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Dynamics of supercooled melts treated in terms of the random-walk concept

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Abstract. The concept of random walk of an excitation within a Gaussian density of states (DOS) is applied to treat diffusion and viscous motion of glass-forming elements controlled by the random potential established upon supercooling a melt. It relates the super-Arrhenius-type temperature dependence observed for viscosity and related properties at $T > T_g$ (the glass transition temperature) to the energetic relaxation of the glass elements within the DOS. The resulting relaxation pattern implies that the system must become non-ergodic at the temperature where the time required to relax to dynamic equilibrium exceeds the experimental time-scale. The model is able to explain quantitatively (i) $\eta(T)$ data in the temperature range $T_c > T \geq T_g$ (T_c being a critical temperature above which collective effects, tractable within the mode-coupling concept, become important), (ii) the dependence of T_g on cooling rate and (iii) the Arrhenius-type T dependence of molecular motion below T_g , and qualitatively (iv) the occurrence of physical aging and (v) non-exponential relaxation patterns.

1. Introduction

The dynamics of supercooled melts exhibit features not found with their solid or liquid counterpart structures (for a survey see [1–3]): (i) the relaxation to the ground state after a perturbation is non-exponential in time [4–8] following a Kohlrausch–Williams–Watts (kww) pattern [9–11] indicative of a broad distribution of relaxation frequencies [12]. (ii) The temperature dependence of the average relaxation time is non-Arrhenius-like [7, 8, 13–16] and often successfully expressed in terms of the Vogel–Fulcher law [17] or its analogue, the Williams–Landel–Ferry (wLF) equation [1, 18]. (iii) At a given temperature the dynamic behaviour depends on the thermal history of the sample, at variance with the concept of linear response [5, 6, 19–22]. Despite considerable experimental and theoretical effort, a general theory for rationalising these phenomena in a coherent way is still missing. One reason appears to be that functional dependences are often neither unambiguous nor specific for a particular model. A textbook example is the kww behaviour, which can result from a variety of reasons [23].

A central aspect of the present work is concerned with the temperature dependence of the rates governing dynamic processes like mass transport, revealed by diffusion and viscosity, as well as relaxation phenomena like dipole or ultrasonic relaxation. Despite its shortcomings the most commonly used concept for data interpretation is the free-volume model [1, 24, 25]. It relates the molecular transport to the exchange of free volume among the ‘cells’ of a supercooled liquid. Its central assumption is that the

free volume exceeding a critical value v_c can be regarded as free in the sense that its redistribution among the cells does not cost energy. This implies a linear relationship between the local free energy and the cell volume, in contrast to what is known about inter-molecular potentials. Temperature enters the picture phenomenologically via the T dependence of the free volume, expressed in terms of the thermal expansion of the sample above the glass transition temperature T_g . A statistical optimisation procedure in analogy to that yielding the Boltzmann distribution finally leads to the famous Vogel-Fulcher (VF) law for the viscosity,

$$\eta = A \exp[B/(T - T_{VF})] \quad (1)$$

implying that η diverges as T approaches T_{VF} .

Being a three-parameter equation, equation (1) is quite a flexible operational tool for characterising temperature dependences that are steeper than Arrhenius' law would predict, leaving it open to conjecture whether or not its application is legitimate in terms of physical principles. If applied to explain experimental data in the vicinity of T_g , T_{VF} comes out considerably lower than T_g [26, 27], typically $T_g - 50$ K for a T_g of order 300 K, and thus close to the Kauzmann temperature T_K where the entropy of the glass would match that of a crystal [28]. In reality, supercooled melts fall out of thermodynamic equilibrium, i.e. become non-ergodic, at $T_g > T_K$ already if subjected to a finite cooling rate. In its original version the free-volume concept is unable to account for this effect.

A more realistic picture of what happens in a supercooled melt at $T \geq T_g$ derives from the concept of activated transport within a multi-dimensional configuration space, originally introduced by Goldstein [28]. When a liquid is cooled under suppression of crystallisation an extremely complicated potential energy surface is gradually established. It results from the variation of the interaction energy among the glass-forming constituents on their mutual orientation and position. In the low-viscosity regime this energy surface changes with time, involving non-linear coupling between a given element and its environment. As T approaches T_g upon cooling, the energetically more favourable arrangements of the entire manifold of configurations will be realised and, depending on temperature and observation time, a more or less static distribution of site energies will be established. Any kind of transport occurring on a molecular or submolecular level must involve thermally activated transitions among adjacent local energy minima, the transition state being identified as a configuration with a free volume sufficiently large to permit molecular rearrangement. Generation and redistribution of free volume are, therefore, related processes associated with an activation energy, which, by virtue of the random nature of the system, is a statistical quantity. Elaborating upon these ideas, a framework for rationalising the temperature dependence of viscous flow in supercooled melts has recently been laid out [30] resting on a theory of random walks on disordered lattices [31].

This paper deals with the dynamics of supercooled melts in the vicinity of the glass transition treated in terms of the random-walk concept. It is organised as follows. Section 2 presents an outline of relevant aspects of the concepts of random walks in disordered media while § 3 establishes the criteria for applying this concept to motional processes in supercooled melts. In § 4 literature results on the temperature dependence of the viscosity of a large number of systems are analysed in terms of the present model, yet going beyond the scope of a previous analysis [30] by considering the relations to mode-coupling theories explicitly. Section 5 extends application of the model to rationalising the freezing effect occurring at the glass transition while in § 6 motional phenomena present below T_g will be discussed. In the concluding section (§ 7) we summarise the

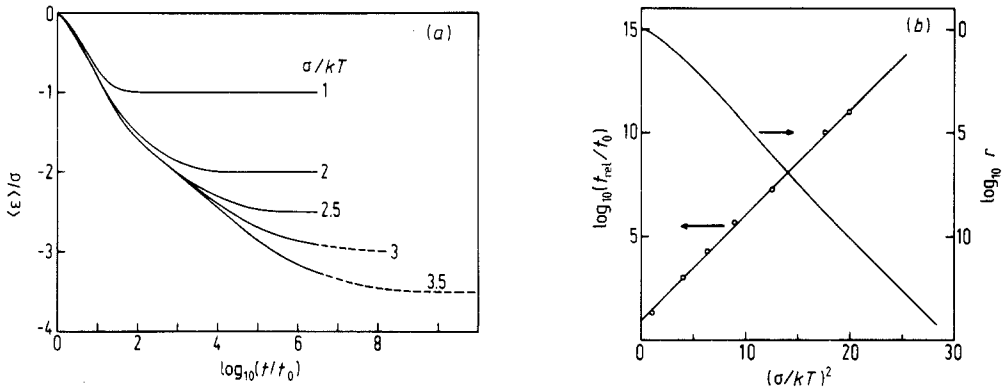


Figure 1. (a) Time dependence of the mean energy of an ensemble of non-interacting excitations started at random within a Gaussian DOS of width σ and centred at $\epsilon = 0$ in the course of a Monte Carlo computer simulation. Time t_0 is the dwell time of an excitation in a lattice with isoenergetic sites. (b) Monte Carlo simulation data for the time t_{rel} required by an ensemble of excitations to relax to dynamic equilibrium at variable σ/kT . Time t_{rel} has been determined from the intersection of slopes in (a) and r is the relaxation rate refined by equation (11).

results, focusing on the establishment of a consistent framework for delimiting glass properties in the vicinity of T_g under inclusion of collective effects tractable in terms of the mode-coupling theory.

2. The model

Since the gist of the arguments of this work will be based on the understanding of random walks in random media, we begin with a survey of results relevant in the present context. A universal feature of glasses is their built-in disorder, prototypically documented by their inhomogeneously broadened optical absorption bands. In general, their profiles are appropriately mapped by Gaussians [32, 33]. This is a plausible result since the intramolecular contribution to the energy of a glass element depends on a large number of configurational coordinates each varying randomly by small amounts. We generalise this result by postulating that the density of states profiles in glasses (henceforth abbreviated as DOS) are of Gaussian shape, for both excited and ground states. A measure for the degree of disorder is the quantity σ/kT , where σ denotes the Gaussian width of the DOS.

Consider now an optical excitation or an excess charge carrier generated at an arbitrary site within the DOS and migrating within the array of hopping sites assumed static on the timescale of the transport process. Its random walk is governed by rates ν_{ij} of the form

$$\nu_{ij} = \begin{cases} \nu_0 \exp[-(\epsilon_j - \epsilon_i)/kT] & \epsilon_j > \epsilon_i \\ \nu_0 & \epsilon_j < \epsilon_i \end{cases} \quad (2)$$

for transitions between nearest-neighbour sites [34, 35]. While hopping, the excitation will relax energetically within the DOS. After a certain time, henceforth referred to as the energetic relaxation time t_{rel} , the probability for making a jump to a site of still lower energy will be balanced by that for a thermally activated jump to a site of higher energy,

indicating that the excitation has attained dynamic equilibrium within the manifold of hopping states. It is easy to show analytically that for $t > t_{\text{rel}}$ an excitation will on average occupy a site located at energy

$$\lim_{t > t_{\text{rel}}} \langle \varepsilon(t) \rangle = \langle \varepsilon_{\infty} \rangle = -\sigma^2/kT \quad (3)$$

relative to the centre of the DOS [31]. Qualitatively, $\langle \varepsilon_{\infty} \rangle$ must decrease with temperature, because thermally activated jumps are progressively eliminated. Figure 1(a) shows how in a Monte Carlo computer experiment an ensemble of excitations started randomly and independently within a cubic array of hopping sites whose energies are distributed according to a Gaussian profiles relaxes within the DOS as a function of time to attain finally dynamic equilibrium. Energy relaxation is paralleled by the temporal decrease of the mean hopping rate and, hence, the diffusivity, crudely following the pattern characteristic of dispersive transport, $D(t) = D_0(t/t_0)^{\alpha-1} + D_{\infty}$ [34], $0 < \alpha < 1$, α being the dispersion parameter and $D_{\infty} = \lim_{t \rightarrow \infty} D(t)$. The t_0 is the dwell time of an excitation in a lattice composed of isoenergetic hopping sites, typically of the order of a reciprocal-lattice frequency (10^{-12} s). A recent analytic effective-medium approach (EMA) [31, 36] confirmed these results, which have meanwhile been verified experimentally by monitoring both the spatial [37] and the spectral [38, 39] diffusion of triplet excitations in a benzophenone glass.

Steady-state transport requires transitions into regimes of the DOS where the number of states is larger. It is, therefore, thermally activated. The activation energy E_A is a statistical quantity because the occupied sites within the DOS form a distribution having the same width as the DOS itself. Most importantly, the ensemble-averaged value $\langle E_A \rangle$ is proportional to $\langle \varepsilon_{\infty} \rangle$. Both Monte Carlo simulations and analytic theory have shown [31] that to a good approximation $\langle E_A \rangle \approx (2/3)^2 \langle \varepsilon_{\infty} \rangle$. The fact that $\langle \varepsilon_{\infty} \rangle$ and, concomitantly, $\langle E_A \rangle$ vary inversely with temperature leads to a non-Arrhenius type of T dependence for the mean transition rate in the diffusive transport regime,

$$\nu(T) = \nu_0 \exp[-(T_0/T)^2] \quad (4a)$$

where

$$kT_0 \approx (2/3)\sigma. \quad (4b)$$

Of particular interest in the present context is the temperature dependence of the relaxation time t_{rel} . The Monte Carlo data, shown in figure 1(b), bear out a quadratic relation between $\ln t_{\text{rel}}$ and the disorder parameter σ/kT ,

$$t_{\text{rel}}/t_0 = 10 \exp(1.07\sigma/kT)^2 \quad (5)$$

the parameters being empirical. It compares quantitatively with the analytic EMA result. Equation (5) predicts that, for a moderate degree of disorder, $\sigma/kT \approx 5.5$, t_{rel} is already of the order of 3 h! This extremely strong T dependence of t_{rel} is a consequence of the importance of occasional activated jumps that help in excitation find new pathways for further relaxation. Their rate of occurrence is drastically diminished as the excitation becomes localised in deeper tail states of the DOS. This feature of an energetically random system will turn out to be of vital importance for the relaxation in a system that is subject to cooling.

3. Adaptation of the random-walk concept to supercooled melts

Following Goldstein's [29] argument, a random N -particle system is characterised by a $(3N + 1)$ -dimensional potential energy surface with local minima and maxima. It arises

from the dependence of the potential energy of a given element—a molecule or a subunit thereof—on a multitude of internal coordinates such as inter-molecular distances and angles. At temperatures low enough to exclude motional collective effects, the elements will occupy a small fraction of the local energy minima, the distribution of occupied states being governed by both the form of the DOS and the thermal energy. Transitions between metastable adjacent configurations are hindered by energy barriers, the local maxima of the potential surface, which are subject to a distribution. This picture readily translates into a distribution of thermally activated transition rates as well. This situation is analogous to that described in § 2 except that now (i) the moving particle has to be identified with either an atom, a group of atoms or a microscopic region of the system and (ii) motion will occur in configuration space rather than in real space. However, this is irrelevant for applying the random-walk model outlined above, since it specifies neither the nature of the moving element nor the explicit type of its motion. The only restrictions are that (i) motion is incoherent and tractable in terms of a linear kinetic master equation, (ii) rates are in accord with equation (2), (iii) the Pauli principle plays no role, i.e. the particle may carry a spin yet migrate in an otherwise empty DOS, implying that the density of particles is much less than the density of available states, and (iv) the DOS, i.e. the local configuration surrounding an occupied site, remains static on the timescale of a hopping event.

Thermally activated transitions within the multi-dimensional potential energy surface, illustrated in figure 2, are in accord with the above premises. Since the glass element sees a new environment after having executed a jump in configuration space, phase memory is lost after each step, as is characteristic of incoherent transport. By virtue of the large number of internal coordinates, jumps occur within a virtually empty DOS and may involve low-energy transitions within double-well potentials as well as displacive motions. The latter are the ones that are likely to contribute to viscous flow and related dynamic properties [8]. On a microscopic scale displacive transitions will, however, be the final effect of a large number of angular and, perhaps, small translational displacements each leaving the manifold of configurational states virtually unaffected. (In § 5 the width of the DOS for these elementary events will be designated σ^{el} .) After having executed a displacive jump, an element sees a new environment within the manifold of available states, as does an electronic excitation when moving among uncorrelated sites of an energetically random system. The average barrier height that an element has to overcome in order to jump from one local minimum of the energy surface to an adjacent one in configuration space is determined by the energy of those configurations representing the transition state. Within the context of the random-walk picture these will be sites close to the centre of the DOS. Combining equations (3) and (4b) yields an average, temperature-dependent activation energy

$$\langle E_A \rangle = (kT_0)^2/kT = (2\sigma/3)^2/kT \quad (6)$$

provided that the environment of an element does not change before the jump has occurred (static DOS approximation). Otherwise the jump rate will be determined by the time required to establish a configuration favouring a transition.

4. Behaviour of supercooled melts at $T > T_g$

To document that the random-walk concept provides a satisfactory explanation for transport processes in supercooled melts near T_g , we extend the analysis of [3] to a

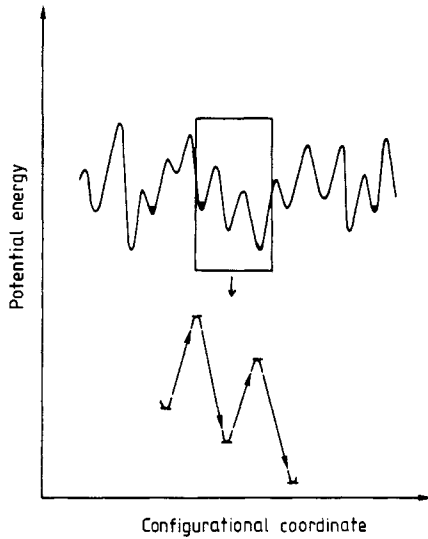


Figure 2. Schematic translation of transport on a potential energy surface representing the configurational disorder in glasses into hopping within a manifold of discrete sites whose energies match the local minima and maxima of the potential. A Gaussian density of states (DOS) of the hopping sites accounts for the statistics of the energy fluctuations.

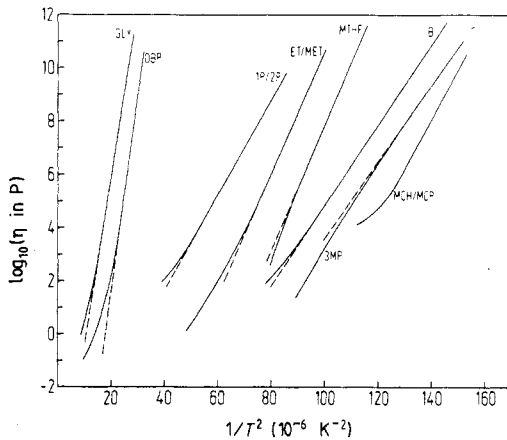


Figure 3. Compilation of literature data for the viscosity of a series of supercooled melts in $\log \eta$ versus T^{-2} representation: GLY, glycerol; DBP, di(*n*-butyl)phthalate; 1P/2P, 1-propanol/2-propanol(1:1 mixture); ET/MET, ethanol/methanol(1:1 mixture); MTHF, methyltetrahydrofuran; B, *B*,methylcyclohexane/3-methylpentane(1:1 mixture); 3MP, 3-methylpentane; MCH/MCP, methylcyclohexane / methylcyclopentane(1:1 mixture) (from [14]).

broader class of systems for which viscosity data are available in the literature, also extending the range to higher temperatures. This analysis will not only confirm the gist of the previous reasoning but will further allow (i) defining the temperature range where the random-walk model is applicable and (ii) discussing its relation to mode-coupling theories.

Figures 3 and 4 show a compilation of literature data for the temperature dependence of the viscosity for a broad variety of supercooled melts, both organic and inorganic as well as network formers such as B_2O_3 and molecular glasses like *o*-terphenyl. The straight lines observed in $\log \eta$ versus T^{-2} plots indicate that $\eta(T)$ follows

$$\eta \propto \exp[(T_0/T)^2] \quad (7)$$

in the high-viscosity regime ranging from typically 10^3 – 10^5 P to about 10^{13} P at T_g . To demonstrate that this thermal behaviour is quite universally observed with dynamic properties of supercooled melts, the T dependences of various relaxation frequencies collected by Jeong *et al* [7] and of the viscosity, respectively, are compared in figure 5 for glycerol. Remarkably, relaxation frequencies obtained by such different techniques

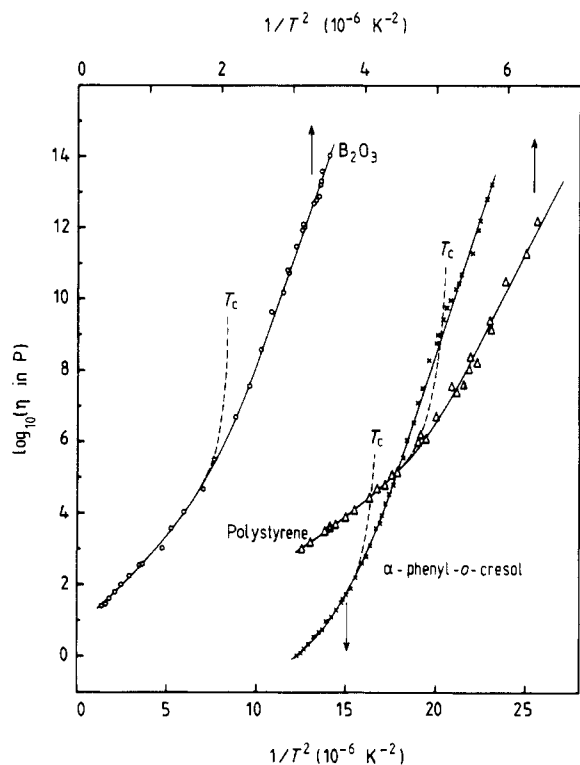


Figure 4. Viscosity data for B_2O_3 [15], polystyrene [59] and α -phenyl-*o*-cresol [16] in $\log \eta$ versus T^{-2} representation. Broken curves are extrapolations according to mode-coupling theory (equation (9)).

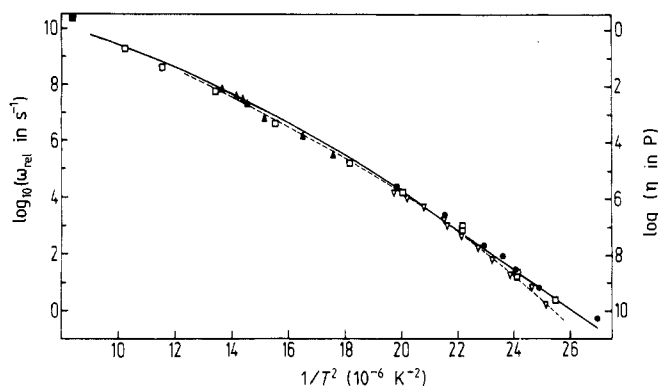


Figure 5. A $\log \omega$ versus T^{-2} plot of the relaxation frequencies in glycerol, obtained by dielectric relaxation (\square), ultrasonic attenuation (\triangle), digital correlation spectroscopy (\bullet), Brillouin scattering (\blacksquare) and frequency-dependent specific heat (∇). Data are taken from [7].) The full curve is the reciprocal viscosity [59]; the broken curve is the VF fit of [7].

as dielectric and ultrasonic relaxation, photon correlation and Brillouin as well as specific-heat spectroscopy fit quantitatively the same behaviour, indicating that correlated microscopic processes are involved in a variety of macroscopic phenomena. In figure 5 we included the Vogel-Fulcher (VF) fit of [7] based on the parameter set $B = 2130$ K and $T_{VF} = 129$ K (see equation (1)). It provides a good description of the data over essentially the entire temperature range covered by experiment, while the $\ln \eta \propto T^{-2}$ fit is good for the high-viscosity/low-frequency regime only. In this range,

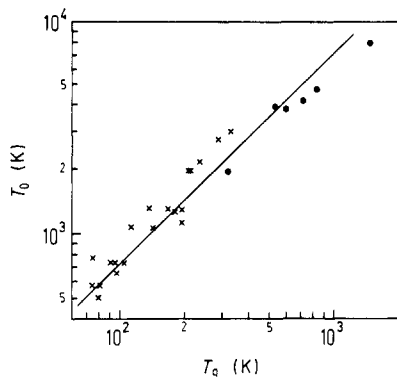


Figure 6. Correlation between the characteristic temperature T_0 defined by equation (7) and the glass transition temperature T_g for a series of organic glass formers (×) and the inorganic glasses Se, B_2O_3 , BeF_2 , Natrisilicate, GeO_2 and SiO_2 (●), listed in the sequence of increasing T_g .

however, the VF fit shows a slight but systematic deviation, although it is a two-parameter equation as far as the slope is concerned. Note, however, that for limited temperature intervals both approaches, the VF law and equation (7), can be matched by appropriate parameter choice. The fact that a scaling law derived from completely different principles can provide an equally good fit to experimental data, albeit with an unrealistically large value of the critical exponent ($\gamma = 12.5$) [7], illustrates that the quality of a fit cannot be used to discriminate among various models unless physical arguments are considered in addition. One of the conclusions of this work is that, upon varying the viscosity of a system over, say, 15 orders of magnitude, the dynamic behaviour changes to an extent prohibitive for applying a single concept for data interpretation.

Before embarking on a discussion of the low-viscosity regime, a compilation of data for the characteristic temperature T_0 (see equation (7)) will be given. Previous analysis [30] revealed a linear correlation between T_0 and T_g , $T_0 = CT_g$, yet suggested that there are two classes of materials—molecular glasses and network formers—differing with respect to the proportionality factor C , the former yielding $C \approx 9$ and the latter $C \approx 6$. Extension of the analysis to a broader class of materials argues against this distinction. Instead, figure 6 indicates a single linear relationship

$$T_0 = (7 + 2/-1)T_g \quad (8)$$

with the tendency of the organic glasses to exhibit larger values of C .

Figures 3 and 4 argue in favour of the applicability of the concept of stochastic transport in a Gaussian DOS for rationalising molecular transport involved in viscous flow, yet do show that this description breaks down in the low-viscosity regime. This is a necessary consequence of the model. The master equation governing the transition among configurations has been applied under the premise that the transition rates are time-independent, implying that the environment of a generalised jumping particle be constant on the timescale of the process. Otherwise the temperature dependence of the mean jump rate must become weaker. Consider an element sitting in a deep potential well. If the environment were to be redefined before the average time needed for a transition had elapsed, the new site configuration may become more favourable, i.e. the effective activation barrier is reduced. This situation is realised if the structure becomes less viscous. Structural relaxation will then have a feedback effect on the individual transition. The method of choice for treating this case is the mode-coupling (MC) theory [40–44]. It describes the viscosity in terms of density fluctuations whose decay is governed by the viscosity in a self-consistent way. Bengtzelius *et al* [40] predicted that $\eta(T)$ should obey a scaling law characteristic of critical phenomena

$$\eta(T) \propto (T - T_c)^{-\gamma}. \quad (9)$$

A successful application of the MC theory to aqueous low-viscosity systems [44]

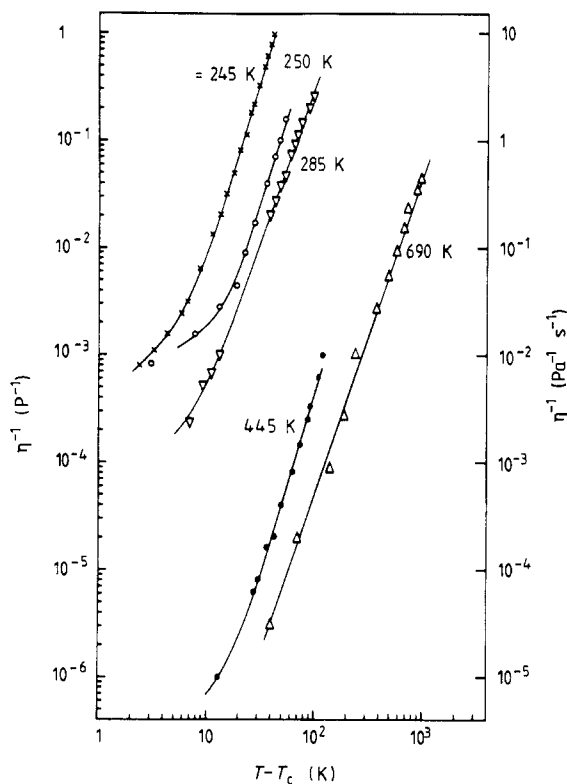


Figure 7. The low-viscosity regime of a selection of supercooled melts plotted on a $\log \eta^{-1}$ versus $\log(T - T_c)$ scale appropriate to test applicability of the mode-coupling theory: B_2O_3 (Δ); polystyrene (\bullet); *o*-terphenyl (∇); glycerol (\circ); α -phenyl-*o*-cresol (\times).

Table 1. Values for critical exponent γ , critical temperature T_c and glass transition temperature T_g for the systems of figure 7.

System	γ	T_c (K)	T_g (K)	T_c/T_g
B_2O_3	3.0	707	534	1.32
Glycerol	3.2	250	186	1.33
<i>o</i> -Terphenyl	3.0	285	238	1.20
<i>o</i> -Cresol	3.6	243	208	1.17
Polystyrene	3.45	445	384	1.16

prompted us to reanalyse the low-viscosity data of a variety of organic and inorganic supercooled melts. The results, shown in figure 7, indicate that equation (9) fits $\eta(T)$ data up to viscosities of typically 10^3 P (10^5 P in the case of polystyrene) with a universal critical exponent $\gamma = 3.3 \pm 0.3$. It is only slightly larger than the values around $\gamma = 2$ found by Taborek *et al* [43] for aqueous LiCl melts and $\gamma = 2.8$ reported by Götze and Sjögren [44] for a 3- α -naphthylbenzene. To illustrate that successful application of the MC theory with a realistic value for γ is restricted to the low-viscosity regime, extrapolated $\eta(T)$ curves have been included in figure 4. This demonstrates erosion of criticality near T_g because uncoupled transport takes over and explains the difficulties encountered upon trying to fit high-viscosity $\eta(T)$ data by the MC theory [45].

Values for the critical exponent γ and the critical temperature T_c are summarised in table 1 together with T_g data. This data set indicates that application of the mode-coupling concept is by no means restricted to atomic or molecular glasses. Network

formers via covalent (B_2O_3) or hydrogen bonding (glycerol) follow the same general pattern as also does a typical polymer (polystyrene). Various types of systems seem, however, to differ with regard to the T_c/T_g ratio. While network formers including aqueous ionic systems [43] yield $T_c/T_g \approx 1.3$, van der Waals systems including polystyrene are characterised by a lower T_c/T_g ratio (1.16–1.20). This indicates that configurational constraints imposed by the network topology obstruct collective motions. Their onset will, therefore, require higher reduced temperatures $T - T_c$.

5. The freezing effect occurring at T_g

The random-walk concept can readily be extended to provide an explanation for the observation that supercooled melts become non-ergodic at a certain temperature (T_g), which depends on experimental parameters like, for instance, the cooling rate. Consider an ensemble of glass elements occupying lower-lying local minima of the DOS and having attained dynamic equilibrium. Upon lowering the temperature the occupational density of states has to readjust in order to guarantee that the average energy of the elements is maintained at $-\sigma^2/kT$ relative to the centre of the DOS as required by the condition of dynamic equilibrium. This readjustment requires time, called the relaxation time t_{rel} , which itself increases with decreasing temperature following a $\ln(t_{rel}/t_0) \propto T^{-2}$ law. The reciprocal temperature derivative of t_{rel}/t_0 ,

$$r = [d(t_{rel}/t_0)/dT]^{-1} \quad (10)$$

defines the maximum rate in time units normalised to t_0 at which the system temperature can be lowered under maintenance of equilibrium conditions. Numerical differentiation in equation (10) yields

$$r = r_0 \exp[-(1.07\sigma/kT)^2] \quad (11)$$

where r_0 (in units of K) is a constant of the order of unity. *If the cooling rate exceeds the maximum rate r of excitation relaxation, the system must move away from equilibrium, i.e. become non-ergodic.* Because the latter rate is a function of T , the transition from ergodic to non-ergodic behaviour occurs at a certain temperature T_r defined by the condition

$$r(T_r) = [d(t_{rel}/t_0)/dT]^{-1}|_{T=T_r} = qt_0 \quad (12)$$

where qt_0 is the sample cooling rate normalised to the elementary jump rate t_0^{-1} . By its definition it is straightforward to identify T_r with the glass transition temperature T_g , with equation (12) relating T_g to the cooling rate and the degree of disorder in a quantitative fashion. The glass transition can, therefore, be considered as a dynamic freezing effect that prevents the supercooled melt from relaxing to a dynamic equilibrium state set by the DOS and temperature. This argument is similar to Dyre's [46], who utilises the concept of the T -dependent demarcation energy separating permanently from non-permanently trapped charge carriers within the density of tail states in an amorphous inorganic semiconductor [47]. The present approach extends that of Dyre because it allows quantitative rather than qualitative predictions. From the Monte Carlo simulation data of figure 1(b) the critical disorder parameter σ^{el}/kT_r and, if σ^{el} is known, the critical temperature T_r at which the system 'freezes' at a given cooling rate can immediately be determined. Here the symbol σ^{el} is used to characterise the width of the DOS for the elementary motional process (see below). By combining equations (5) and (12) and after identifying T_r with the glass transition temperature T_g , we arrive at

$$kT_g = 1.07\sigma[-\ln(qt_0r_0^{-1})]^{-1/2}. \quad (13)$$

For $t_0 = 10^{-12}$ s, $r_0 = 1$ and a representative value $q = 10^{-1}$ K s $^{-1}$, $\sigma^{el}/kT_g = 5.2$ is

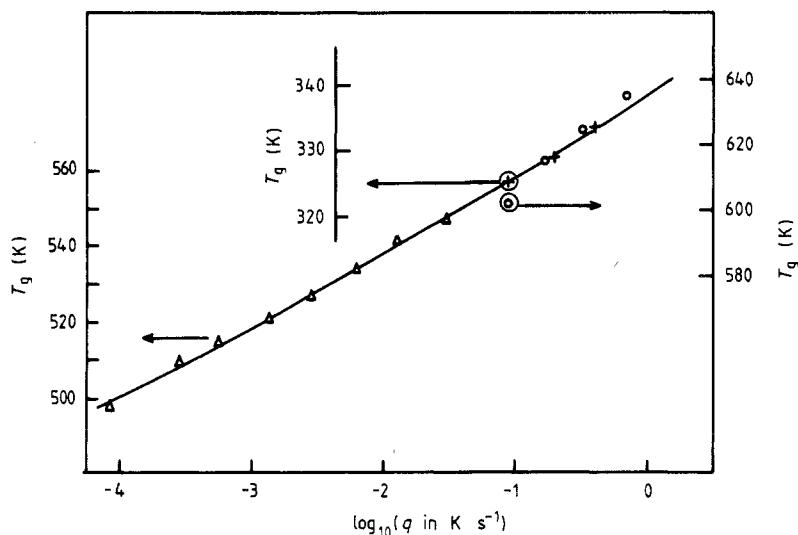


Figure 8. Glass transition temperature as a function of cooling rate q . Data points are for a borosilicate glass (Δ) [47], Aroclor (+) [46] and P_2O_5 (\circ) [45]. The full curve is calculated from equation (13), the adjustable parameter being the width σ^{el} of the DOS (for details see text).

obtained. In figure 8 experimental T_g data, measured for three different systems (P_2O_5 [48]; a commercial polymer, Aroclor [48]; and a borosilicate glass [50]) at variable cooling/heating rate employing differential scanning calorimetry, have been fitted by equation (13). Note that the only adjustable parameter is σ^{el} . Data fitting yields $\sigma^{el} = 0.144$ eV (Aroclor), 0.270 eV (P_2O_5) and 0.246 eV (borosilicate), respectively. The success of the model for rationalising the dependence of T_g on the cooling rate in a quantitative fashion is obvious.

At this stage we have to readdress the problem of how the characteristic temperature T_0 that determines the T dependence of a transport rate in the non-Arrhenius-like transport regime above T_g depends on the width of the DOS, i.e. on the degree of disorder. Combining the experimental result expressed by equation (8) with equation (4b) yields $\sigma/kT_g = 9\text{--}13.5$. At first glance this is in conflict with the above freezing condition $\sigma^{el}/kT_g = 5.2$. The apparent contradiction is solved by recognising that the freezing condition refers to the *elementary* configurational motions of a glass element while the displacive motion responsible for viscous flow will require several of these events acting cooperatively. Consider, for instance, the isotropic rotational diffusion of an *o*-terphenyl matrix that gives rise to the α -transition. It certainly involves the simultaneous occurrence of elementary displacements of the cage molecules. The fact that the apparent 'activation energy' of the viscosity near T_g , defined via $k d \ln \eta / d(1/T)$, is a multiple of the heat of vaporisation [51] can be considered as a consequence of the same phenomenon. Making the simplifying assumption that all elementary steps are of the same kind, the total activation energy for a displacive step is

$$\langle E_A \rangle = \sum_{i=1}^n (\frac{2}{3}\sigma_i^{el})^2 / kT \approx n(\frac{2}{3}\sigma^{el})^2. \quad (14)$$

It immediately follows that the σ determined from T_0 via equation (4b) is a cumulative

quantity, related to the width σ^{el} of the DOS for the elementary step by

$$\sigma = n^{1/2} \sigma^{\text{el}} \quad (15)$$

with n reflecting the degree of cooperation in the high-viscosity regime. By comparing $\sigma/kT_g \approx 11 \pm 2.5$ with the ratio $\sigma^{\text{el}}/kT_g = 5.2$ following from the freezing condition, $n = 3-7$ is obtained. Being of the order of the number of nearest neighbours this is a realistic result. This approach also offers a straightforward explanation for the observation that the proportionality factor C relating T_0 and T_g is slightly different for different materials although the freezing condition (equation (13)) allows for marginal variations of σ^{el}/kT_g only. It also predicts that the T_0 determined, for instance, from the T dependence of the diffusion of a tracer molecule (see § 6) be different from the T_0 inferred from viscosity data.

6. Glass behaviour at $T < T_g$

If a melt is cooled to a temperature below T_g without crystallisation, thermally activated relaxation processes required to readjust the occupational density of states to the new temperature are eliminated. Neglecting tunnelling transitions in a first-order approach implies that the system must, therefore, preserve the state it had when passing the glass transition temperature. In terms of the average energy of the structure-forming elements occupying the DOS this means that

$$\langle \varepsilon_\infty \rangle = \begin{cases} -\sigma^2/\theta T & T > T_g \\ -\sigma^2/kT_g & T \leq T_g. \end{cases} \quad (16)$$

Below T_g the system should, therefore, behave similarly to a conventional solid, at least as far as properties that are related to the degrees of freedom that freeze at T_g are concerned, i.e. α -relaxation processes. A property that follows this rule is the specific sample volume. While at $T > T_g$ the thermal contraction upon cooling exceeds that of an ordinary solid because the progressive occupation of the more stable inter-molecular conformation goes hand in hand with the elimination of structural excess volume, the thermal contraction does approach that of an ordinary solid at $T < T_g$ [2].

As far as displacive motions are concerned, their average activation energy $\langle E_A \rangle$ is related to $\langle \varepsilon_\infty \rangle$ by $\langle E_A \rangle = (2/3)^2 \langle \varepsilon_\infty \rangle$ (see § 2), yielding

$$\langle E_A \rangle = \begin{cases} (\frac{2}{3}\sigma)^2/kT = (kT_0)^2/kT & T > T_g \\ (\frac{2}{3}\sigma)^2/kT_g = (kT_0)^2/kT_g & T \leq T_g. \end{cases} \quad (17)$$

The model, therefore, predicts that (i) the temperature dependence of dynamic processes related to motional freedoms that freeze at T_g become Arrhenius-like below T_g and (ii) the activation energy in the sub- T_g regime is determined by the T dependence at $T \leq T_g$. The experimental result $T_0/T_g \approx 7$ (equation (8)) translates into $E_{A, T \leq T_g} \approx 50 kT_g$.

A beautiful demonstration of this effect is provided by the experiments on the diffusion of photochromic dye molecules employing the holographic grating technique [52]. It allows the measurement of molecular diffusion coefficients in the range 10^{-8} to $10^{-17} \text{ cm}^2 \text{ s}^{-1}$. Figure 9 presents data for the diffusion of tetrahydrothiophenindigo (TTI) in a polycarbonate matrix plotted in a $\log D$ versus T^{-1} scale (part (a)) and a $\log D$ versus T^{-2} scale (part (b)). Near T_g there is a significant change in the T dependence of D , which becomes Arrhenius-like for $T < T_g$. Remarkably, the activation energy in the sub- T_g regime is exactly what one would expect from equation (17) if the conformational

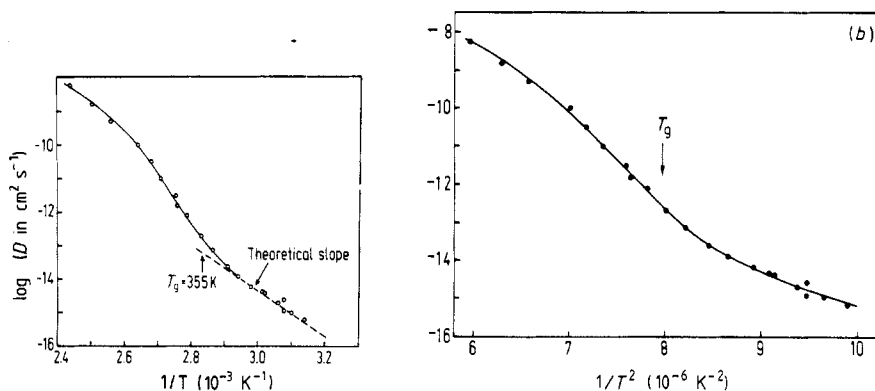


Figure 9. Diffusion coefficient for tetrahydrothiophenindigo in a polycarbonate matrix plotted on $\log D$ versus T^{-1} (part (a)) and $\log D$ versus T^{-2} (part (b)) scales, respectively. The broken line represents the slope that equation (17) predicts for $T < T_g$. Data taken from [52].

structure realised at T_g is preserved below T_g . This is another manifestation that the random-walk concept provides a unified description of molecular dynamics in supercooled melts above and below T_g without invoking additional conceptual elements.

Further examples for this category of observations can be found in the work of Eisenbach [53] and Smets [54] on photochemical reactions in polymeric matrices probing either the *cis-trans* isomerisation of azobenzene derivatives or the ring-closure reaction in a merocyanine molecule. The steepness of the T dependence of the average reaction rate changes abruptly near T_g in the same fashion as does the diffusivity of a tracer molecule (see above). Quantitative data analysis in terms of the present model is, however, more intricate, because the activation energy of the entire process is the sum of a molecule-inherent electronic contribution and the conformational barrier set up by the cage molecules [55].

On an extended timescale, some residual relaxation will continue to occur even at $T < T_g$, leading to the phenomenon of physical aging at an aging temperature $T_a < T_g$. Being consistent with any random potential concept not invoking cut-off conditions for the DOS, aging effects readily arise from the present model. Intuitively it is clear that further relaxation of a formerly equilibrated state must reveal a highly dispersive temporal pattern by means of the following notion. The initial ensemble of states will occupy a distribution of sites which, on the energy scale, exceeds the span of kT . By virtue of a demarcation energy ϵ_d , in analogy to the notion of Dyre [46], this ensemble subdivides into mobile states above ϵ_d and states trapped in the lower wing of the DOS. While the former states contribute to the relaxation in the short-time domain, subsequent progress is increasingly frustrated by gradually increasing trap release times. Dispensing with a detailed comparison, we only mention that the pattern reported by Straff and Uhlmann [56] for isothermal enthalpy relaxation in rigid poly(vinyl chloride) (PVC) is in accord with the above reasonings.

7. Conclusions

The present work suggests the following scenario for the dynamics involved in the formation of a glass from a melt under suppression of crystallisation. At temperatures not too far below the melting point, the viscosity is determined by density fluctuations

in a non-linear fashion. This case is appropriately described by the mode-coupling theory, predicting a divergence of η at a critical temperature T_c where the collective motion vanishes. Below T_c motion becomes gradually cooperative, paralleling the establishment of a quasi-static random potential constraining motion to the level of elementary steps within the manifold of potential states. The states reflect the multitude of configurations among the structural elements within a static random potential. Although no longer allowing for coupled motion it still permits displacive transitions of the glass-forming elements as elementary steps involved in phenomena like viscous flow, molecular transport or dipole relaxation. For $T < T_c$ dynamics are controlled by transitions within the density-of-states distribution, tractable in terms of a random walk in configuration space obeying a linear kinetic master equation. Of central importance for the temperature dependence of dynamic properties is the fact that the average configurational state of the system depends on temperature, because at any given temperature the ensemble of glass elements occupies a different subset of available states of the DOS in accord with the principle of dynamic equilibrium under the conditions of detailed balance. It implies that in the steady-state approximation the mean energy of the elements decreases as T^{-1} and so does the ensemble-averaged activation energy for molecular motion. This leads to a T dependence of the type $\exp[-(T_0/T)^2]$ for the rate of an elementary kinetic event, revealed, for example, by viscous flow.

This reasoning concurs with independent evidence provided by both molecular dynamics [57] and neutron scattering studies [44]. Both indicate that the essential discontinuity in the behaviour of a supercooled melt occurs at a temperature T_c between T_g and the melting temperature T_m , where the character of the many-body dynamics changes. Simulations [57] confirm that below T_c the elements of the structure no longer execute collective motions but are temporarily trapped in local minima of the configurational energy surface set up by the quasi-static arrangement of the entire manifold of structure-forming elements [51]. The anomaly near T_c can, however, only be revealed by experiments probing long-range density fluctuations such as quasi-elastic neutron scattering or Rayleigh scattering of Mössbauer radiation [58], yet not by experiments probing local displacive acts of individual structural units, such as viscous flow, because the latter persist below T_c , albeit following a characteristically different temperature behaviour.

The random-walk picture also offers a conceptually simple explanation for the long-standing question regarding the nature of the phenomena occurring at the conventionally defined glass transition. Pursuing the argument that a system of elements subject to stochastic motion in a random potential must fall out of dynamic equilibrium once the cooling rate exceeds the maximum rate of readjustment of the total internal energy of the system, we have been able to show that a supercooled melt must become non-ergodic below a certain temperature, identified as T_g . The relation of T_g to the width of the DOS, i.e. to the inherent degree of disorder, and to the cooling rate can be cast into a simple analytic expression. While at $T_c > T > T_g$ the system is able to relax energetically it can no longer do so at $T < T_g$ because the structure existing at T_g will be frozen-in upon further cooling below T_g . As a consequence its behaviour approaches that of a conventional solid with an Arrhenius-type temperature dependence for kinetic processes. This alleviates the necessity to invoke the existence of liquid-like clusters below T_g as relicts of the free-volume percolation cluster proposed to exist above T_g in order to explain motional processes still active below T_g .

So far the distribution of rates, which is another feature of supercooled melts and random systems in general, has not been considered explicitly. Suffice to mention at this

stage that the present concept requires the rates of elementary processes to be distributed rather than single-valued quantities because activation energies are subject to a distribution as governed by the complicated potential surface of the system. It will be the intention of subsequent work to demonstrate how this distribution translates into non-exponential relaxation patterns.

Finally, it has to be emphasised that modelling glass dynamics in terms of stochastic transport theories remains a somewhat arbitrary approach. Despite accounting for the complicated random potential and consequently for the statistics to which elementary processes are subject, no molecular details of a glass can be translated in a straightforward manner into the model. In view of the conceptual simplicity of the model advanced herein, together with the diverse results reproducing features characteristic of the glassy nature, we believe that application of the model can be justified on a more microscopic level in the future.

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