceeded the value v_e which the system would have if it was in equilibrium at $T_e = 370$ K. The system was then brought to $T^* = 370$ K. In the course of the second relaxation starting at this point, v increases beyond the equilibrium value v_e , reaches a maximum and then drops back to v_e . The cause for this behaviour can be found in the opposing contribution of the material structure and the free volume at the beginning of the process with respect to the rate of the volume change (64). ξ , ϕ , and T_f lie above the equilibrium and, there-

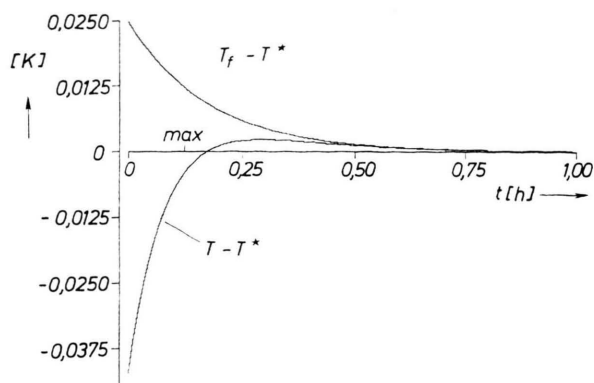


Fig. 6. Temperature differences $T_f - T^*$ and $T - T^*$ during the non-monotonous volume relaxation shown in Figure 5. T_f : fictive temperature according to (40); T : thermostatic temperature; T^* : thermodynamic temperature. "max" denotes the time at which the maximum in the volume occurs.

fore, continuously decrease during the second relaxation. Thus, the contribution of the free volume in (64) is negative. The static temperature, which relaxes faster than ζ , ϕ , and T_f in the first half of the relaxation process, is below the equilibrium value at the beginning of the second process, and consequently increases during the second relaxation process. The contribution of the material structure in (64) is positive. If the contributions of the free volume and the material structure become equal in magnitude, $\dot{v} = 0$ follows from (64). The volume passes through a maximum. Moreover, T cannot reach its equilibrium value $T_e = T^* = 370$ K from below, whereas T_f strives to reach this value from above. According to (52), T must converge faster towards T_f than towards T^* . *i.e.* T must necessarily intersect the equilibrium value $T_e = T^*$, pass through a maximum and then, together with T_f , strive to reach the equilibrium value from above (see Figure 6). $\dot{T} = 0$ with $\dot{\zeta} \neq 0$ holds at the maximum of T , *i.e.*, $\Delta\alpha$ has to pass through a singularity at this point.

The non-monotonous effect depicted in Fig. 5 is relatively small. The maximum of v becomes the larger, the larger the difference $T_f - T$ is at the beginning of the second relaxation. Since the difference $T_f - T$ passes through a maximum during the first relaxation, the height of the maximum in v during the second relaxation depends on the position of the temperature T^* . Furthermore, the maximum in v becomes the larger, the lower the temperature T_1^* . It can possibly become significantly larger if the initial state at T_0^* is not an internal equilibrium state.

If, instead of τ , one inserts the Debye relaxation time τ_{Tp}^e referring to the respective final state into (62), T relaxes considerably slower than T_f . The non-monotonous effect is then particularly pronounced, but points in the wrong direction (when cooling, as described above, one obtains a minimum instead of the experimentally determined maximum). If, instead of τ , one inserts the relaxation time τ_{Tp} according to (26b) into (62), $T \equiv T_f$ becomes valid for all relaxation processes which proceed from an internal equilibrium state. Non-monotonous relaxation is then only possible if the initial state at T_0^* was a non-equilibrium state.

5. Conclusion

Relaxation processes in the glass transition region are non-linear. This becomes immediately clear if one considers that the relaxation times change by factors of ten within the relatively small temperature range of the glass transition (Table 1). As the solutions of non-linear differential equations are not additive, it does not appear very useful to describe the processes in the glass transition region using additively superimposed linear mechanisms. The term "normal modes", which is linked to linear differential equations, loses its validity, as does the linear response theory. We do not wish to deny that several molecular degrees of freedom are possibly involved in the relaxation processes in the glass transition region. It was shown here, however, that some modes of behaviour which led to the assumption of a multiplicity of degrees of freedom in the literature, can also be described by a single internal variable.

Comments:

- 1) The differential equations (63) and (23) were solved by means of the Runge-Kutta method of the second and fourth order [25]. Within the accuracy of the figures, a difference between the two methods could not be detected.
- 2) The formulation in (60) should definitely be preferred to the VFTH-equation (58). For example, if one anneals a glass and then heats it up at a constant temperature rate, the experimental data (see *e.g.* Fig. 13 in [1]) are described much better by (60) than by the VFTH-equation (Fig. 8 in [1]).
- 3) When describing the relaxation processes in the glass transition region within the framework of the thermodynamics of irreversible processes, it is essential to realize that the so-called phenomenological coefficients cannot be constants. I didn't take this into consideration in two previous papers [26, 27]. I would, therefore, like to withdraw these papers.

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