Original Paper

Thermodynamic approach to viscosity in the glass transition

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The glass transition is re-investigated by means of the formalism of linear nonequilibrium thermodynamics. The process is treated for melts cooled down below their liquidus temperatures in terms of three events. These events are, in the order of decreasing temperature: by-passing of crystallization, freezing-in of stress relaxation, and freezing-in of near-range structural relaxation. Conditions for the viscosity levels are derived at which each of these events is accomplished. The model is tested against data of five one-component, three simple binary and ternary, and three multicomponent systems. Within the scope of this test, it is confirmed that the model correctly describes the viscosity levels typical of the glass transition, as well as their dependence on the cooling rate. An explanation for the 10^{13} dPa · s rule at T_g is included.

Thermodynamischer Zugang zur Viskosität im Glasübergang

Der Glasübergang wird mittels des Formalismus der linearen Thermodynamik der Nichtgleichgewichte erneut untersucht. Er wird für Schmelzen behandelt, die unterhalb der Liquidustemperatur abgekühlt werden, und wird durch drei Ereignisse erfaßt. Dabei handelt es sich, in der Reihenfolge abnehmender Temperatur, um das „Überspielen" der Kristallisation, das Einfrieren der Spannungsrelaxation und das Einfrieren der Nahordnungsrelaxation. Es werden Bedingungen für die Viskositäten hergeleitet, bei denen die jeweiligen Ereignisse sich einstellen. Das Modell wird einer Prüfung durch Daten von fünf Einkomponenten-, drei einfachen binären und ternären und drei Vielkomponentensystemen unterzogen. Innerhalb des Rahmens dieser Prüfung bestätigt sich, daß das Modell die für den Glasübergang typischen Viskositäten und ihre Abhängigkeit von der Abkühlgeschwindigkeit richtig beschreibt. Das schließt eine Deutung der 10^{13} dPa · s-Regel für T_g mit ein.

1. Introduction

"In the physicochemical sense, glass is a frozen-in undercooled liquid" [1]. This sentence is an attempt to summarize the essentials of the nature of glass. The pursuit of this topic has been a challenge for generations of scientists. Relatively early, the large temperature coefficient of viscosity with its more or less pronounced deviation from Arrhenius behavior has been identified as one particularly important feature of glass forming systems. The most successful description of this feature is the three-parameter presentation known as the VFT equation. It was first discovered by Vogel [2], Fulcher [3], and Tammann and Hesse [4], and later verified by countless experiments, and justified by different theoretical concepts [5]. Another likewise fundamental aspect of the nature of glass is the dependence of density and heat capacity on temperature. This dependence is the most immediate expression of the phenomenon called glass transition. It also applies to glasses not produced from a melt and is widely used to characterize glass forming systems by a glass transformation temperature T_g. Quite in contrast to a phase transition temperature, T_g explicitly depends on the parameter time, i.e., on the history of glass genesis. Yet, if this is allowed for by a suitable instruction like DIN 52324 [44], then T_g becomes an unambiguous material property. Fundamental work on the glass transition dates back to Simon [6] who coined the term "freezing-in", Tammann [7] who introduced the symbol T_g, and other pioneers like Jenckel, Lillie, Littleton, Morey, Richards, and others referenced in [8] (total number of references: 104). Drawing from these sources, Kauzmann [8] compiled the following observations and conclusions:

a) The glass transition is a relaxation phenomenon.

b) The temperature coefficient of the relaxation time is very large.

c) The molecular movement related to freezing-in is essentially a molecular rotation, hence closely related to dielectric relaxation.

d) The T_g values determined by means of dilatometry and calorimetry are nearly identical.

e) At T_g, liquids assume viscosities of about 10^{13} dPa · s.

f) If extended far below the liquidus temperature T_{liq}, liquids would assume entropies, heat contents, and molar volumes significantly lower than the corresponding crystalline states; hence the occurrence of a transition changing the temperature coefficients of the said properties, i.e., the heat capacity and the thermal expansion coefficient, is plausible.

The transition occurs at approximately 2/3 of T_{liq} (T in K). This relation between T_g and T_{liq}, known as the "2/3 rule", is another typical feature of many glass forming systems. An extended documentation is found

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in [9]. By now, numerous theories of the glass transition have been developed. They are based on free volume, configurational entropy, phenomenological nonequilibrium thermodynamics, defect structure, or dielectric response [10]. A compilation and detailed discussion of 89 references covering the period until 1988 is found in [11]. An important question refers to the number of independent mechanisms which have to be taken into consideration in an adequate description of the glass transition. Experimental [12 and 13] as well as theoretical [14 to 16] results confirm that, in general, a two-mechanisms approach is sufficient. Some of the most common observations related to the glass transition, i.e. $\eta(T_g) \approx \approx 10^{13}\,\text{dPa}\cdot\text{s}$ and $T_g \approx {}^2/_3 \cdot T_{\text{liq}}$, have hardly been explained by anyone [8 and 17]. It is thus the purpose of the present paper to reconsider the glass transition by means of the formalism of linear nonequilibrium thermodynamics, and to complement existing theories with a few new aspects. For the sake of applicability, conclusive formulae are kept strictly phenomenological in such a way that only data from standard tables, or otherwise easily accessible data, are used. Specifically, an attempt is made to understand the viscosity values typical of the glass transition.

2. Theory

2.1. Entropy generation, equilibrium, and freezing-in

The entropy change $\mathrm{d}S$ in a closed system (no exchange of matter with the environment) during a real process reads [18 and 19]

$$T \cdot \mathrm{d}S = \mathrm{d}U - \mathrm{d}W + \mathrm{d}Y = \mathrm{d}Q + \mathrm{d}Y \geq 0 \tag{1}$$

where U is the inner energy of the system, W the work externally applied, and Q the heat transferred from the environment to the system. The term $\mathrm{d}Y$ comprises the heat and work turnover within the system. It can be presented as a sum of products of generalized forces f_k and internal coordinates (or order parameters) L_k conventionally written in a form

$$\mathrm{d}Y = \Sigma f_k \cdot \mathrm{d}L_k\,. \tag{2}$$

L_k are representatives of the inner structure of the system. A set of k springs compressed to respective lengths L_k by the action of forces f_k may serve as an illustration. The indices k count all internal mechanisms necessary to describe the internal state of a system. Each mechanism k provides a way (or: a degree of freedom) by which the system can change its internal state even after a complete shut-off from the environment. From the point of view of equilibrium thermodynamics, the term $\mathrm{d}Y$ is obsolete since the internal state of a system is thought to be in perfect tune with any changes of its boundary conditions. Internal equilibrium is thought to be established "instantaneously", hence, time does not appear as an explicit parameter in the theory. This idealization becomes invalid when the time required for the establishment of inner equilibrium cannot be neglected against the time of observation any more. Then, the discussion of the term $\mathrm{d}Y$, and its variation with time, becomes a key issue. From the point of view of linear nonequilibrium thermodynamics, the constituents of $\mathrm{d}Y$, i.e., L_k and f_k, are linked by linear flow-force relations of the type

$$\frac{\mathrm{d}L_k}{\mathrm{d}t} = -\,a_k \cdot f_k = -\,\frac{L_k - L_k^0}{\tau_k} \tag{3}$$

with phenomenological coefficients a_k and relaxation times τ_k; L_k^0 is the equilibrium value of L_k; the potential interdependence of mechanisms is not elaborated here. Now the concept of inner equilibrium, which is valid under any boundary conditions, shall be illustrated for an isolated system. Any internal changes will obey the law $T \cdot \mathrm{d}S = \mathrm{d}Y \rightarrow 0$, hence S approaches a maximum $S_{\max}$. It is vital to note that the condition $\mathrm{d}S \rightarrow 0$ can be verified by three substantially different types of state:

a) Type 1: All $\mathrm{d}L_k$ approach zero, and along with this, the complementary f_k approach zero after equation (3). The corresponding state is a stable inner equilibrium. All L_k reach their respective equilibrium values L_k^0, and the corresponding entropy maximum $S_{\max}$ cannot be changed by any further internal variation.

b) Type 2: All $\mathrm{d}L_k$ approach zero like before, while f_k remains non-zero, at least for one process k. This means that mechanism k is halted by some inner constraint, and the respective L_k cannot reach its equilibrium value L_k^0. The constraint consists in an energy barrier E_A of the type of an activation energy. The corresponding state is a metastable inner equilibrium. The system remains in this state until a sufficiently large local disturbance lifts the constraint, and the system "spontaneously" relaxes towards a new state of higher entropy. The spontaneity is governed by the value of the relaxation time. A typical example for a type 2 mechanism is nucleation and crystallization from a supercooled melt.

c) Type 3: Like in type 2, at least one f_k remains non-zero, while all $\mathrm{d}L_k$ approach zero. So, mechanism k is halted by an internal constraint. However, quite in contrast to type 2, the constraint chiefly consists in a relaxation time τ_k reaching far beyond the time of observation or application t_{obs}. The presence of an energy barrier is typical, but not necessary. The type 3 state is a frozen-in state, also called an apparent, or false equilibrium.

The mentioned systematics strains the term equilibrium a little bit. But one has to yield to the fact that from the outside, i.e., by measuring macroscopic properties, there is no way to distinguish among the three types of equilibria, unless a relaxation process is directly observed, or else, a relaxed duplicate of the system is available for comparative measurements. Thus, the materials properties related to reversible changes of entropy S, volume V, temperature T, and pressure P, i.e.: heat capacities, densities, thermal expansion coefficients, and elastic moduli, can be measured for a frozen-in phase (respectively glass) like for a true equilibrium phase. Yet, the existence of a crystalline counterpart, or the occurrence of relaxation phenomena far below T_g (like the thermometer zero point displacement, or effects related to ion migration [20]) are remainders of the type 3 nature of the "glass equilibrium".

2.2 Draft of a model

In a glass melt cooling down from above the liquidus temperature T_{liq} to below the glass transition temperature T_g, the following types of relaxation phenomena are to be taken into consideration:

- viscous volume flow;
- far-range structural relaxation (chiefly nucleation and crystallization);
- stress relaxation;
- near-range structural, or positional relaxation (within a basically established structure).

The phenomena are listed in the order of their predominance during cooling.

a) Ultimate freezing-in

At temperatures below T_g, all four mechanisms are frozen-in, the term "ultimate" being used with reservation to the effects mentioned at the end of section 2.1. It was assumed that the cooling process prior to ultimate freezing-in was fast enough so as to constrain the far-range structural relaxation, but slow enough so as to permit stress relaxation. This premise is identical to demanding a well-annealed glass free of crystalline defects. Then, the only mechanism contributing to the entropy generation is near-range structural relaxation. The available driving force stems from overall structural relaxation. It is summarized by a single overall devitrification reaction "glass" → "completely crystallized matter", which is permissible according to [18]. The said overall reaction is characterized by a Gibbs free energy difference of devitrification ΔG_{dev} representing the affinity, and a dimensionless reaction variable z. For this case, equation (1) takes the specific form

$$T \cdot \frac{dS}{dt} = \left[\frac{\partial Q}{\partial T}\right]_P \cdot \frac{dT}{dt} + \Delta G_{dev} \cdot \frac{dz}{dt} \to 0\,. \tag{4}$$

Under the assumption of a constant cooling rate $dT/dt = -q_0$, and with the abbreviation $w \equiv dz/dt$, w in s^{-1}, this results in

$$T \cdot \frac{dS}{dt} = -c_P \cdot q_0 + \Delta G_{dev} \cdot w \to 0\,, \tag{5}$$

with c_P as the heat capacity of the system. The remaining problem consists in assessing a realistic value for w for the temperature range $T \leq T_g$. According to Maxwell's theory of viscoelasticity, the shear relaxation time τ_0 in a continuum is given by

$$\tau_0 \equiv \eta / G \tag{6}$$

where η is the viscosity and G is the shear modulus. It is true, G is collapsed for $T > T_g$, and the value of the rigid material is only established during the glass transition. But since equation (5) does not depend on any particular path $dS \to 0$, the use of the value from equation (6) is justified. The inverse of τ_0 shall be adopted as a measure of w. Thus, when dS has reached zero, the viscosity of the system takes the value

$$\eta_1 \equiv \frac{\Delta G_{dev} \cdot G}{c_P \cdot q_0}\,. \tag{7}$$

The term

$$\tau_1 \equiv \Delta G_{dev} / (c_P \cdot q_0) \tag{8}$$

may be considered as a relaxation time threshold for complete freezing-in, the freezing-in condition becoming $\tau_0 = \tau_1$.

b) Freezing-in of stress relaxation

For this event, the less strict premise is made that no previous crystallization occurred. Stresses may be frozen-in permanently, or relax prior to being frozen-in at zero driving force. In any case, the mechanism of stress release contributes to entropy generation, either by stored elastic energy, or by internally dissipated heat. It is more convenient to describe the effect in terms of a stress changing at an approximately constant volume (stress relaxation), than by a volume change at constant stress (volume relaxation) as suggested in equation (2). This is permissible as much or as little as the relation $c_V \approx c_P$ is valid. The change of internal stress s with temperature is approximated by the adiabatic gradient

$$ds = \frac{c_P}{V \cdot \alpha' \cdot T} \cdot dT \tag{9}$$

where α' is the linear expansion coefficient of the supercooled melt. Expressions like equation (9) derived from a $dS(T, P) = 0$ rationale have been found to be more successful in describing phenomena in glasses, such as the pressure dependence of T_g, than expressions based on a $dV(T, P) = 0$ rationale [21]. The contribution of the stress s to the entropy balance thus takes the form $V \cdot ds/dt$, and equation (1) becomes

$$T \cdot \frac{dS}{dt} = -c_P \cdot q_0 \cdot [1 + 1/(\alpha' \cdot T)] + \\ + \Delta G_{dev} \cdot G/\eta \to 0\,. \tag{10}$$

As the temperature where dS becomes zero is located somewhere close to T_g, T is replaced by $(2/3) \cdot T_{liq}$. The thermal expansion coefficient α' is approximated by three times the coefficient α of the rigid glass. With $1 \ll 1/(\alpha' \cdot T_{liq})$, equation (10) yields the following condition for the viscosity η_2 at which the volume relaxation mechanism is frozen-in:

Table 1. Oxide composition of three multicomponent glasses in wt%

oxide	DGG-I	753-C	basalt
SiO_2	71.7	63.4	46.2
TiO_2	0.1	–	2.8
Al_2O_3	1.2	5.1	13.2
B_2O_3	–	4.8	–
Fe_2O_3	0.2	–	12.5
MgO	4.2	3.1	9.8
CaO	6.7	6.2	10.9
Na_2O	15.0	15.6	2.7
K_2O	0.4	1.0	1.3
SO_3	0.4	0.2	–

$$\eta_2 \equiv \frac{2 \cdot \Delta G_{\mathrm{dev}} \cdot G \cdot \alpha \cdot T_{\mathrm{liq}}}{c_{\mathrm{P}} \cdot q_0} . \tag{11}$$

The corresponding relaxation time threshold is given by the term

$$\tau_2 \equiv 2 \cdot \Delta G_{\mathrm{dev}} \cdot \alpha \cdot T_{\mathrm{liq}}/(c_{\mathrm{P}} \cdot q_0) , \tag{12}$$

and the freezing-in condition for stress relaxation becomes $\tau_0 = \tau_2$.

c) By-passing of crystallization

The former two mechanisms lead to glass formation only if crystallization did not occur before. Crystallization typically takes place in the vicinity below T_{liq}, yet in principle the entire temperature range down to ultimate freezing-in is prone to crystallization. Thus, with respect to a time scale of application t_{obs}, the crystallization mechanism ultimately freezes-in at η_1. It can, however, be frozen-in at $\eta < \eta_1$ on a temporary basis with respect to the process time scale $t' = (T_{\mathrm{liq}} - T_{\mathrm{g}})/q_0$ as long as the cooling rate q_0 is maintained. Since t' is significantly shorter than t_{obs}, the term "by-passing" is preferred to the term freezing-in in this context. Equation (10) already provides the framework for the description of the process; but the reaction frequency $w = G/\eta$, valid for the rigid regime only, has to be replaced by an appropriate term w'. The matter is approached as follows: The frequency w' is essentially determined by a diffusion coefficient D, the value of which is estimated by the Stokes-Einstein relation. However, instead of the molecular dimension r, the critical radius r_{c} from nucleation theory is employed. Thus, D stands for the mobility of entire structural units rather than for the mobility of individual atoms. The expression for w' becomes

$$w' = D/r_{\mathrm{c}}^2 = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot r_{\mathrm{c}}^3} \tag{13}$$

with

$$r_{\mathrm{c}} = \frac{2 \cdot \sigma \cdot V_{\mathrm{M}}}{H^{\mathrm{m}} \cdot (1 - T/T_{\mathrm{liq}})} , \tag{14}$$

and k = Boltzmann's constant, σ = surface tension, V_{M} = molar volume = molar mass M divided by density ϱ, H^{m} = heat of melting. Like before, the freezing-in condition $\mathrm{d}S \rightarrow 0$ yields, in turn, a condition for the viscosity η_3 beyond which crystallization cannot occur anymore at the given cooling rate. As w' strongly depends on temperature, the condition is averaged over the temperature interval from T_{liq} to $(2/3) \cdot T_{\mathrm{liq}}$ by elementary integration, resulting in the somewhat bulky expression

$$\eta_3 \approx 3.3 \cdot 10^{-5} \cdot \frac{\Delta G_{\mathrm{dev}} \cdot (H^{\mathrm{m}})^3 \cdot k \cdot \alpha \cdot T_{\mathrm{liq}}^2}{c_{\mathrm{P}} \cdot q_0 \cdot \sigma^3 \cdot V_{\mathrm{M}}^3} . \tag{15}$$

3. Comparison with experimental data

3.1. Selection of glass forming systems

The model sketched in section 2.2. needs to be tested against a representative number of glass forming systems. The well-known one-component systems SiO_2, B_2O_3, P_2O_5, GeO_2, and BeF_2 were selected in first place. Sodium disilicate, albite, lead metasilicate, and three technical multicomponent glasses were added. The first one is the standard glass no. I (DGG-I) [30], the second one the marble glass 753-C by Manville-Schuller, Denver, CO (USA), used in insulation fiber production, the third one is a basalt of German origin, likewise used in mineral fiber production. The compositions of the technical glasses are given in table 1. The list of systems is completed by NaCl and LiF, two systems with very poor glass forming ability, if at all.

3.2. Data acquisition

Table 2 summarizes all data required for testing the model of equations (7, 11, and 15). Along with the data, an account of their origin is provided. For the heat capacities, the Dulong-Petit limit $c_{\mathrm{P}} \approx 3 \cdot N \cdot R$ (N = number of atoms in the formula, R = gas constant) is sufficient. This may be surprising since other models focus on the change of heat capacity during the glass transition. However, the information critical for the glass transition is already contained in the overall value ΔG_{dev}. The c_{P} values are merely used to estimate the heat transfer rate during cooling. ΔG_{dev} can be derived directly from the difference of standard Gibbs free energies of formation, if such data are available for a representative glassy state, e.g., from [22 and 23]. By breaking these data down to partial molar quantities of oxides, and composing them again in the way as described in [24], ΔG_{dev} values can be found for the multicomponent glasses, too. For the remaining systems, ΔG_{dev} is estimated by 1/2 of the enthalpy of melting H^{m}. All other data are available from standard books or by well-established procedures. Additional data used for the discussion of results, not for their derivation, are compiled in table 3. These are, firstly, experimental T_{g} values, and secondly, the VFT constants A, B, T_0. The origin of these data is documented in table 3.

Table 2. System properties required for the test of equations (7, 11, and 15)

system	c_P(a) in J/K*)	ΔG_{dev} in J/K*)	E in 10^{10} Pa	μ	α in 10^{-6} K^{-1}	T_{liq}(q) in °C	H^m(q) in kJ*)	ϱ(u) in g/cm^3	σ(v) in N/m
SiO_2	124.5	13.37(b)	7.20(g)	0.170(g)	0.5(h)	1723	23.68	2.20	0.28
B_2O_3	180.7	16.24(b)	1.75(h)	0.284(h)	15.0(h)	450	31.88	1.84	0.08
P_2O_5	123.0	8.50(c)	7.00(i)	0.215(i)	13.1(m)	570	16.96	2.25	0.08
GeO_2	71.5	21.00(c)	4.33(h)	0.256(h)	8.0(m)	1049	42.02	3.65	0.40
BeF_2	159.2	5.10(d)	16.45(k)	0.237(k)	13.9(k)	542	10.21	2.00	0.20
$Na_2Si_2O_5$	124.0	20.18(b)	5.97(l)	0.242(l)	16.0(n)	874	28.67	2.50	0.28
$NaAlSi_3O_8$	123.7	17.69(e)	7.44(l)	0.239(l)	6.8(n)	1118	22.61	2.40	0.37
$PbSiO_3$	44.0	2.38(b)	4.25(l)	0.231(l)	8.4(n)	767	12.18	5.70	0.17
DGG-I	121.1	15.71(f)	6.78(l)	0.246(l)	9.0(o)	961(r)	29.80(f)	2.50	0.34
753-C	123.6	15.41(f)	7.19(l)	0.254(l)	9.7(n)	921(s)	29.70(f)	2.52	0.33
basalt	113.0	16.12(f)	7.75(l)	0.250(l)	6.2(p)	1142(t)	47.10(f)	2.96	0.43
NaCl	86.5	24.00(c)	3.62(l)	0.256(l)	39.2(k)	800	47.95	2.16	≈0.1
LiF	161.4	52.30(c)	11.94(l)	0.217(l)	32.6(k)	848	104.57	2.64	≈0.1

*) per 100 g of material
(a) Dulong-Petit limit
(b) per difference of standard Gibbs free energies of formation, from [22]
(c) as $^1/_2$ of tabulated H^m value [22]
(d) as $^1/_2$ of tabulated H^m value [25]
(e) per difference of standard Gibbs free energies of formation, from [23]
(f) calculated as explained in [24]
(g) from [26]
(h) from data compiled in [1]
(i) estimated by respective oxide increment from [27 and 28]
(k) extrapolated from data in [26]
(l) calculated from the composition after [27 and 28]
(m) estimated by $\alpha \cdot 10^6 \approx 11800/T - 0.9$ (T in K)
(n) calculated from the composition after [29]
(o) from [30]
(p) author's experiment
(q) from standard tables [22, 25, 31, and 32]
(r) calculated after [33]
(s) communicated by Manville-Schuller
(t) calculated after [34]
(u) from data compiled in [1, 35, and 36], or calculated after [37]
(v] calculated from composition, or estimated from increment after [38]

Table 3. Glass transition temperature and VFT constants for different glass forming systems

system	T_g in °C	A	B	T_0 (c)
SiO_2	1222 [1]	−2.490	15004.0	253.0 [1]
B_2O_3	257 [1]	−2.030	2816.0	69.7 [1]
P_2O_5	380 [39]	−2.000	4950.0	50.0 [1]
GeO_2	545 [21]	−1.761	8003.5	2.8 [1]
BeF_2	319 [21]	−8.083	11454.0	−219.9 [41]
$Na_2Si_2O_5$	451 [1]	−2.041	4250.2	168.4 [1 and 40]
$NaAlSi_3O_8$	538 [1]	−1.336	5572.5	195.4 [42]
$PbSiO_3$	422 [9]	–	–	–
DGG-I	538 [30]	−1.584	4331.6	247.6 [30]
753-C	539 [42]	−1.008	2983.6	325.5 (b)
basalt	685 (a)	−4.000	5502.8	361.3 [43]

(a) author's experiment
(b) viscosities communicated by Manville-Schuller
(c) VFT constants recalculated based on T_g and the data drawn from given references

Table 4. Decadic logarithms of viscosities η_1, η_2, η_3, calculated according to equations (7, 11, and 15), respectively; η_{liq} is the viscosity at liquidus temperature, and Z_{cryst} is the difference between $\lg \eta_3$ and $\lg \eta_{liq}$; η in dPa · s

system	$\lg \eta_1$	$\lg \eta_2$	$\lg \eta_3$	$\lg \eta_{liq}$	Z_{cryst}
SiO_2	15.0	12.3	5.3	7.7	<0
B_2O_3	14.3	12.6	7.6	5.4	2.2
P_2O_5	14.8	13.1	7.0	7.5	<0
GeO_2	15.2	13.5	7.5	5.9	1.6
BeF_2	14.8	13.2	4.6	7.0	<0
$Na_2Si_2O_5$	15.1	13.6	6.9	4.0	2.9
$NaAlSi_3O_8$	15.1	13.4	5.9	4.7	1.2
$PbSiO_3$	14.4	12.7	6.7	–	–
DGG-I	15.0	13.4	6.4	4.5	1.9
753-C	15.0	13.4	6.5	4.0	2.5
basalt	15.1	13.4	6.9	3.0	3.9
NaCl	15.1	14.0	7.8	≈−2	≈10
LiF	15.7	14.5	9.1	≈−2	≈11

3.3. Results and discussion

Numerical values of the viscosities (in dPa · s) η_1 (ultimate freezing-in), η_2 (freezing-in of stress relaxation), and η_3 (successful by-passing of crystallization) are calculated by equations (7, 11, und 15), respectively. The decadic logarithms of the viscosities are compiled in table 4. The data are supplemented by the viscosities η_{liq} at the respective liquidus temperatures, calculated by means of the VFT constants in table 3, and by the differences $Z_{cryst} = \lg \eta_3 - \lg \eta_{liq} = \lg(\eta_3/\eta_{liq})$. The viscosity levels $\lg \eta_1$ and $\lg \eta_2$ for all the different glass forming systems are very similar. Beyond this, the relationship of $\lg \eta_1$ to the conventional "lower cooling point" $\lg \eta \approx 14.5$, and especially of $\lg \eta_2$ to the conventional value $\lg \eta(T_g) \approx 13$ is striking. For the glass DGG-I, the T_g value after DIN 52324 [44] determined in a round robin test is $T_g = (537.6 \pm 2)$ °C; viscosities independently determined by the Physikalisch-Technische Bundesanstalt Braunschweig yield $\lg \eta(T_g) = 13.26 \pm 0.09$ [30]. This is in good agreement with the respective $\lg \eta_1$ value from table 4. For the few systems taken into

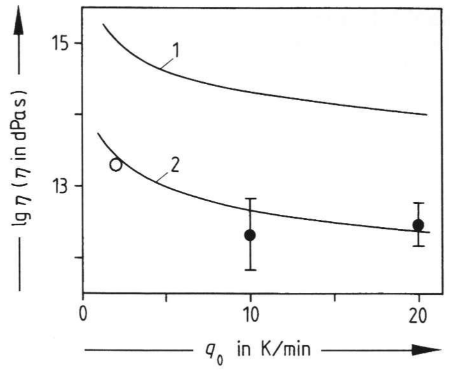

Figure 1. Viscosity levels $\lg \eta_1$ of ultimate freezing-in (curve 1) and $\lg \eta_2$ of freezing-in of stress relaxation (curve 2), calculated for glass DGG-I [30] as a function of the cooling rate q_0. ○: experimental $\lg \eta(T_g)$ value for DGG-I; ●: experimental $\lg \eta(T_g)$ values for a variety of other glasses after [44], means and standard deviations.

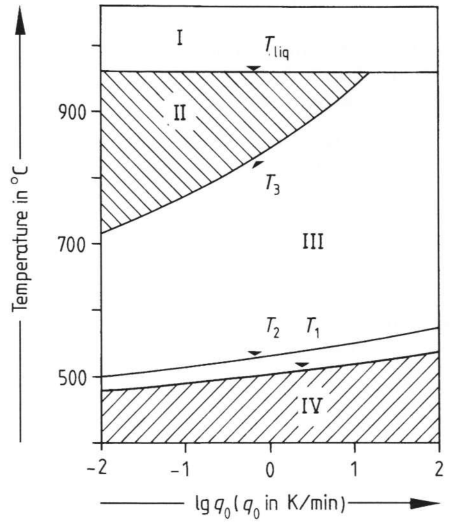

Figure 2. Temperatures of the viscosity levels 1, 2, and 3 as a function of the cooling rate q_0; T_{liq} = liquidus temperature. Field I: stable liquid; field II: system prone to crystallization, field III: crystallization is by-passed; field IV: ultimately frozen-in phase.

consideration, equation (11) indeed provides an understanding of the 10^{13} dPa · s rule in terms of a small set of materials properties. It is a surprising outcome that a relatively crude model based on the consecutive freezing-in of two overall mechanisms is capable of reproducing the key viscosity levels of glass transition. The finding that two order parameters are typically involved in the glass transition is thus supported again from a different perspective. Relaxation times calculated from equations (8 and 12), respectively, range from 10^3 to 10^4 s at the level of η_1, and from 5 to 200 s at the level of η_2. The data qualitatively agree with the typical finding of a relatively fast versus a relatively slow relaxation mechanism. A re-evaluation [1] of the crossover experiments on B_2O_3 [12 and 13] mentioned earlier yielded 7500 and 270 s, compared to 2700 and 60 s in this work.

A comment is necessary with respect to the cooling rate of $q_0 = 2$ K/min used in all calculations, which was selected in agreement with DIN 52324 [44]. As the model explicitly contains the cooling rate, the dependence of the key viscosity levels on q_0 can be readily predicted. The model predicts $\eta \cdot q_0 \approx$ const with different constants for the viscosity levels 1 to 3. Figure 1 shows the values of $\lg \eta_1$ (ultimate freezing-in) and $\lg \eta_2$ (freezing-in of stress relaxation) for the glass DGG-I as a function of temperature. The experimental value $\lg (T_g)$ for DGG-I at 2 K/min is included. The curves suggest that the key viscosity levels change considerably, even within the narrow range of cooling rates 1 to 20 K/min. Experimental data on a variety of 17 other glasses by [45] cooled down at 10 to 20 K confirm the trend. In figure 2, the viscosity levels 1 to 3 of the glass DGG-I were translated into temperatures by means of the VFT equation. In addition to this, the liquidus temperature is shown, too. For $T_1 = T(\eta_1)$ and $T_2 = T(\eta_2)$, an increase of the cooling rate by a factor of 10 brings about an increase by approximately 20 K. $T_3 = T(\eta_3)$ displays a much stronger dependence on the cooling rate. The temperature curves divide the diagram into stability fields of true and apparent equilibria. Field I is the field of the stable liquid. In field II, the system is prone to crystallization, while in field III crystallization is successfully by-passed. Field IV is the field of the ultimately frozen-in phase.

As to the salt melts NaCl and LiF: Their viscosity levels for a hypothetical freezing-in in table 4 are higher than for the good glass formers. But the deviations are not very pronounced, and may even be due to the fact that, for lack of better data, the elastic constants of the crystalline phases were employed. In no way can they explain the huge differences in glass forming ability. The true reason for these differences is seen in the ability to by-pass crystallization. This is already indicated by the viscosities η_{liq}: The good glass formers reach $\lg \eta \geq 4$, basalt as a poorer candidate has 3, but the ionic salt melts have $\lg \eta \approx -2$ (Stokes-Einstein estimates based on the average ionic radii). The degree of glass forming ability becomes very clear when η_3 is taken into consideration, and the ratio (or logarithmic difference) Z_{cryst} is discussed. For a given cooling rate, Z_{cryst} represents the viscosity range which has to be crossed before crystallization can be considered as successfully by-passed. Alternatively, Z_{cryst} can be viewed as a logarithmic measure of the cooling rate necessary to make η_3 match with η_{liq} (at which condition crystallization is reliably by-passed). The interval is small or even zero (for $Z_{cryst} \leq 0$) for the good glass formers. Systems used in fibrization processes (753-C, basalt) have a wider range, hence require higher cooling rates. The range for the ionic salt melts exceeds by far any of the other systems. In a diagram of the type of figure 2, the glass forming ability expresses itself by the extensions and relative positions of the fields I to IV. For systems with good glass forming ability, the field II retires towards the upper left corner, while for poor glass formers, it expands at the expense of field III towards higher cooling rates and lower temperatures.

4. Conclusion

The glass transition was re-investigated by means of the formalism of linear nonequilibrium thermodynamics. The process was treated for melts cooled down from their liquidus temperatures in terms of three key events. These comprise the successful by-passing of crystallization and two independent relaxation mechanisms, i.e., stress relaxation, and near-range structural relaxation. A model was developed which predicts the viscosity levels at which each of these key events is accomplished. The model was tested against data of the five one-component glasses SiO_2, B_2O_3, P_2O_5, GeO_2, and BeF_2, the systems sodium–disilicate, albite, and lead–metasilicate, and three multicomponent glasses of the types soda–lime–silicate, sodium–borosilicate, and basalt. The following results were obtained:

a) Freezing-in of stress relaxation at a cooling rate of 2 K/min is predicted by equation (11) to occur for all systems at viscosities close to 10^{13} dPa · s (for the standard glass DGG-I: $10^{13.4}$ dPa · s predicted versus $10^{13.3}$ dPa · s measured [30]). Thus, within the scope of this work, an explanation for the rule $\lg \eta(T_g) \approx 13$ is obtained.

b) Freezing-in of the near-range structural relaxation at 2 K/min is predicted by equation (7) for $\lg \eta \approx 14.5$ to 15. Here, the model provides a rationale for the technological concept of the lower cooling point.

c) The viscosities at the key levels of freezing-in are inversely proportional to the cooling rate.

d) For systems hardly able to form glasses, the predicted viscosity levels for hypothetical freezing-in are not significantly different from those of the good glass formers.

e) The ability of a system to form a glass is chiefly determined by the ability to by-pass crystallization. This is described by the ratio of the viscosity at the liquidus temperature and a characteristic viscosity threshold given by equation (15). The ratio sharply reflects the difference between good glass formers (like SiO_2), less good glass formers (like basalt), and systems hardly able to form glasses (like NaCl).

5. Nomenclature

5.1. Symbols

a	phenomenological coefficient of flow-force relation
A, B, T_0	constants of the Vogel-Fulcher-Tammann equation
c	specific heat
D	diffusion coefficient
E	elasticity modulus
E_A	energy barrier
f	generalized force
G	shear modulus
ΔG_{dev}	Gibbs free energy difference of devitrification
H^m	enthalpy of melting
k	Boltzmann's constant
L	generalized path (internal coordinate); the product $f \cdot L$ has the dimension of an energy
L^0	equilibrium value of L
M	molar mass
N	number of atoms
P	pressure
Q	heat transferred from the environment to a system
q_0	cooling rate
R	gas constant
r	molecular dimension
r_c	critical radius
S	entropy
S_{max}	maximal entropy value
s	stress
T	temperature
T_g	glass transition temperature
t	time
t'	process time (time required to cool down a melt from liquidus to glass transition temperature)
t_{obs}	time of observation (experimentation, application)
U	inner energy
V	volume
V_M	molar volume
W	work applied to a system by the environment
w	frequency related to a chemical reaction
w'	frequency related to a diffusion process
Y	energy dissipated within a system
Z_{cryst}	the difference $\lg \eta_3 - \lg \eta_{liq}$
z	dimensionless reaction variable
α	linear thermal expansion coefficient of the rigid glass
α'	linear thermal expansion coefficient of the supercooled melt
η	viscosity
μ	Poisson's ratio
ϱ	density
σ	surface tension
τ	relaxation time
τ_0	shear relaxation time

5.2. Subscripts

1	ultimate freezing-in
2	freezing-in of stress relaxation
3	successful by-passing of crystallization
k	individual relaxation mechanism
liq	liquidus
P	constant pressure
V	constant volume

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