

Microscopic dynamics of glass-forming polymers

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TOPICAL REVIEW

Microscopic dynamics of glass-forming polymers

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Online at stacks.iop.org/JPhysCM/15/R1025**Abstract**

The microscopic dynamics of glass-forming materials, especially polymers, is a topic of strong current interest and often heated debate. In this review an overview of the most common dynamical phenomena in glass-forming polymers will be presented: α relaxation, β relaxation, ‘boson peak’, and ‘fast process’ (β_{fast} relaxation). The experimental results presented will be mainly from inelastic and quasielastic neutron scattering. Several mostly unanswered questions arise from the experimental findings, e.g.: Is the α relaxation of heterogeneous or homogeneous origin? Is there any relation between the ubiquitous low-temperature vibrational properties of glasses and the α relaxation? Different theoretical and model approaches will be mentioned, e.g. mode-coupling theory, the coupling model, the vibration–relaxation model. The limitations of these attempts will be demonstrated leading to the conclusion that currently there is no theory describing the microscopic dynamics of polymers completely over the whole temperature range from the glassy to the liquid (rubbery) state. Nevertheless, for certain temperature ranges or individual phenomena, especially the β relaxation, successful concepts could be developed.

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1. Introduction

Glass formation, i.e. the solidification of a liquid without forming a crystal, is a very common phenomenon [1]. The range of materials forming glasses includes silicates (window glass), polymers (e.g. polystyrene), elements (selenium), metals, biological materials, and many more. From computer simulations it may even be speculated that any material vitrifies if it is cooled down sufficiently fast. Nevertheless, the glass transition and the related molecular dynamics are still poorly understood [2].

This topical review is restricted to the materials class of *polymers*. These are firstly of interest because of their technological applications and secondly because polymers are often 'good' glass formers, meaning that their tendency to crystallization is effectively suppressed by a disordered molecular microstructure.

Probably the most important experimental technique for studying the microscopic dynamics of glass-forming systems is the *inelastic and quasielastic neutron scattering* technique, because it gives simultaneous information about the dynamics and structure of the substances [3, 4]. There has been an immense amount of experimental work on this subject which cannot be completely included in this review. Therefore, the reader is advised to consult other literature [5] for completeness and alternative approaches.

Figure 1 shows the generic regions of microscopic dynamics which can be observed in nearly all glass-forming materials, especially polymers. Represented is the logarithm of the characteristic time of the dynamics versus the reciprocal temperature. In this kind of plot an activated (Arrhenius) process appears as a straight line. The absolute values on both axes are valid for 1,4-polybutadiene. Nevertheless, the times are universal with a spread of about one decade, so the 'fast process' (fp) is always at about 1 ps, the merging of α and β relaxation occurs at about 1 ns, etc.

Omitted from this map and the discussion are processes which are related to the chain nature of the polymer, e.g. Rouse modes and reptation [6]. Usually, these processes just follow the temperature dependence of the α relaxation with a scaling factor which depends only on the molecular weight. Polymer-specific side-group relaxations [7, 8] will also not be discussed because they are not a general phenomenon. Also there are some glass-transition-related dynamical processes in polymers which are still debated, most importantly the 'slow modes' (Fischer modes) [9]. These will also not be included in this article.

The discussion in this article will follow the sequence of dynamical phenomena in the following order:

- (i) At the longest timescale considered here the α relaxation related to the glass transition itself can be found. For polymers it always shows a non-Arrhenius behaviour.
- (ii) At shorter times one can usually find the β relaxation. It has an Arrhenius temperature dependence and occurs also in polymers that completely lack side-groups and low-molecular-weight liquids.
- (iii) The vibrational density of states (DOS) in polymeric glasses shows a distinctive excess over the result expected from sound waves which is termed 'boson peak' (bp) or 'low-energy excitations'.
- (iv) Adjacent to this vibrational feature a fp can be found which increases in intensity upon heating but does not show a strong temperature dependence of its characteristic time.

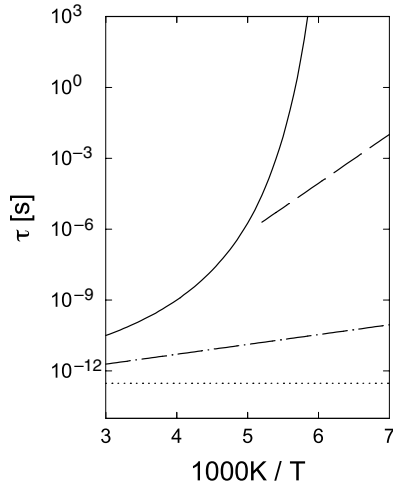


Figure 1. A generic map of the microscopic dynamical processes in glass-forming polymers. Continuous curve: α relaxation; dashed line: β relaxation; dotted line: ‘boson peak’; dash-dotted line: ‘fast process’. The exact values are those from 1,4-polybutadiene at a scattering vector of $q = 1.48 \text{ \AA}^{-1}$ corresponding to a length scale of $2\pi/q \approx 4 \text{ \AA}$.

2. α relaxation

2.1. Phenomenology of the α relaxation

The central and most important dynamical phenomenon in glass-forming polymers is the α relaxation. It is undoubted that any polymer (if not any material at all) which solidifies without crystallization shows this type of dynamics and that certain characteristics are always observed.

2.1.1. Non-exponentiality. This feature is the one known of for the longest time in the history of glass research. In the 19th century Kohlrausch had already discovered [10] that the decay of the charge of a Leyden flask, a capacitor made from silica glass, is not exponential but can be described by the expression

$$\Phi(t) = \exp(-(t/\tau_K)^\beta), \quad (1)$$

with $\beta < 1$. It is remarkable that this expression is still used successfully today in the description of various aspects of the dynamics of glasses, especially polymeric ones. It applies as well to macroscopic quantities such as the dynamic shear compliance [11] and the dynamic light scattering correlation function [12] as to microscopic correlation functions from neutron scattering [13]. Only in studies covering very large frequency ranges, mostly by dielectric spectroscopy, can differences be found:

- (1) The susceptibility shows deviations from the asymptotic behaviour¹ $\chi'' \propto \omega^{-\beta}$ corresponding to (1) at high frequencies, $\omega \approx 10^4/\tau_K$ [15]. This could also be due to the onset of the β relaxation (see section 3).
- (2) At low frequencies especially for polymers the asymptotics $\chi'' \propto \omega$ following from (1) is not well fulfilled but rather $\chi'' \propto \omega^{-m}$ with $m = 0.8-1$ [16].

¹ Williams and Watts have published a series of papers about the frequency domain representation of the Kohlrausch function (which is why it is often called Kohlrausch–Williams–Watts). In [14] they give a series expression for $\chi^*(\omega)$ from which the asymptotic power law at high frequencies follows.

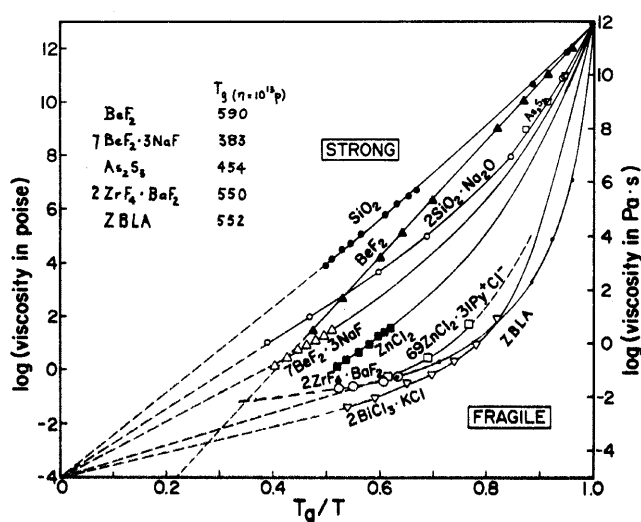


Figure 2. A plot of logarithmic α relaxation times of various glass-forming materials versus the reciprocal temperature normalized to the respective glass temperature T_g , defined here as the temperature at which the viscosity $\eta(T_g) = 10^{12}$ Pa s (equivalent to $\tau \approx 10^3$ s). Reprinted with permission from [25].

The success of the ‘Kohlrausch law’ (1) is even more surprising considering that there is no theory that *exactly* predicts it. MCT [17] states it as limiting approximation to but not the solution of its dynamical equations [18]. The coupling model (CM) of Ngai [19] uses the expression only stating heuristic arguments for it. Approximately or asymptotically the Kohlrausch law could be derived for dynamics in fractal structures (especially polymers) [20], fractal time [21], hierarchical models [22], and percolation models [23]. The special ubiquitous role of the form (1) may be related to its mathematical importance as the characteristic function of Levy’s stable distributions [24] but this property has never been exploited in a rigorous derivation but rather only as a motivation for the widespread use of the Kohlrausch law [21].

2.1.2. Non-Arrhenius temperature dependence. Another characteristic feature distinguishing the α relaxation of glass-forming polymers from relaxations in ‘simple’ systems is the deviation of its temperature dependence from that expected for thermally activated processes, namely the Arrhenius law

$$\tau \propto \exp(E/k_B T). \quad (2)$$

The degree of this deviation is very different for different glass-forming materials leading to a categorization by Angell [25, 26] into ‘strong’ glasses following relation (2) closely to ‘fragile’ ones which show a bent curve in the normalized activation plot $\log \tau$ versus T_g/T [25–27] (figure 2).

In this framework all polymeric glasses appear to be more or less ‘fragile’. The temperature dependence of their α relaxation can be described empirically by the Vogel–Fulcher [28, 29] expression

$$\tau \propto \exp\left(\frac{A}{T - T_{VF}}\right). \quad (3)$$

This formula was developed for non-polymeric glasses. In the context of polymers, often the mathematically equivalent expression of Williams *et al* [30] is preferred.

At this point, a remark about the ‘glass transition’ in general is in order: equation (3) suggests that there is complete vitrification at T_{VF} . This behaviour is experimentally unobservable because (i) most methods cease to be feasible for $\tau > 10^4$ s because of prohibitive experiment duration, (ii) samples have to be equilibrated before the experiments and the time required for this (ageing time) increases in the same way as the α relaxation time τ itself. It is therefore unclear whether equation (3) holds up to the singularity; most recent experiments even seem to deny this possibility [31]. For that reason the empirical glass ‘transition’ temperature T_g is defined as that where $\tau(T_g) = 10\text{--}10^4$ s.

Also high-precision measurements combined with an analysis of the derivatives of $\tau(T)$ show clear deviations from the VF expression (3) for high as well as low temperatures [32, 33]. Nevertheless, it seems to be an excellent description in an intermediate temperature range.

Empirically, a relation between non-exponentiality and non-Arrhenius temperature dependence can be found for glassy polymers [34] and well as for glass-forming materials in general [35]: ‘fragile’ glasses seem to show the higher deviation from exponentiality.

Here, the CM offers a simple explanation: from heuristic arguments [36] and motivated by simplified models [37] it is deduced that the relaxation in glass-forming materials consists of an initial exponential (Debye) part followed by a Kohlrausch law:

$$\Phi(t) = \begin{cases} \exp(-t/\tau_D) & \text{for } t < t_c \\ \exp(-(t/\tau_K)^\beta) & \text{for } t > t_c. \end{cases} \quad (4)$$

Here, $\Phi(t)$ can be any normalized relaxation function, e.g. $(\varepsilon - \varepsilon(t))/(\varepsilon - \varepsilon(0))$ from dielectric spectroscopy or $S(q, t)/S(q)$ from inelastic neutron scattering. τ_D is the elementary relaxation time of a microscopic unit (to be visualized as a molecule or monomer) and t_c the (temperature-independent) crossover time to a cooperative relaxation. The continuity of $\Phi(t)$ at t_c imposes a relation between the time constants:

$$\tau_K = (t_c^{\beta-1} \tau_D)^{1/\beta}. \quad (5)$$

Because the exponent $1/\beta$ is larger than one, the time constant of the α relaxation τ_K shows a stronger temperature dependence² than τ_D . Supposing that the temperature dependence of $\tau_D(T)$ does not vary much within a family of materials (e.g. polymers), that of $\tau_K(T)$ is determined by β . The smaller β , the larger the temperature dependence $\tau_K(T)$. Despite that qualitative agreement, it has to be noted that the *quantitative* fragility $m = d \log \tau / d(T_g/T)|_{T_g}$ does not show the expected proportionality to $1/\beta$ but rather a linear behaviour $m = m_0 - s\beta$ [11, 35].

2.1.3. Time–temperature superposition principle. Despite being non-exponential the α relaxation usually exhibits the same shape over a large temperature range. This means that the relaxation can be described by a master function Φ_α which is only rescaled to the individual temperatures:

$$\Phi(t, T) = \Phi_\alpha(t/\tau_\alpha(T)). \quad (6)$$

For the Kohlrausch expression (1) this means that β does not depend on temperature. This implies that the loss part of the susceptibility corresponding to the α relaxation obeys the inverse scaling law

$$\chi''(\omega, T) = \chi''_\alpha(\omega\tau_\alpha(T)). \quad (7)$$

² Of course, this is only a single aspect of glass-typical behaviour. For example, the molecular origin of non-exponentiality and non-Arrhenius temperature dependence are left open. The limitations of the CM are outlined by the principal author himself in [38].

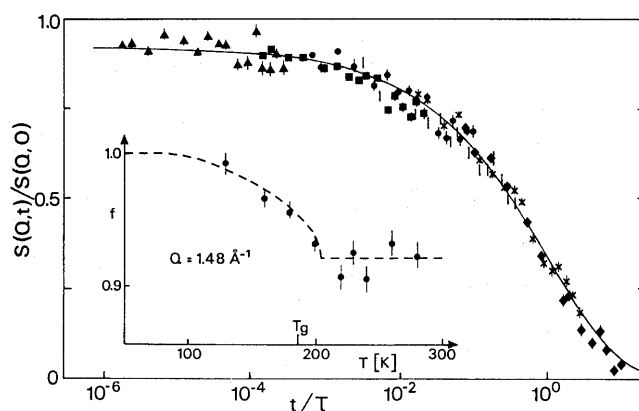


Figure 3. A scaling representation of the neutron spin-echo data $S(q, t)$ for 1,4-polybutadiene at $q = 1.48 \text{ \AA}^{-1}$. (\blacktriangle , 200 K; \blacksquare , 220 K; \bullet , 230 K; \mid , 240 K; \times , 260 K; \blacklozenge , 280 K). The scale $\tau(T)$ is taken from a macroscopic viscosity measurement. Inset: the temperature dependence of the non-ergodicity parameter f_q . (Reprinted from [13]. Copyright (1988) by the American Physical Society.)

This principle was first found from rheological measurements of the dynamic moduli [39]. It is still applied as a standard way to overcome the restricted dynamical range of such experiments. Measurements at different temperatures are spliced together to obtain a master curve which spans 12–14 decades.

The time–temperature superposition principle obviously applies as well to the microscopic dynamics seen in a neutron scattering experiment [13] (figure 3).

Nevertheless, experiments covering a large dynamical range by themselves show that deviations from time–temperature superposition occur. Although they are less pronounced for polymers than for simple liquids [15] they can be detected in dielectric spectroscopy [40] as well as rheological measurements [11].

2.1.4. α relaxation universality. Finally, the timescale $\tau(T)$ is usually universal for all relaxation processes—macroscopic (rheological, dielectric, etc) and microscopic. This can be recognized from figure 3: the fact that the (microscopic) relaxation curves from neutron scattering superimpose when the (macroscopic) shift factor from rheology [41] is used is by no means trivial. The former data reflect the loss of correlation on a length scale of $2\pi/q \approx 4 \text{ \AA}$ while the latter are obtained from a macroscopic sample. This shows that there is indeed a universality of the α relaxation timescale covering all levels of motion from that of an individual polymer segment to the bulk.

Also in the case of the α relaxation universality it should not be concealed that high-resolution experiments show a deviation from its strict validity. Even the mechanical relaxation of the whole chain has a different temperature dependence such as the mechanical relaxation of an individual segment for certain polymers such as polystyrene [42]. This result can be explained in the framework of the CM by a different stretching coefficient β causing a different $\tau(T)$ dependence via relation (5) [43].

2.2. Mode-coupling theory

The only theory which is currently able to predict all above-mentioned features of the α relaxation from microscopic equations at least qualitatively is the MCT [17]. Time–

temperature superposition and α relaxation universality follow directly from the mathematical properties of the MCT. Stretching is found except for the simplest models of the MCT.

A strict ergodic–non-ergodic transition is predicted for a temperature T_c . At this temperature the caging effect caused by neighbouring particles becomes so strong that a structural arrest takes place. Close to T_c the α relaxation timescale diverges with a power law

$$\tau_\alpha(T) \sim (T_c - T)^{-\gamma} \quad (8)$$

with a high exponent $\gamma > 1.76 \dots$. Experimentally, such a power law can usually only be found in a small temperature region [32]. The extrapolated T_c is about 20% higher than the glass temperature T_g . This is an indication of thermally activated (‘hopping’) processes which are included in a more extended formulation of MCT [44]. These processes restore ergodicity even at temperatures below T_c where the ‘ideal’ MCT predicts a non-ergodic behaviour.

Besides the prediction of the temperature dependence of macroscopic properties the MCT is able to predict properties of the (microscopic) density correlation function observable by means of coherent inelastic neutron scattering:

$$\Phi_q(t) = \frac{\langle \delta\rho_q^*(0) \delta\rho_q(t) \rangle}{\langle \delta\rho_q^*(0) \delta\rho_q(0) \rangle} = \frac{S(q, t)}{S(q)}. \quad (9)$$

Here the $\delta\rho_q(t)$ are the Fourier components of the microscopic density fluctuations. $S(q, t)$ is the inverse Fourier transform of the scattering function observed in the inelastic neutron scattering experiment $S(q, \omega)$ and $S(q)$ is the static structure factor $S(q, t = 0)$. Note that neutron spin-echo experiments yield the normalized quantity $S(q, t)/S(q)$ directly [45].

The most important prediction with respect to the α relaxation is that of the behaviour of the non-ergodicity parameter f_q . This quantity is defined as the degree of correlation remaining at infinite time in the non-ergodic state, $f_q = \lim_{t \rightarrow \infty} \Phi_q(t)$, and in the ergodic state as the amplitude of the α relaxation decay obtained by extrapolating the incipient decay using the von Schweidler law [46]

$$\Phi_q(t) = f_q + h_q t^{-b}. \quad (10)$$

With high generality the temperature dependence of the non-ergodicity parameter should be

$$f_q(T) = \begin{cases} f_q^c & \text{for } T > T_c \\ f_q^c + \tilde{h}_q (T_c - T)^{1/2} & \text{for } T < T_c. \end{cases} \quad (11)$$

Note that this expression does not contain a material-dependent exponent as the power law (8) does; the value 1/2 follows solely from the topological nature of the singularity at T_c . The inset of figure 3 shows as an example the validity of this ‘square-root law’. It has been confirmed in various studies for different q -values [47], different polymers [48], and non-polymeric glass formers [49].

2.3. Dynamical heterogeneity

Currently the probably most discussed question concerning the α relaxation is whether it is of homogeneous or heterogeneous origin [51]. This question was first asked in categorizing the attempts to explain non-exponential relaxation [50]: ordinary diffusion generates a self-correlation function $S(q, t) = \exp(-Dq^2t)$. There are basically two ways to obtain from this a non-exponential relaxation. Heterogeneous: a distribution of diffusion constants can be assumed. In this case the (unobservable) self-correlation function for an individual particle would still be exponential. But due to the averaging of exponentials with different decay times $\tau(q) = 1/Dq^2$, a non-exponential result is obtained. Homogeneous: by

modifying the linear increase of the mean square displacement implied by normal diffusion, $\langle r^2 \rangle = 6Dt$, to a sublinear dependence $\langle r^2 \rangle = 6Dt^\beta$, one can derive the Kohlrausch expression $S(q, t) = \exp(-Dq^2t^\beta)$.

The experimental answering of this question is rather difficult because it involves the identification of faster and slower ‘populations’ of particles. This is usually impossible due to the implied particle averaging in the experiment and the restriction to two-point correlation functions. Attempts to devise experimental techniques overcoming this restriction are listed in [51]. They all suffer from certain limitations which prevent a clear answer: NMR experiments are able to define fast and slow subensembles but only on grounds of rotational dynamics [52]; solvation dynamics experiments [50] observe the motion of probe molecules only, etc. Nevertheless, it should be noted that all these experiments hint at a heterogeneous component in the origin of the anomalous dynamics of glass-forming liquids.

The only clear evidence for heterogeneous dynamics comes from computer simulations [53] which were first carried out on Lennard-Jones model systems [54] but now also extend to polymer models [55]. In the computer ‘experiment’ it is possible to identify mobility populations [54] as well as to access higher-order density correlation functions [53]. All approaches yield consistent results:

- (i) Dynamical heterogeneity exists on a timescale t^* corresponding to the ‘early α relaxation’ [56]. At t^* the mean square displacement is about 1/10 of the square of the next-neighbour distance. The associated microscopic picture may be that for shorter times $t \ll t^*$ particles are confined to rather uniform cages of neighbouring particles and for longer times $t \gg t^*$ individual motion steps add up to a regular diffusive motion. Only for the time when a particle is about to break out of its ‘cage’ is the heterogeneity pronounced.
- (ii) As temperature is lowered t^* increases similarly to the α relaxation timescale τ . Also the peak values of all numerical measures of heterogeneity increase with decreasing temperature often with power laws indicating a divergence at T_c , the critical temperature of the MCT (see section 2.2).
- (iii) The population of more mobile particles is not randomly distributed. It tends to cluster on a length scale ξ which increases with decreasing temperature. (Note that this was predicted to be the fundamental origin of the glass transition in earlier theories [57].) A closer look at the clusters shows that they are not compact but string-like [58].

A related but not identical question is whether the relaxation process is Gaussian in space or not, i.e. whether the self-correlation function can be written as $S(q, t) = \exp(-q^2 \langle r^2(t) \rangle / 6)$ at any time. It is clear that in the case of a heterogeneous origin the individual self-correlation functions will not add up to a Gaussian function. On the other hand, the sublinear diffusion model above leads to a Gaussian expression and so do other homogeneous models, e.g. the Rouse and Zimm models for the large-scale motion of polymers [6]. Nevertheless, Gaussianity is not implied by all homogeneous models.

The question of Gaussianity is simpler because it should be possible to answer it from the two-point correlation function $S(q, t)$. But even this question turned out to be not undisputed. An analysis of high- q inelastic neutron scattering data using the Rahman–Singwi–Sjölander expansion [59] of the self-correlation function in a liquid

$$S(q, t) = \exp\left(-\frac{\langle r^2(t) \rangle}{6}q^2 + \frac{\alpha_2(t)\langle r^2(t) \rangle^2}{72}q^4\right) \quad (12)$$

yields a parameter $\alpha_2(t) > 0$ clearly indicating non-Gaussianity for 1,2–1,4-polybutadiene [60]. In contrast, fits of the Kohlrausch expression with a power law dependence of the

characteristic time

$$S(q, t) = \exp\left(-\left(\frac{t}{\tau_0(q/q_0)^n}\right)^\beta\right) \quad (13)$$

for lower q -values give $n = -2/\beta$ in agreement with the (Gaussian) sublinear diffusion model for several polymers [61].

But at least this contradiction seems to be resolved. Most recent results show a crossover from $\tau \propto q^{-2/\beta}$ to a weaker q -dependence at $q \gtrsim 1 \text{ \AA}^{-1}$ [62]. The whole dependence $\tau(q)$ could be described by a surprisingly simple sublinear *jump* diffusion model with an average jump length of 0.42 \AA in 3,4-polyisoprene. This model also agrees qualitatively with the non-Gaussian parameter $\alpha_2(t)$ calculated from a computer simulation of the same polymer [63]. So the introduction of a finite length scale is sufficient to create the non-Gaussianity in a homogeneous model.

3. β relaxation

It is well known that glass-forming liquids, besides the α relaxation, show *secondary* relaxations [64, 65]. Because of their widespread occurrence and because they often cannot be immediately assigned to specific chemical groups they were soon considered as another ‘intrinsic property of the glassy state’ [64]. Recent wide-band dielectric spectroscopy measurements reveal these processes also in materials which do not show explicit additional peaks in the spectra as an excess wing to the α relaxation [66, 67]. These relaxations are at a given temperature faster (or for methods with a fixed frequency, occur at lower temperature) than the α relaxation. Traditionally, they are labelled $\beta, \gamma, \delta, \dots$ in the sequence of their timescales.

There are also some more subtle differences distinguishing the secondary relaxations from the α relaxation:

- (i) The temperature dependence is usually Arrhenius-like following equation (2) or at least less ‘fragile’ [67]. But it has to be noted that the values of the activation energy E_A and pre-exponential factor are often out of the range allowing interpretation as a microscopic activated process.
- (ii) The secondary relaxations are also non-exponential but usually ‘symmetrically broadened’.

The latter term refers to the representation of the relaxation function as the Laplace transform of a relaxation time spectrum $g(\ln \tau)$:

$$\Phi(t) = \int_{-\infty}^{+\infty} d \ln \tau g(\ln \tau) \exp(-t/\tau). \quad (14)$$

In this representation the variance $\sigma_{\ln \tau}^2$ of the distribution $g(\ln \tau)$ indicates the deviation from exponentiality. For expressions fitting the α relaxation, the third centralized moment of $g(\ln \tau)$ is usually negative, e.g. $\mu_{3 \ln \tau} = 2\zeta(3)(1 - 1/\beta^3)$ (ζ being Riemann’s zeta function) for the Kohlrausch expression [68]. In contrast, expressions describing the β relaxation as the Cole–Cole function [69] or the log-normal distribution [70] usually have $\mu_{3 \ln \tau} = 0$.

The MCT (see section 2) also uses the term ‘ β relaxation’. In the beginning it was identified with the Johari–Goldstein type of relaxation discussed in this section. Later studies showed that this identification was wrong for two reasons:

- (i) The relaxation is expected to take place at a much faster timescale immediately adjacent to the vibration frequencies of the system. Therefore, it is more natural to identify it with the ‘fp’ (section 6).

- (ii) The MCT equations usually do not produce solutions which correspond to a peak in the susceptibility which is the actual experimental finding.

In order to get such a peak in the framework of MCT it is necessary to introduce a rather complicated two-correlator model [71].

A step towards the understanding of the β relaxation could be made in polymers by proving its local nature [72]. In this study 1,2-1,4-polybutadienes with a random sequence of different monomeric units (*cis*-1,4, *trans*-1,4, and vinyl (1,2)) were used. In these materials the α relaxation does not reflect the microscopic irregularity. There is only one α relaxation corresponding to a single T_g which is a monotonic function of the composition. In contrast, the β relaxation is a superposition of independent contributions from the different monomer species. This indicates that the process of the β relaxation takes place on a local length scale not larger than a monomeric unit.

In the case of 1,4-polybutadiene the microscopic mechanism of the β relaxation could be identified more clearly by using the spatial sensitivity of quasielastic neutron scattering. In a first study the jump length involved could be identified as about 1.5 Å [73]. A two-site hopping model with this site distance and the energy barrier distribution obtained from dielectric spectroscopy yields a satisfactory description of neutron spin-echo data over a large range of q and temperature. Using the structure of the monomer the motion could be identified more closely as a rotation of 60°–90° around the centre of mass [74]. It has to be noted that the detailed β relaxation mechanism seems to be particular for each polymer, e.g. polyisobutylene shows a significantly smaller jump length, 0.5–0.9 Å [75].

4. α - β merging

Because the temperature dependence of the β relaxation is weaker than that of the α relaxation, they are expected to merge at a certain temperature when their timescales become equal. Several scenarios have been devised regarding how this happens in detail [76], e.g. one of the relaxations may vanish and be replaced by the other

The influence of the β relaxation on the microscopic density correlation function $S(q, t)$ was first detected in neutron spin-echo (NSE) experiments [77]. At that time only a decoupling of the temperature dependence of the timescales of $S(q, t)$ and the macroscopic viscosity could be stated. In later dielectric experiments it could be shown that the temperature dependence in the ‘decoupled’ range is that of the β relaxation [70].

A quantitative description of $S(q, t)$ in the α - β merging regime could be derived from the two-site hopping model of the β relaxation cited in the preceding section combined with the Kohlrausch function (1) for the α relaxation [74]. The crucial (yet still debated [78]) point is that the two contributions are not simply added but rather *convoluted* in the frequency domain. This corresponds to a factorization

$$S(q, t) = S_\alpha(q, t)S_\beta(q, t) \quad (15)$$

for the density correlation function which is the rule for combining intermediate scattering functions of statistically independent motions [4]. For the case of the dielectric susceptibility Williams had already suggested an equivalent way to merge α and β relaxations in 1979 [79]. Figures 4 and 5 show that the convolution model for the merging is successfully applicable to 1,4-polybutadiene for NSE as well as dielectric spectroscopy. It has to be noted that the same parameters were used for both fits. A major consequence of the convolution model is that the ‘decoupling’ discontinuity of the α relaxation temperature dependence vanishes. A continuous description of the α and β relaxation by a VF (3) and an Arrhenius law is possible over the whole temperature range.

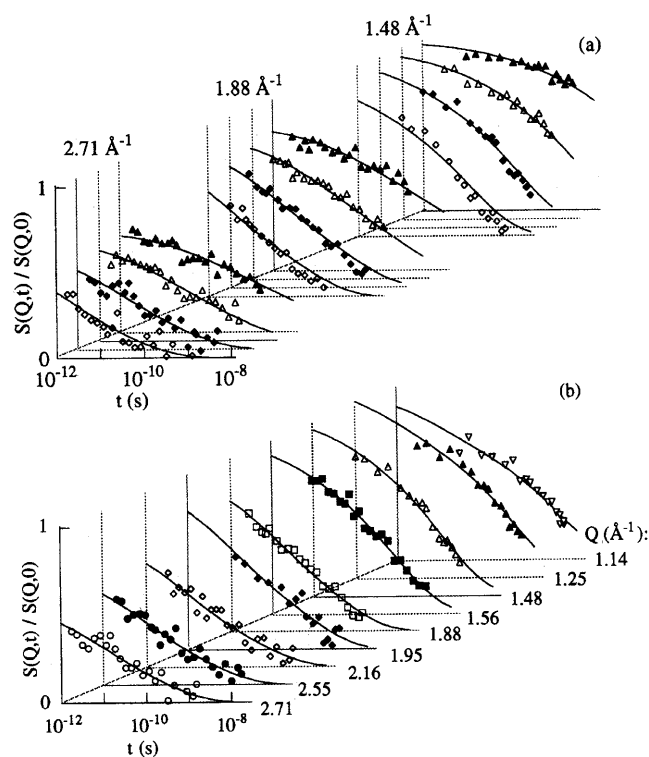


Figure 4. (a) NSE spectra of 1,4-polybutadiene for the q -values indicated at 220 K (\blacktriangle), 240 K (\triangle), 260 K (\blacklozenge), and 280 K (\diamond), (b) at 260 K for the q -values indicated. The solid curves are fitting curves obtained with the convolution model based on equation (15). (Reprinted with permission from [74]. Copyright (1996) by the American Physical Society.)

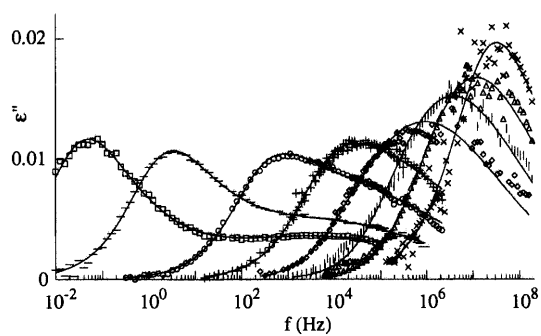


Figure 5. Dielectric loss curves obtained for 1,4-polybutadiene at 175 K (\square), 180 K ($-$), 190 K (\circ), 200 K ($+$), 210 K (\diamond), 220 K (l), 230 K (\triangle), and 240 K (\times). The solid curves are fits with the convolution model. (Reprinted with permission from [74]. Copyright (1996) by the American Physical Society.)

5. Vibrations: 'boson peak'

The first evidence that the vibrational properties of glasses are distinctively different from those of crystalline materials were found by measurements of the thermal conductivity and specific

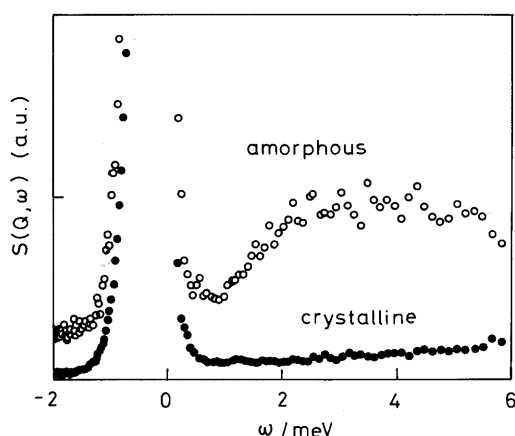


Figure 6. Inelastic neutron scattering spectra $S(q, \omega) \sim g(\omega)/\omega^2$ for the amorphous and crystalline phases of polyethylene. The spectra were calculated from two experiments at 10 K on polyethylene with 46 and 96% crystallinity. (Reprinted from [85]. 'Low-energy excitations in polyethylene: comparison between amorphous and crystalline phases', pp 334–338. Copyright (1988), with permission from Elsevier.)

heat of amorphous materials [80]. These show a clear excess compared to their crystalline counterparts. While for crystals the power laws $\kappa \propto T^3$ and $c_p \propto T^3$ expected from the Debye model are obeyed well at low temperatures, glasses show positive deviations at about 10–20 K. (There are even stronger deviations below 1 K. The reason for these is clearly identified: tunnelling states [81, 82].)

The origin of this behaviour was found by means of Raman light scattering [83] and inelastic neutron scattering [84] in an anomaly of the vibrational DOS. Glasses show a peak in the representation $g(\omega)/\omega^2$ around $\hbar\omega = 1\text{--}4$ meV which is expected to be a constant for low energies in the Debye model. The neutron and Raman spectra follow the scaling with the Bose factor over a large range of low temperatures. This led to the somewhat awkward naming of 'bp' which has been adopted in a large part of the glass scientists' community. The Bose scaling property led to the conclusion that low-lying vibrational modes are the origin of the bp. (It has to be noted that the maximum of the bp usually corresponds to optical wavenumbers of $10\text{--}30\text{ cm}^{-1}$ which are considerably lower than for usual molecular vibrations.)

Shortly after the discovery of the bp in anorganic network glasses it was shown to exist in glassy polymers too. A comparison of semicrystalline and highly crystalline polyethylene showed that the amorphous part gives rise to a bp at about 4 meV while the crystalline fraction only shows a flat $g(\omega)/\omega^2$ in the same range [85] (figure 6). This result was later confirmed for several different amorphous polymers [86].

Hitherto, there is no complete theory of this peculiarity in the density of vibrational states of glasses. There is an ongoing widespread debate on the origin of the bp and here only a few aspects can be presented.

For only one material the microscopic mechanism of motion underlying the bp could be unambiguously identified, amorphous SiO_2 . For this anorganic network glass, coherent inelastic neutron scattering experiments [87] showed that coupled librations of the corner-connected SiO_4 tetrahedra make up for the difference between bp and pure sound waves.

In all other cases the picture derived from inelastic neutron scattering is more vague, namely that of in-phase motion of string-like groups of atoms [88]. This picture is supported by computer simulation using model potentials [89, 90] as well as 'realistic' potentials, e.g. for selenium [91]. It can also be intuitively understood that the low frequencies of the bp vibrations

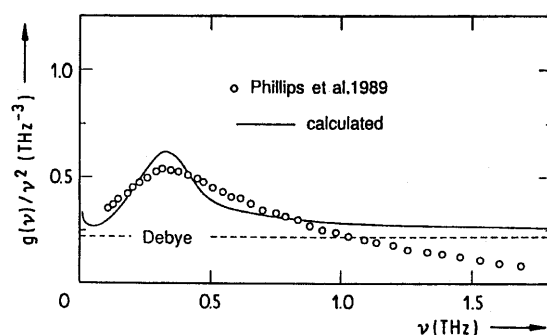


Figure 7. Comparison of the vibrational DOS calculated from the soft-potential model [94] to data from inelastic neutron scattering [93] for selenium. (Adapted with permission from [94].)

require small spring constants. These in turn can only be attained for motions which do not lead to a strong stretching of interatomic bonds. This condition immediately suggests a chain-like nature of the motion.

As stated above, there is no generally accepted theory of the bp. Nevertheless, one can distinguish two approaches to the problem, the soft-potential model and models based on the disorder of force constants. While the former assumes the existence of local modes interacting with sound waves, the latter regard the boson peak as a result of the disorder of the force constants between the atoms of an amorphous material. It is currently difficult to say whether at some point there will be a crucial experiment to decide between them or whether there will be a reconciliation of the two views.

The variants of the soft-potential model [92] start by assuming the existence of modes containing a strong fourth-order contribution in their potential

$$V(x) = W(D_1x + D_2x^2 + x^4). \quad (16)$$

Here, x is the normal coordinate of the mode, W , D_1 , and D_2 the parameters specifying the potential. For different choices of these parameters the potential may be of single-well or double-well type, symmetric or asymmetric. While the parameter W is usually assumed to be constant, for D_1 and D_2 distributions are assumed which result from the disorder of the glassy material.

The strength of the soft-potential model is that it allows the description of the low-temperature tunnelling phenomena and the bp region on the same assumptions. It is possible to derive a numerical expression for the DOS which can be compared to experimental results from inelastic neutron scattering [94, 95]. Figure 7 shows a comparison for selenium where parameters derived from the tunnelling region were used to predict the DOS without further parameters.

The soft-potential model also allows an estimate of the number of atoms partaking in a vibrational mode [96]. Depending on the material-specific parameters, it lies in the range 10–100. These values agree with simulation results (e.g. [91]) as well as a model-free determination from the wavevector dependence of inelastic neutron scattering [97]. There a mode of about six monomers (96 atoms) was calculated for polystyrene.

The second approach explains the vibrational anomalies in amorphous materials on the basis of the fluctuations of the elastic constants in such materials. Numerical calculations of such models are usually based on randomly changing the force constants of a crystalline lattice. (The fact that this change alone is able to produce a bp is in agreement with experiments where the presence of orientational disorder in the orientational glass phase of methanol is sufficient to create a bp [98].) The vibrational DOS resulting from diagonalization of the matrix of force

constants can be well described in terms of the coherent potential approximation (CPA) [99]. The CPA in turn is able to describe the DOS obtained from numerical simulation of Lennard-Jones glasses [100]. Although a comparison with experimental data has not yet been attempted it can be expected that the CPA will work there as well. In a very recent development the MCT (see section 2) was also able to describe the bp [101]. Since this theory needs the structure factor $S(q)$ as an input it can currently only be applied to simple systems, e.g. Lennard-Jones potential glasses, and no comparison with experiments is possible.

The reader may ask why these low-temperature vibrational properties are considered so important and whether they have any relevance to the technologically relevant properties of glasses at room temperature. The first indications that this is the case came from systematic correlation of inelastic neutron and Raman light scattering spectra with the fragility (see section 2) of the materials [102]. The qualitative result was that the more the temperature dependence of the α relaxation deviates from the Arrhenius relation (i.e. the more ‘fragile’ the glass is), the less pronounced is the bp. In this first study it was still thought necessary to relate the bp intensity to a quantity at T_g : in [102] the ratio R between the height of the bp and the minimum between bp and elastic line was calculated from spectra at T_g . At that temperature the scattering at the minimum position contains mainly quasielastic intensity from the ‘fp’ (section 6). So R was interpreted as a relaxation/vibration ratio. Later [103] it was shown that the ratio of excess DOS and the Debye value also shows this correlation. A similar correlation was found for the position of bp in a series of 1,2–1,4-polybutadienes [104]. This means that vibrational quantities obtained at temperatures far below T_g are linked in some way to the glass transition properties. A relation between the bp and the α relaxation is also indicated by the striking similarity between the clusters of the low-energy modes mentioned above and those of the mobile particles close to the α relaxation (compare figures in [91] and [58]). There is no theoretical concept of that linkage except for a few attempts based on mode-coupling theories [105] and energy-landscape pictures [106]. Nevertheless, it seems to be a well-established experimental fact which has to be taken into account in any future theory of glass-forming materials.

6. ‘Fast process’

The characteristic scaling of the inelastic neutron scattering spectra with the Bose factor breaks down above a certain temperature (often called T_x) [107] as figure 8 shows with an example. At higher temperatures additional scattering occurs between the bp and the elastic line. At the same temperature the mean square displacement of atoms begins to increase more strongly than the linear relation $\langle u^2 \rangle \propto T$ expected for harmonic vibrations [108].

The origin of this change in the spectrum, often called vaguely ‘fp’ in order to avoid any prejudice regarding the theoretical explanation, is highly debated. Here the conflicting views will be reported briefly.

Because the spectral features occur so close to the elastic line it is difficult to tell whether they are quasielastic (which would suggest a relaxation as origin) or inelastic (favouring an interpretation as overdamped vibrations). Only in the case of polyisobutylene it was found unambiguously inelastic: at temperatures where the Bose scaling already fails the bp is still separated from the elastic line by a minimum [111].

Nevertheless, most theoretical attempts to explain the fp prefer a combination of relaxation possibly combined with a softening of the bp modes as the origin. Among these the MCT is the most developed [17]. In MCT the fp is *the* β relaxation. (This nomenclature stands in contrast with that of most experimentalists who use this name for the slower relaxation discussed in section 3. Therefore, it will be called β_{fast} to distinguish it in the following.)

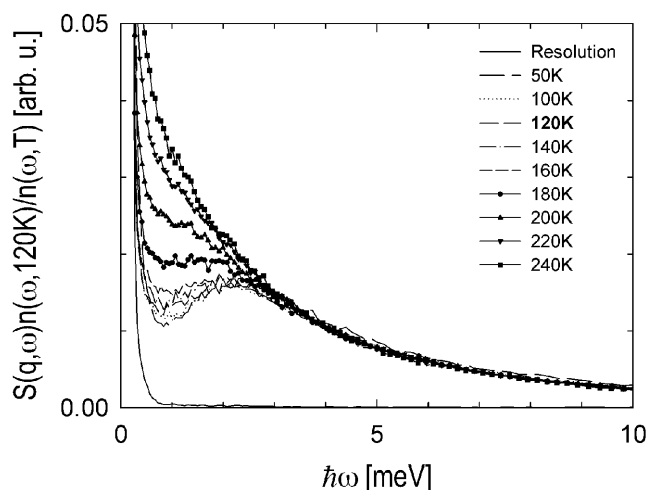


Figure 8. Incoherent inelastic neutron scattering spectra ($q = 2.2 \text{ \AA}^{-1}$) of 1,4-polybutadiene scaled by the Bose occupation factor $n(\omega, T) = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ to a reference temperature of 120 K. Plain curve: resolution function; other curves: temperatures 20–240 K as listed in the figure. It can be seen that for low temperatures the spectra superimpose while at higher temperatures there is an increasing component close to the elastic line [109].

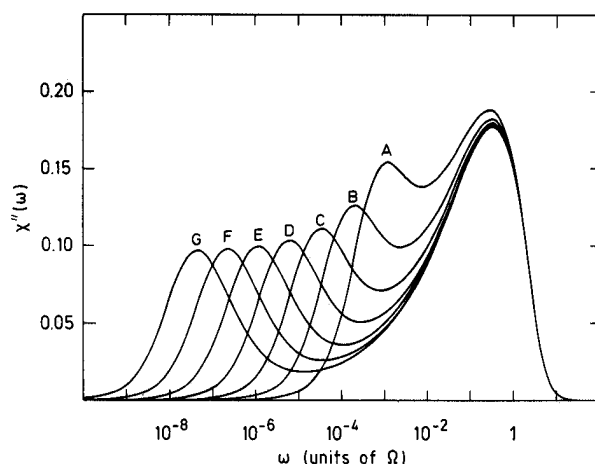


Figure 9. The mode-coupling calculation of the susceptibility in the simplest so-called F_{12} model. The labels A–G correspond to separation parameters $\sigma = -0.2/2^n, n = 0, \dots, 6$. σ is proportional to $\epsilon = (T_c - T)/T_c$ used in the text but the proportionality constant cannot be fixed within this schematic model. (Reprinted with permission from [110].)

According to MCT it is a universal feature occurring in any glass former and deeply related to the α relaxation.

Figure 9 shows a calculation of the susceptibility in the simplest version (the F_{12} -model) of MCT which is able to describe the essential features of the glass transition. In this plot the β_{fast} relaxation is the feature which starts to extend the low-frequency wing of the vibrational peak which is present at all temperatures. In figure 10 for comparison the coherent inelastic

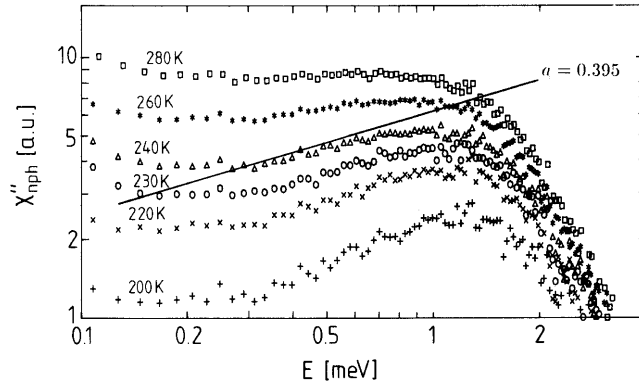


Figure 10. A double-logarithmic plot of the susceptibility of 1,4-polybutadiene for temperatures 200–280 K at the wavevector $q = 1.48 \text{ \AA}^{-1}$. The line indicates the maximal slope $a = 0.395$ consistent with MCT which should describe the asymptotic slope of the susceptibility as well as the shift of the minimum in a log/log plot. (Reprinted from [112]. Copyright (1993), with permission from Elsevier.)

neutron scattering spectra of 1,4-polybutadiene are shown converted to a susceptibility via

$$\chi''_q(\omega) = \omega S(q, \omega). \quad (17)$$

Here it is assumed that the majority of vibrations at low temperature (bp) are not those relevant for MCT. Therefore this part of the spectra was subtracted. Nevertheless, the picture with inclusion of the bp does not look qualitatively different. It can be seen that the emerging extra intensity behaves qualitatively similarly to the result of the schematic model shown in figure 9.

One of the quantitative predictions of MCT is that the relaxations (α and β_{fast}) behave asymptotically as power laws with exponents related by

$$\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \lambda = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \quad \gamma = \frac{1}{2a} + \frac{1}{2b},$$

with $1/2 < \lambda \leq 1$. Here, a is the exponent which relates to the β_{fast} relaxation while b and γ determine the α relaxation discussed in section 2 (equations (8) and (10) respectively). Note that the equations impose the restriction $0 < a < 0.395 \dots$. From figure 10 one can see that a power law $\chi''(\omega) \sim \omega^a$ can be found but it seems that the limit on a is exceeded. This result is also found by means of light scattering for various materials, e.g. polypropyleneglycol [113].

A further prediction of MCT concerns the shift of the minimum in the susceptibility which is visible in figures 9 and 10 close to the resolution limit of $\hbar\omega = 0.1 \text{ meV}$:

$$\omega_{\text{min}} \sim |\epsilon|^{1/2a} \quad (18)$$

$$\chi''_{\text{min}} \sim |\epsilon|^{1/2} \quad (19)$$

where $\epsilon = (T_c - T)/T_c$ is the normalized distance from the critical temperature of MCT. Similarly to the case for expression (11), the exponent $1/2$ in (19) is universal while (18) contains the material-dependent parameter a . To investigate the scaling prediction for χ''_{min} the squares of the minima of the susceptibility have been plotted versus temperature in figure 11. Those should be proportional to $|\epsilon|$ and thus form straight lines intersecting the T -axis at T_c . One can see that linearity is fulfilled only in the range $220 \text{ K} \leq T \leq 250\text{--}260 \text{ K}$ with $T_c \approx 213 \text{ K}$. The deviation for large T can be explained by a breakdown of the validity of the asymptotic laws. On the other hand, also close to $T = T_c$, χ''_{min} does not completely drop to zero as predicted by equation (19). This is again an indication of the necessity of an extended formulation of MCT [44] including ‘hopping’ processes.

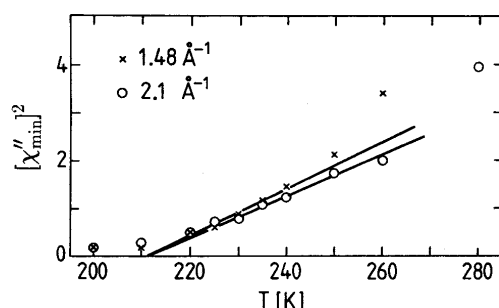


Figure 11. The temperature dependence of the square of the minimum in the dynamic susceptibility χ''_{\min} of 1,4-polybutadiene for $q = 1.48$ and 2.1 \AA^{-1} . (Reprinted from [112]. Copyright (1993), with permission from Elsevier.)

The scaling law (18) for ω_{\min} cannot be fulfilled at all with an exponent a allowed by MCT. This becomes immediately clear from the susceptibility data (figure 10): the minima shift much *less* than indicated by the $a = 0.395$ line.

In the framework of the CM (see section 2) the fp is the initial part of expression (4). In the early development of the CM, no direct experimental evidence of this fast Debye relaxation could be found. Because the crossover time t_c is of the order of a picosecond, classical relaxation methods were not able to access it. It took about a decade until the fp was found and identified as interpretable as the CM fast relaxation by means of neutron scattering [114] and high-frequency dynamic conductivity measurements [115].

Figure 12 shows data from inelastic neutron scattering interpreted according to the CM. Firstly, the data which are originally $\tilde{S}(q, \omega)$ from a time-of-flight spectrometer were Fourier transformed into the time domain. Then it was assumed that they are a convolution of three parts: a relaxational contribution (the object of the CM), a vibrational spectrum (bp), and the instrumental resolution. From the convolution theorem it follows that then the functions in the time domain are a product:

$$\tilde{S}(q, t) = S_{\text{rel}}(q, t)S_{\text{vib}}(q, t)R(q, t). \quad (20)$$

While the last contribution enters undoubtedly by convolution, the convolution of the vibrational and relaxational part assumes their unrelatedness [4]. Because $R(q, \omega)$ can be obtained experimentally and $S_{\text{vib}}(q, \omega)$ by extrapolation using the Bose statistics, it is possible to calculate $S_{\text{rel}}(q, t)$ in this framework [116]. As the fits in figure 12 show, expression (4) describes the relaxation perfectly. But it has to be noted that it cannot be considered an *explanation* of the fp because there is no microscopic theory behind it as is the case for MCT.

Nevertheless, a microscopic picture was supplied for polymers later [117]. It was found that the onset temperature T_x of the fp correlates clearly with the C–C rotation torsional barrier. From this it is concluded that the elementary mechanism of the fp is just the jump over this barrier. But one has to consider that the fp is a universal phenomenon also present e.g. in glass-forming salt melts which cannot exhibit any mechanism even similar to a C–C rotation. Although the authors of [117] address this question it remains ultimately unclear what the counterpart of the C–C rotation could be in these cases.

One of the few approaches not interpreting the fp as a pure relaxational phenomenon is the vibration relaxation model (VRM) [114, 118]. This model is an extension of the soft-potential model mentioned in section 5. In the VRM the single-well potentials resulting from expression (16) for certain parameter combinations are seen as the source of vibrations while the double-well potentials give rise to a combination of vibration in the minima and over-the-

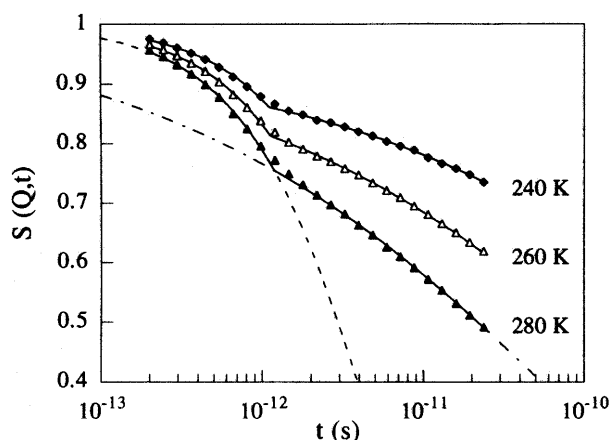


Figure 12. $S_{\text{rel}}(q, t)$ for 1,4-polybutadiene at $q = 1.4 \text{ \AA}^{-1}$. The curves through the points are fits according to the CM expression (4). (Reprinted with permission from [114]. Copyright (1995) by the American Physical Society.)

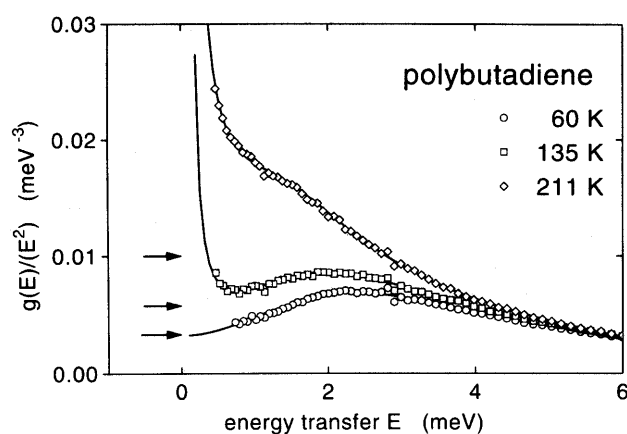


Figure 13. Fits by the VRM to inelastic neutron scattering spectra of 1,4-polybutadiene. The spectra have been converted to a pseudo-vibrational DOS by applying the relation between $g(\omega)$ and $S(q, \omega)$ not considering whether the spectra do indeed contain only vibrations. The plotted quantity $g(\omega)/\omega^2$ is approximately proportional to $S(q, \omega)$. The arrows indicate the contribution of sound waves to the DOS. (Reprinted with permission from [114]. Copyright (1995) by the American Physical Society.)

barrier relaxations. The dynamic structure factor can be calculated in this model by integrating over the distribution of parameters. Figure 13 shows fits of $S(q, \omega)$ from inelastic neutron scattering for 1,4-polybutadiene [114]. The VRM was subsequently successfully applied to several polymeric systems [119, 120].

A weak point of the VRM may be that it needs four parameters for the description of a neutron spectrum: density of eigenvalues of the force matrix, sound velocity, bp position, and phonon damping coefficient. But it has to be noted that the sound velocity can be obtained by independent measurements and the phonon damping compared to estimates based on the mean square amplitude of vibrations [114]. In this way a more stringent check of the model is possible than just by a free fit of all parameters. Another drawback of the model is that

it fails for the combination of high temperatures and long times whereas e.g. the Kohlrausch expression is often valid up to the complete decay of the relaxation function $\Phi(t) \rightarrow 0$. The reason for this intrinsic limitation of the VRM is that it only includes the ‘elementary step’ of the structural relaxation, a hopping between two potential minima, but not a true flow which would be necessary for describing the α relaxation.

Recently, coherent inelastic neutron scattering has also been deployed to investigate the nature of the fp. This technique should be able to detect on which length scale a molecular motion is in phase. But the results are still contradictory: while measurements on 1,4-polybutadiene [121] indicate mostly sound-wave-like extended motions, a study on polymethylmethacrylate let the authors conclude on a length scale of ≈ 7 Å, about two monomeric units [122].

7. Summary

Glass-forming polymers show a large variety of dynamical phenomena on widespread timescales which are mostly not well understood. In particular, the α relaxation which is the dynamics most characteristic for glass formation cannot be explained completely by current theories. The most developed approach is that of the MCT [17] extending the theory of the *liquid* state towards lower temperatures. Despite its success at temperatures significantly higher than T_g , the empirical glass ‘transition’ temperature, it needs additional uncontrolled assumptions about thermally activated processes at lower temperatures to sustain its validity. On the other hand, approaches from the disordered solid such as the soft-potential model or the VRM [118] fail towards higher temperatures. Therefore, it is correct to say that there is currently no valid theory with predictive strength close to T_g which—at least from the empirical point of view—is the distinctive temperature range of glass-forming polymers.

Similarly unexplained remains the region of fast (picosecond) dynamics. There is currently no generally accepted theory on the low-frequency vibrations (so-called bp) which are a feature distinguishing between glassy and crystalline polymers. The development of a fast relaxational component at a slightly slower timescale can be derived from MCT, but also competing models (VRM, CM [19]) include this feature. An open question is how the empirical relation between these fast processes and the much slower α relaxation can be explained, e.g. on the grounds of differences in the intermolecular potential or the potential energy surface.

The only dynamical phenomenon which is quite well understood are (surprisingly) the secondary relaxations, e.g. the β relaxation. Here, the experiments clearly support a picture of a local relaxation which has a distributed activation energy due to a disorder in the environment [72, 73]. In some cases the underlying molecular motion can even be identified. This model is quite similar to that for polymer side-group relaxations [8]. Here, the only open question may be why the β relaxation is such a general phenomenon occurring in nearly all glass formers. This fact may point to an interpretation of the β relaxation as a necessary precursor of the α relaxation.

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