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A mode-coupling theory catastrophe scenario description of relaxations in semicrystalline nylons

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Abstract. In the conception of mode-coupling theory the liquid–glass transition is due to topological singularities (mathematical catastrophes) in a system’s parameter space. It is shown that previously published dielectric relaxation data for a number of semicrystalline polymers (polyalanine, polyglycine, nylon 3 and nylon 4) exhibit the characteristic signatures for an A_4 -singularity: inflection points, linear regions in $\ln(\omega)$, $1/f$ noise regions, as well as a double minimum. Besides agreeing qualitatively with mode-coupling theory predictions, the data can also be described quantitatively with the A_4 -scenario.

1. Introduction

During the past decade, the mode-coupling theory (MCT) of supercooled liquid dynamics [1, 2] has evolved as a powerful theoretical tool for the study of the liquid–glass transition. MCT is not only able to account for various time-honoured experimental results (like the Kohlrausch–Williams–Watts stretched exponential [3, 4], the Curie–von Schweidler law [5], or the Cole–Cole relaxation function [6]), but its highly non-trivial and empirically non-obvious predictions have inspired a whole new set of experiments and instilled vigorous activity in this long-researched area of condensed matter physics [7, 8]. Indeed, MCT offers a new conceptual framework for a field in which empirical curve-fitting reigned supreme for almost a century and a half.

From the very beginning, mode-coupling models for the liquid–glass transition were controversial and the early simplified versions elicited much criticism, with the debate carried on mainly by theorists [9, 10]. While there is substantial experimental support for the most counter-intuitive predictions for the type B transition in the so-called F_{12} -model of MCT from neutron and light scattering experiments in several materials [11–18], MCT is still the centre of much controversy, with the attention shifting to experiments [19–23]. Although the basic MCT equation can be derived from first principles for simple liquids (i.e. monatomic fluids), theoretical results have been compared against relaxation data from more complicated systems such as molecular liquids and amorphous, as well as semicrystalline, polymers. While a basic assumption of the model, such as ‘monatomic liquid’ seems to be flagrantly violated, the solution of the MCT equation entails a number of assumptions whose dependence on (and sole derivability from) this simplifying assumption is not at all clear. This brings to the fore a number of interesting questions pertaining to the validity of various assumptions of MCT and the range of applicability of its results. Moreover, the questions are moving targets since the theory is still evolving, and new questions continue to arise.

A key new idea introduced by MCT is that the universally observed features of the glass transition are due to topological singularities (mathematical catastrophes [24, 25]) in a system's parameter space. Close to a singularity, a system's behaviour is governed solely by the generic topological features of the singularity and is largely independent of its microscopic make-up. The simplest types of mathematical catastrophe are of the cuspid type, and can describe relaxation spectra in materials as diverse as molecular and ionic glasses (A_2 -singularity or Whitney fold) [1, 2], spin glasses (A_3 -singularity or Whitney cusp) [26], and amorphous as well as semicrystalline polymers (A_3 -, A_4 -cuspid) [27, 28]. Such a breadth of applicability for MCT results raises the prospect for a unified approach to the immensely diverse field of relaxations in disordered systems.

It was suggested by Johari [29] that the notion of amorphous or disordered state be extended from the classic random network (Zachariasen-type) and randomly packed spheres (Bernal-type) materials, to encompass orientationally disordered crystals, liquid-crystalline polymers, and even semicrystalline materials made of crystallites embedded in an amorphous matrix. While Johari's challenge has been partially picked up in the fields of orientationally disordered crystals and liquid-crystalline polymers, until the advent of MCT there had been little progress in the theoretical description of relaxations in semicrystalline materials, and new insights were wanting. The applicability of MCT results to semicrystalline polymers is quite controversial, and previous publications on this subject [27, 28] bring only plausibility arguments in favour of MCT catastrophe scenarios. Questions concerning the microscopic justification for the observed behaviour and the applicability of a model derived initially for monatomic structureless liquids to complex systems such as polymers and, moreover, to heterogeneous systems such as semicrystalline materials, were left largely unanswered. At the present stage in the development of the theory some of these questions are probably intractable, and the analysis of experimental data exhibiting the predicted patterns in a variety of materials ought to shed more light on the problem and provide guidance for the construction of new theoretical models. In as far as MCT results represent universal features of the ubiquitous glass transition, the fact that they were derived with the simplest possible models does not represent a major objection to their wider applicability, and should therefore not impede the search for the predicted behaviour in experimental data.

It is the purpose of this paper to bring additional support for a catastrophe scenario description of relaxations in disordered systems. As we shall see, the MCT description can account for features in data which have no other analytical description. Moreover, MCT-inspired analyses require fewer parameters than any of the popular fitting functions in cases where data can also be described with empirical formulae. It will be shown that previously published dielectric relaxation data on a series of semicrystalline nylons [30] are consistent with the A_4 -singularity scenario of MCT and that the catastrophe scenario offers a coherent picture for relaxation in these complex systems. While this will not answer any of the previously mentioned questions, it will nevertheless increase the plausibility of the MCT scenarios. The analysis presented here can also contribute to the formation of classes of materials according to the mathematical singularities exhibited by their spectra, and this should help in understanding their microscopic underpinnings and offer clues for theoretical model building.

2. Catastrophe scenarios in MCT

The relaxation spectra in glassy systems can be described as bifurcation singularities [24, 25] of the cuspid type A_k ($k = 2, 3, 4, \dots$) [1, 2, 26, 27, 28]. Higher-order singularities A_k contain lower-order singularities A_j ($j < k$) as special limits, and the lower-order relaxation

patterns are distorted due to higher-order precursors. The various singularities exhibit distinct signatures in susceptibility spectra $\epsilon''(\omega)$, through which they can be identified.

In the simplest case, for the schematic (i.e. ignoring all wave-vector contributions to the relaxation term of the memory function, except those from a thin spherical shell close to the peak of the static structure factor) and simplified (or ‘idealized’, that is, not including phonon-assisted hopping effects) model (often mislabelled as ‘the’ mode-coupling theory), the catastrophes are an A_2 -fold or a degenerate A_3 -singularity. At high temperatures ($T > T_c$, with T_c the MCT critical temperature) the theory predicts a white-noise spectrum ($\epsilon'' \sim \omega + 1$) on the low-frequency side of the primary (or α -) relaxation peak and the Curie–von Schweidler law ($\epsilon'' \sim \omega^{-b}$) on its high-frequency side, followed by a power-law ($\epsilon'' \sim \omega^{+a}$) characteristic for the secondary (or β -) relaxation [1, 2]. The value of T_c is not predicted by theory, but has been determined experimentally to be situated 30 K to 60 K above the calorimetric glass transition temperature T_g , and is material dependent. The exponents a and b are not independent; they are uniquely determined by the so-called exponent parameter λ . The two power laws with exponents a and b give rise to a susceptibility minimum at some frequency ω^* , where the spectrum amplitude $\epsilon''(\omega^*; T) = \epsilon''_{\min}$ is predicted to follow a square-root dependence on temperature difference. These signatures can be summarized as follows:

$$\frac{\epsilon''(\omega_s)}{\epsilon''_{\min}} = \frac{1}{a+b} [a\omega_s^{-b} + b\omega_s^a] \quad (1)$$

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

$$\epsilon''_{\min} \propto \sqrt{|T - T_c|} \quad (3)$$

with $\omega_s = \omega/\omega^*$ a scaled frequency and Γ the gamma function. Equation (1) is a convenient interpolation formula for experimental data and indicates that, in the α – β crossover region, spectra corresponding to different temperatures close to T_c will fall on a master curve. At low temperatures ($T < T_c$) the α -peak and the Curie–von Schweidler law in its high-frequency wing disappear. There exists only a white-noise spectrum ($\epsilon'' \sim \omega^{+1}$), followed by the β -relaxation power law ($\epsilon'' \sim \omega^{+a}$). These power laws will yield a ‘knee’ (i.e. break in slope) for $\epsilon''(\omega)$ at some frequency ω^* , with the corresponding susceptibility spectrum value $\epsilon''(\omega^*; T)$ still obeying equation (3). For the extended MCT model (which includes phonon-assisted hopping effects) [31], the minimum persists into the glassy region, and the functional behaviour of the susceptibility spectra becomes more complicated.

In the case of higher-order singularities A_k ($k > 2$), MCT yields a universal description of susceptibilities in terms of elliptic functions [27, 28]:

$$\epsilon = f_c - \epsilon_c p \left[\ln \left(\frac{1}{\omega t_m} \right) \right] \quad (4a)$$

$$\epsilon'' = -\frac{\pi}{2} \epsilon_c p' \left[\ln \left(\frac{1}{\omega t_m} \right) \right]. \quad (4b)$$

Here f_c represents the non-ergodicity (or Edwards–Anderson) parameter on the critical surface which separates the liquid and glassy states in the parameter space of the system, ϵ_c is a critical amplitude and t_m is the microscopic time-scale for the short-time transient motion of the system. $p(u)$ is the inverse function of the elliptic integral:

$$u = \int_p^\infty \frac{ds}{\sqrt{S(s)}} \quad (5)$$

and $p'(u)$ its first derivative.

For an A_4 -singularity, the integrand has the form

$$S(u) = u^4 - g_2 u^2 - g_3 u - g_4. \quad (6)$$

The coefficients g_k are the so-called separation parameters, i.e. mathematical control parameters indicating the distance from the singularity, and represent the coupling constants of the theory. They can be mapped onto the physical control parameters of a system through a smooth non-linear transformation, which can be linearized in the vicinity of the singularities. The pattern which is unique for an A_4 -singularity is characterized by the existence of a horizontal inflection point on either side of the minimum situated at ω^* . Depending on a system's path in parameter space, the spectra can also exhibit linear variations of $\epsilon''(\omega)$ with $\ln(\omega)$, double minima or $1/f$ noise regions (characterized by a 'flat', i.e. frequency-independent spectrum). These patterns result from equations (4)–(6) in various limits [28].

3. Data analysis

Dielectric relaxation data were obtained through digitization of the original figures from an article by Wölfle and Stoll [30]. Log–log plots were used for most data, due to the wide range of variation for $\epsilon''(\omega)$ (almost three decades), for easy detection of the predicted power laws and in order to amplify any distortions of the A_2 -pattern. Semi-logarithmic plots (with linear ordinate) were used in cases where $\epsilon''(\omega)$ has an inflection point or a linear variation in $\log(\omega)$. The data were fitted to the various functional forms with the aid of a Levenberg–Marquardt non-linear least-squares algorithm. The various parameters were determined with relative errors ranging from 5 to 30%, depending mainly on the scatter in the experimental data.

The starting point of the analysis consists of isothermal susceptibility spectra $\epsilon''(\omega)$, covering frequency windows of 8 to 10 decades. As a first step one tries to identify the singularity scenario ($A_k, k \geq 2$) exhibited by the data, using characteristic signatures and asymptotic solutions for MCT models (usually over more limited frequency intervals). This can also yield preliminary values for the various parameters. Once an identification has been achieved, one can proceed with the second step and describe the data with the full solution for the MCT model at hand (numerical, if necessary, as was done in [32]), and in principle determine the path of the system in parameter space, i.e. the space of the separation parameters g_k . In practice the outlined procedure meets with varying degrees of success, depending on the complexity of the spectra. The main stumbling block is the need to provide good initial parameter guesses for the non-linear least-squares fitting algorithm. In the case of an A_2 -singularity starting values for the various parameters can be easily found by reading the values of the spectrum minimum ϵ''_{min} and the corresponding frequency ω_{min} off the curves, and by determining the power-law exponents a and b from linear fits of the high- and low-frequency sides of the spectra, respectively. Fits for the frequency dependence of the A_2 -spectra using the interpolation formula (1) (with or without the Γ -function constraint (2) for the exponents) are then straightforward. Initial guesses for parameters in the case of an A_4 -singularity are not so easily found. The existence of the shift factor t_m between the 'shape function' (i.e. the elliptic function) and the data, as well as the evaluation of the elliptic integral makes the non-linear fitting procedure particularly cumbersome. By using the property $p'(u) = -\sqrt{S(p(u))}$ of elliptic functions one can in part circumvent these difficulties. Instead of fitting both ϵ' and ϵ'' versus frequency, one can fit ϵ'' versus ϵ' , thus eliminating the need for calculating elliptic integrals and for knowing t_m during this stage of the analysis, and obtain $g_2, g_3, g_4, \epsilon_c$ and f_c . This procedure does not always work very

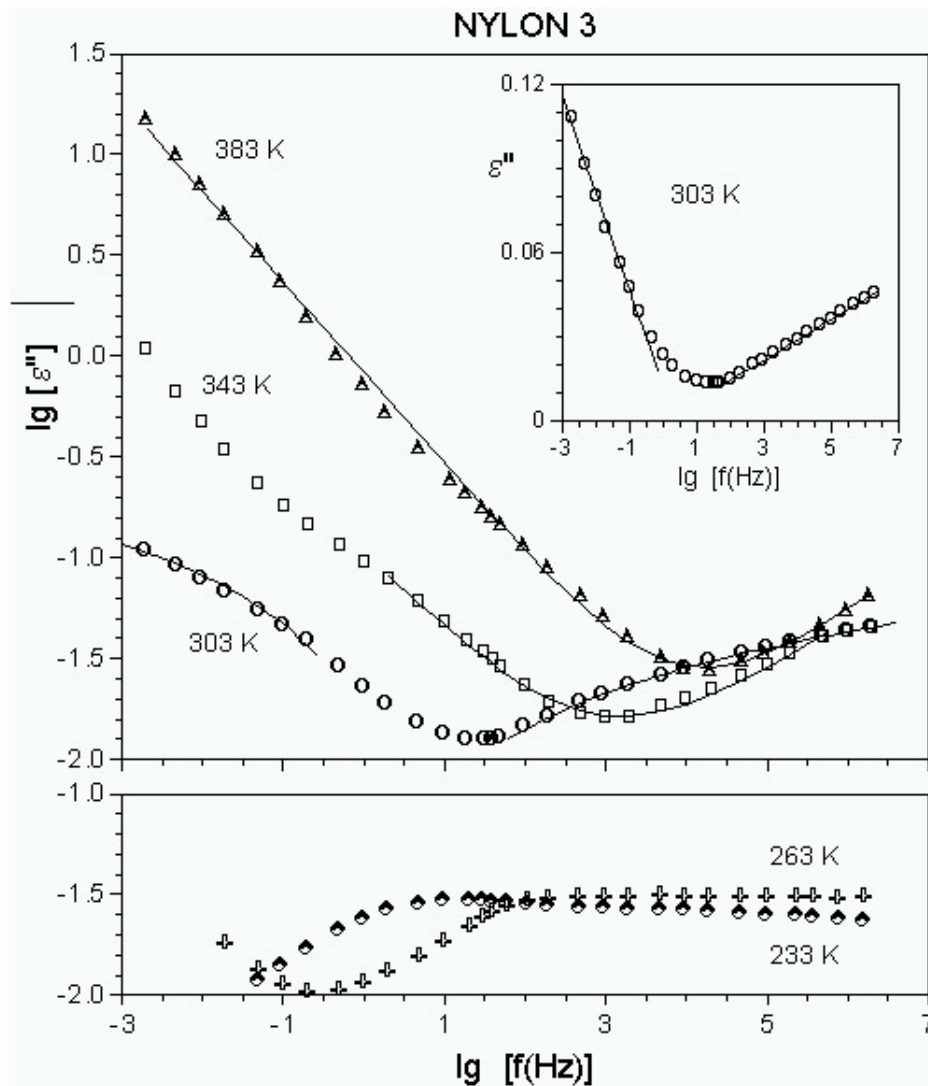


Figure 1. Dielectric loss spectra for nylon 3. The lines for the 383 K and 343 K data represent fits with equations (1) and (2), while the lines at 303 K constitute fits linear in $\log(f)$. At 263 K and 233 K one can observe well developed $1/f$ noise regions (frequency-independent spectra) covering 4–5 decades of frequency.

well, since errors in ϵ' can cause serious difficulties with the non-linear least-squares fitting algorithm. In [30] both ϵ'' and ϵ' versus frequency were displayed on log–log plots. While this data representation is well suited for ϵ'' (which varies by one to three orders of magnitude over the available experimental frequency window, depending on the temperature), it causes a significant loss of detail for ϵ' (which varies from almost constant at low temperatures to one order of magnitude at the highest temperatures, over the same experimental frequency window). Consequently, the digitization errors were larger for ϵ' than for ϵ'' . The double-logarithmic representation for ϵ'' and ϵ' represents a particular handicap for the analysis of ϵ'' -spectra which lack the hallmark signature of the A_4 -singularity (a minimum plus

an inflection point) or a double minimum. This is why only a qualitative analysis was possible for some of the data presented below. In cases where the spectra exhibit either a double minimum, or a minimum and an inflection point, one can find initial guesses for the parameters g_k , ϵ_c and f_c by solving a system of non-linear algebraic equations resulting from the ϵ' - and ϵ'' -values at the given special points and the respective extremum conditions. Once g_2 , g_3 and g_4 are determined, one calculates the elliptic integral (5) and finds the value of the time-scale t_m from a horizontal shift of $(u, \log(\sqrt{S(p)}))$ onto $(\log(f), \log(\epsilon''))$. This also provides a check for the previously determined value of ϵ_c . The value for f_c was checked in a similar fashion, by shifting (u, p) onto $(\log(f), \epsilon')$ on a semi-logarithmic plot.

In figure 1, the ϵ'' -spectra for nylon 3 ($T_g = 383$ K) display a continuous change from a slightly distorted A_2 -spectrum at 383 K (equations (1) and (2) still providing a fair fit over eight decades in frequency, with $a = 0.27$ and $b = 0.45$, or $\lambda = 0.81$), through a strongly distorted A_2 -spectrum but not exhibiting any clear A_4 -signature at 343 K (the data being still well described by equations (1) and (2) over a limited frequency range of five decades, with $a = 0.23$ and $b = 0.36$, or $\lambda = 0.87$), to a spectrum with linear regions in $\log(f)$ at 303 K and spectra with flat high-frequency regions at 263 K and 233 K. The lines for the data at 303 K (inset of figure 1) constitute fits linear in $\log(f)$ covering 2 and 4.5 decades, respectively at low and high frequencies. The $1/f$ noise regions at 263 K and 233 K exceed four decades in frequency, as is evident from the frequency-independent ('flat') spectra. As stated above, part of the data for nylon 3 can also be described by an A_2 -spectrum, but the overall evolution of the spectra for this material indicates a higher-order (A_4 -) singularity.

The ϵ'' -spectra for nylon 4 ($T_g = 353$ K), displayed in figure 2, are very similar to those for nylon 3. A fit with equations (1) and (2) accounts for the data over five decades in frequency at 383 K (solid line) with $a = 0.22$ and $b = 0.33$, corresponding to $\lambda = 0.88$. While at 383 K there is only a hint of distortion in the data, at 343 K it is quite pronounced. The lines at 343 K and 303 K represent linear fits in $\log(f)$, covering two to three decades, both at low and high frequencies. At the lowest temperatures (263 K and 233 K) one can observe once more a well developed $1/f$ noise region, extending over four to five decades in frequency. From these signatures one may again conclude that the spectra for this material are in qualitative agreement with the behaviour of A_4 -singularity spectra.

Dielectric relaxation data for polyglycine ($T_g = 403$ K) are shown in figure 3. At every temperature the ϵ'' -spectra exhibit an inflection point at low frequency, which represents the distinct signature of an A_4 -singularity. There is also a hint of a double minimum in the high-frequency end of the 337 K spectrum, although its existence is not certain. The solid lines represent fits with the A_4 -singularity formulae (4)–(6), with the following parameter values: (∇) $g_2 = 0.037$, $g_3 = 0.0082$, $g_4 = -0.0018$, $\epsilon_c = 1.23$, $f_c = 4.09$, $t_m = 1.2$ ns ($T = 395$ K); (\circ) $g_2 = 0.046$, $g_3 = 0.0057$, $g_4 = -0.0017$, $\epsilon_c = 1.05$, $f_c = 3.98$, $t_m = 9.8$ ns ($T = 369$ K); (\triangle) $g_2 = 0.023$, $g_3 = 0.046$, $g_4 = -0.00084$, $\epsilon_c = 1.33$, $f_c = 3.92$, $t_m = 42$ ns ($T = 337$ K). The A_4 -formulae can account for the data over six decades in frequency, which matches or exceeds the goodness-of-fit range of any of the popular empirical fitting functions. The A_4 -fits depart from the data for 1–2 decades at high frequencies.

In the case of dry polyalanine, fits with equations (1) and (2) (dotted lines) can describe the ϵ'' -spectra for 6–7 decades in frequency (figure 4), with power-law exponents $0.15 \leq a \leq 0.18$ and $0.20 \leq b \leq 0.22$ (corresponding to an exponent parameter $0.93 \leq \lambda \leq 0.95$). The height of the minimum, however, does not vary like the square-root of the absolute value of the temperature difference (as shown in the inset), ϵ''_{min} having a weaker than square-root dependence (figure 4 inset). The small number of data points does not permit the identification of a functional dependence for $\epsilon''_{min}(T)$ and it is not entirely

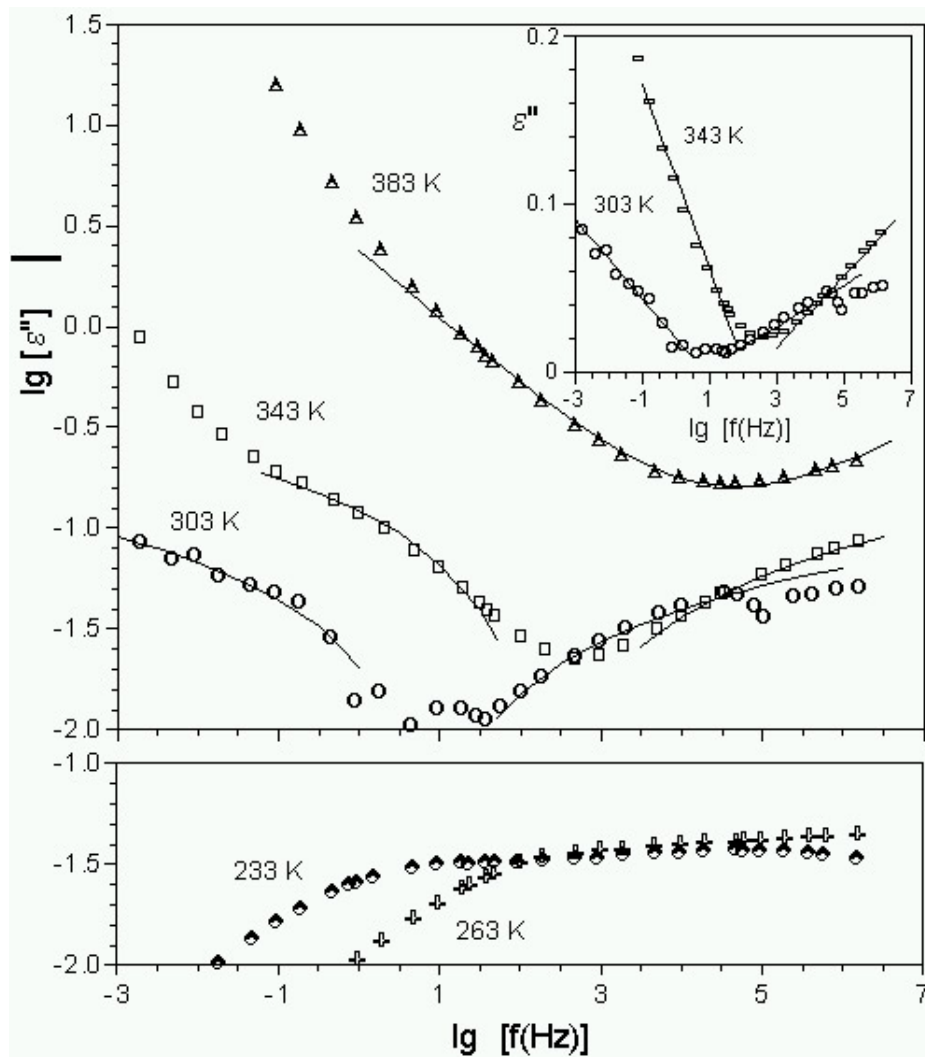


Figure 2. Dielectric loss spectra for nylon 4. The spectrum is already distorted at 383 K, and the fit with equations (1) and (2) is good only over 5–6 decades in frequency. Linear regions in $\lg(f)$ exist in both the 343 K and 303 K data. The $1/f$ noise regions ('flat' spectra), at 263 K and 233 K extend over 4–5 decades of frequency.

clear that the lack of $\sqrt{|\Delta T|}$ -dependence is due exclusively to the existence of a higher-order singularity. Typically, the A_2 -features have been observed to obtain for $T > T_g$. Equations (1) and (2) have been used here in a temperature interval for which they are 'not supposed to work'. Even with this caveat, the fact that the α - β crossover formula (1) with the Γ -function constraint (2) can account for the data over a frequency range which matches or exceeds the goodness-of-fit range for any of the widely used empirical fit formulae (Kohlrausch–Williams–Watts [3, 4], Cole–Cole [6], Cole–Davidson [33], or the generalization of the latter two, Havriliak–Negami [34]), is quite remarkable. A critic of the present analysis might argue that the frequency dependence for these spectra can also be accounted for by a superposition of empirical fit functions. However, a spectrum

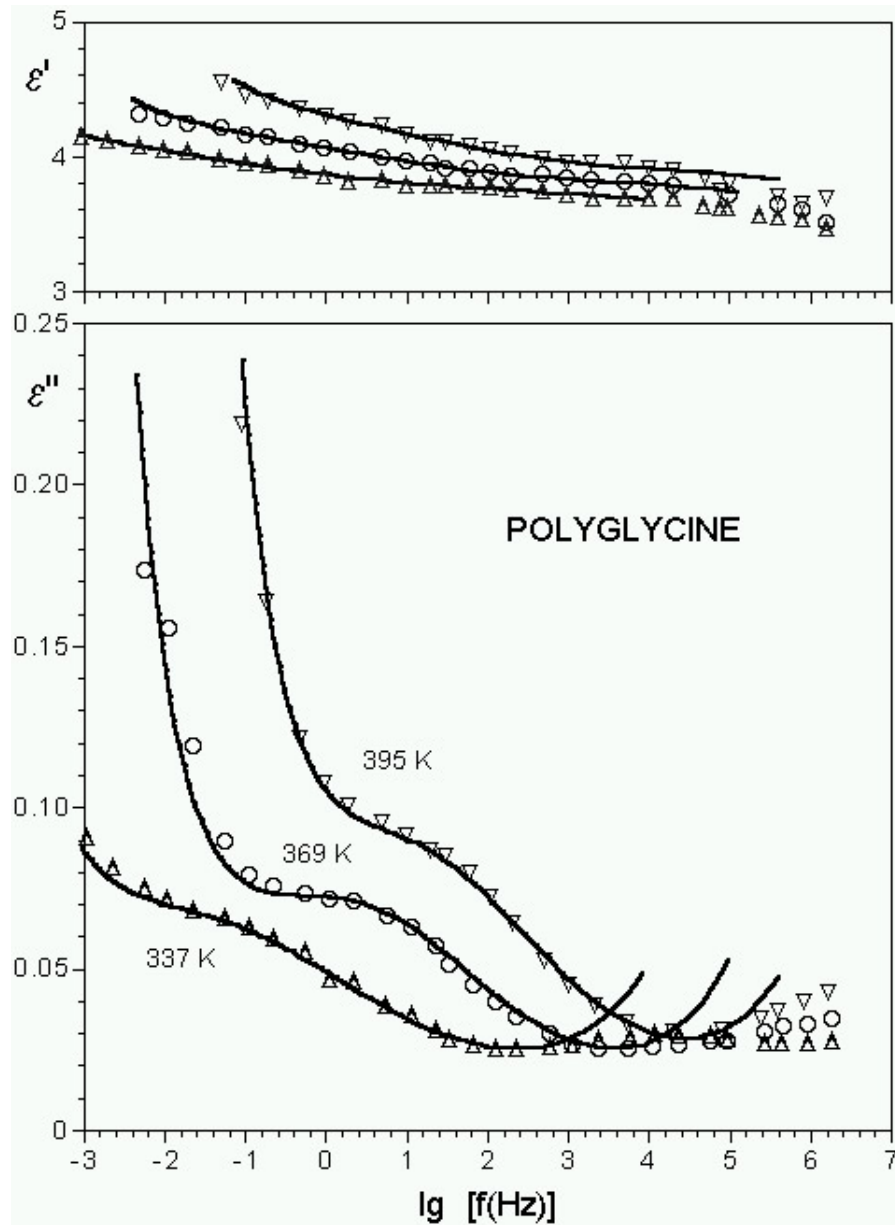


Figure 3. Dielectric relaxation data for polyglycine. All of the spectra exhibit an inflection point (at low frequencies), which is the most distinct signature of the A_4 -singularity. At 337 K there is a hint of double minimum in the data, which represents another A_4 -singularity signature. Solid lines are A_4 -fits with the following parameter values: (∇) $g_2 = 0.037$, $g_3 = 0.0082$, $g_4 = -0.0018$, $\epsilon_c = 1.23$, $f_c = 4.09$, $t_m = 1.2$ ns ($T = 395$ K); (\circ) $g_2 = 0.046$, $g_3 = 0.0057$, $g_4 = -0.0017$, $\epsilon_c = 1.05$, $f_c = 3.98$, $t_m = 9.8$ ns ($T = 369$ K); (\triangle) $g_2 = 0.023$, $g_3 = 0.046$, $g_4 = -0.00084$, $\epsilon_c = 1.33$, $f_c = 3.92$, $t_m = 42$ ns ($T = 337$ K).

which exhibits a minimum necessitates a linear combination of at least two empirical formulae, which will amount to six or more adjustable parameters, i.e. more than double

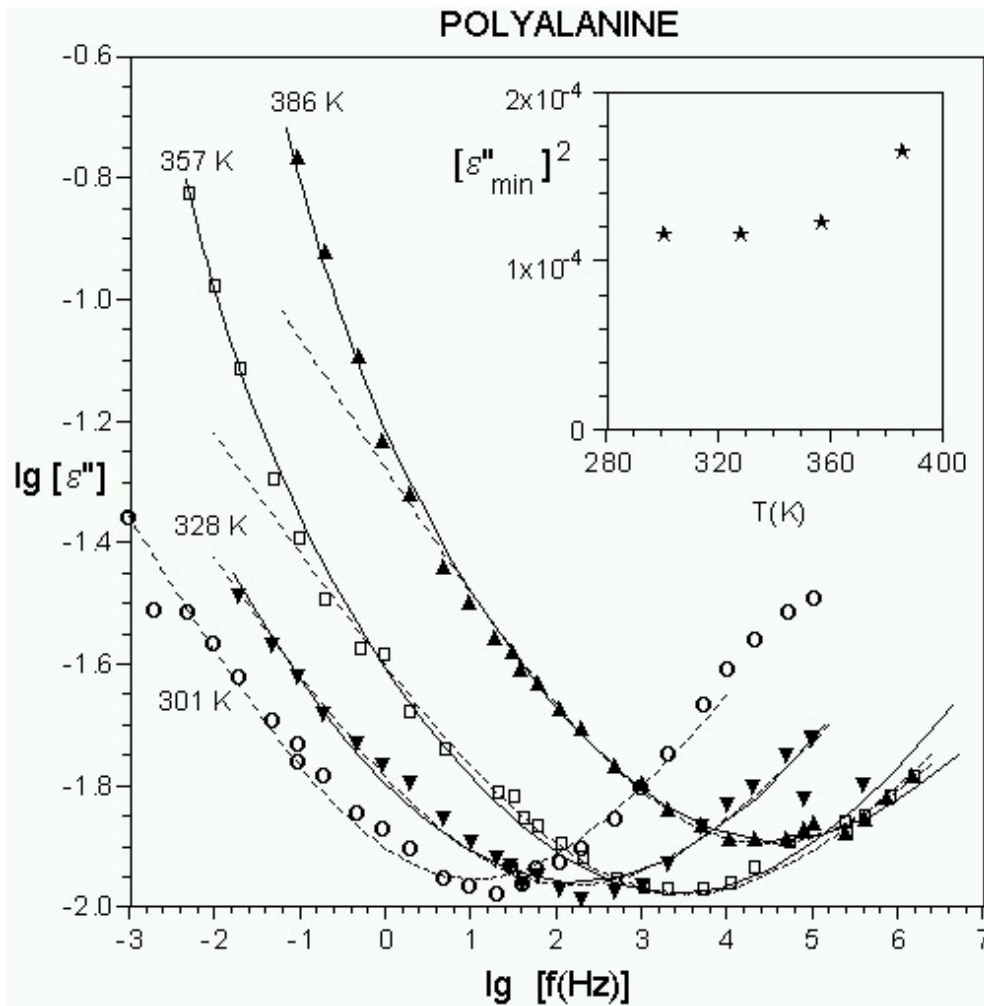


Figure 4. Dielectric loss spectra for dry polyalanine. The lines represent fits with equation (1), subject to the constraint of equation (2). $\sqrt{|\Delta T|}$ -dependence for the susceptibility minimum does not obtain, as shown in the inset. The solid lines represent A_4 -fits with parameters: (\blacktriangle) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 1.18$, $t_m = 160$ fs ($T = 386$ K); (\square) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 0.97$, $t_m = 2.2$ ps ($T = 357$ K); (\blacktriangledown) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 1.01$, $t_m = 34$ ps ($T = 328$ K).

the number required by a fit with equations (1) and (2). (Since the relaxation is stretched, a combination of two Debye relaxations—amounting to fewer parameters—will not do in the present case.) One might suggest that the breakdown of the square-root dependence for ϵ''_{min} could be due to hopping processes. It has been shown [31] that phonon-assisted hopping processes modify the A_2 -spectra quite drastically at temperatures $T < T_c$: the α - β crossover minimum still exists and the functional dependence of the spectrum on frequency becomes more complicated, with two regimes separated by $\lambda_0 = \pi/4$. Exponent parameter values greater than $\pi/4$ (here $\lambda > 0.9 > \pi/4$) would require a constant von Schweidler exponent $b = 0.5$, which is more than twice the values resulting from the fits with equations (1) and (2). It is therefore unlikely that the observed behaviour

can be explained through hopping processes and the data indicate more likely an A_4 -rather than an A_2 -scenario. The solid lines in figure 4 represent fits for the Kramers–Kronig pair (ϵ' , ϵ'') with the A_4 -formulae (4)–(6), corresponding to parameter values: (\blacktriangle) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 1.18$, $t_m = 160$ fs ($T = 386$ K); (\square) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 0.97$, $t_m = 2.2$ ps ($T = 357$ K); (\blacktriangledown) $g_2 = -0.030$, $g_3 = -0.0005$, $g_4 = -0.00005$, $\epsilon_c = 1.01$, $t_m = 34$ ps ($T = 328$ K). As can be seen from the figure, the agreement between data and fits is improved, compared with the A_2 -fits, extending for 6–8 frequency decades. Only the spectra ϵ'' were fitted in this case, since data for ϵ' were not available.

In the case of polyaniline with 6% water content, equations (1) and (2) cannot describe the ϵ'' -spectra at 260 K and 235 K (figure 5, dotted lines). The corresponding parameters for the fits are $a = 0.209$, $b = 0.302$, i.e. $\lambda = 0.90$, at 260 K and $a = 0.240$, $b = 0.371$, i.e. $\lambda = 0.86$, at 235 K. There appears a linear $\log(f)$ -dependence in the spectrum at 203 K (covering four decades), which is a signature of the A_4 -singularity. The failure of the A_2 -scenario to account for these data serves as a good counter-example, showing how non-trivial the predictions embodied in equations (1) and (2) really are. One might argue that it is quite easy to fit many minima with these two equations, as for dry polyaniline. Figure 5 shows quite vividly that this is not the case, making the successful A_2 -fits from figure 4 that much more remarkable. The A_4 -signature exhibited by the spectrum at 203 K in figure 5 is an indication that the failure of the A_2 -fits in this case may be caused by the higher-order singularity, which distorts the A_2 -spectra. The solid lines in figure 5 represent A_4 -fits with the following parameter values: (\blacktriangle) $g_2 = -0.004$, $g_3 = -0.003$, $g_4 = -0.00027$, $\epsilon_c = 3.30$, $f_c = 3.41$, $t_m = 140$ fs at $T = 260$ K; (\circ) $g_2 = -0.004$, $g_3 = -0.003$, $g_4 = -0.00027$, $\epsilon_c = 2.90$, $f_c = 3.47$, $t_m = 3.9$ ps at $T = 235$ K; (\blacktriangledown) $g_2 = -0.001$, $g_3 = -0.0032$, $g_4 = -0.0003$, $\epsilon_c = 2.34$, $f_c = 3.36$, $t_m = 440$ ps at $T = 203$ K. There is good agreement between data and fits over 6–7 decades in frequency, with discrepancies occurring for 1–2 decades at the lowest frequencies.

4. Discussion

Polyglycine (nylon 2), polyaniline (an isomer of nylon 3), nylon 3 and nylon 4 represent the simplest nylons. As can be seen from the figures 1–5, the dielectric relaxations for these related materials exhibit all of the qualitative signatures of the A_4 -singularity and a significant proportion of the data can be described quantitatively by the A_4 -formulae for 6–8 decades in frequency. The temperature dependences for all fit parameters listed in the previous section are displayed in figure 6. While the number of points (three) for each material is insufficient for attempting to derive functional forms for the temperature dependences, it can be seen that the time-scale t_m decreases monotonically with temperature in all cases over 2–4 orders of magnitude, which is physically reasonable. Although the agreement between data and fits occurs over very wide frequency windows, there exist systematic departures of the fits from the data for 1–2 decades at the lowest or highest frequencies. A_4 -fits have also been attempted for nylon 3 and nylon 4 and succeed only for highest-temperature data (383 K). It is also worth noting that some ϵ'' -spectra (for nylon 3 at 303 K, as well as nylon 4 at 343 K and 303 K) exhibit two linear regions in $\log(\omega)$ and that the $1/f$ noise regions in the spectra (nylon 3 and nylon 4, at 263 K and 233 K for both materials) are not bounded by increases in ϵ'' , as predicted for an A_4 -singularity scenario [28], but decrease or have a minimum at the lowest frequencies. There exist several possible causes for these discrepancies. (1) As already stated in section 3, the fitting procedure utilized in the current analysis requires accurate data for both ϵ' and ϵ'' . These

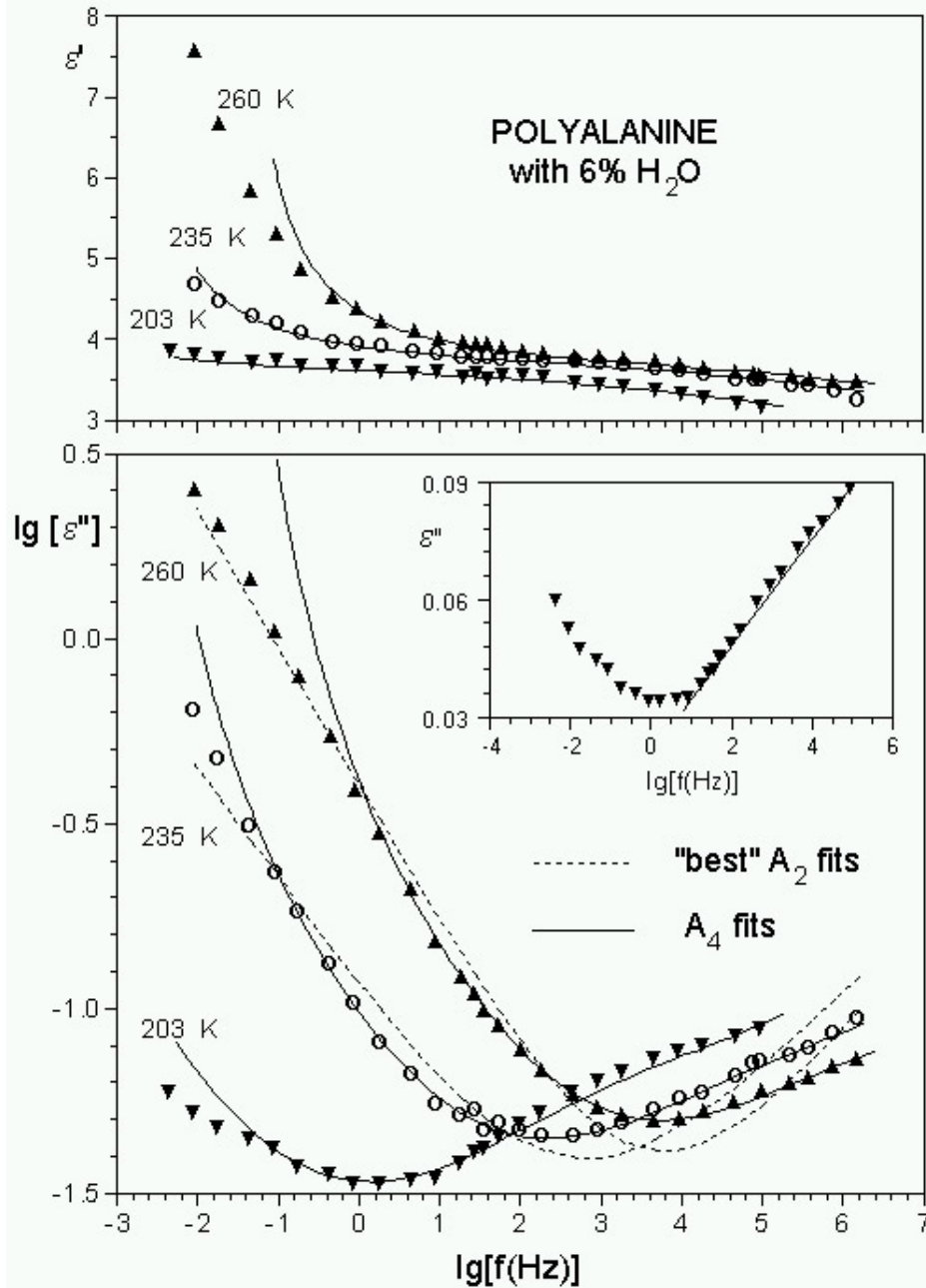


Figure 5. Dielectric relaxation data for polyalanine with 6% water content. The fits with formula (1) and the constraint (2) clearly fail at 260 K ($a = 0.209$, $b = 0.302$, or $\lambda = 0.90$) and 235 K ($a = 0.240$, $b = 0.371$ or $\lambda = 0.86$) (dotted lines). The spectrum at 203 K exhibits a linear region in $\log(\omega)$ over four decades in frequency, which is a signature typical for an A_4 -singularity. The distortion of the A_2 -spectrum by the higher-order (A_4 -) precursor is the probable cause for the poor A_2 -fits at 260 K and 235 K. The solid lines represent A_4 -fits with parameters: (\blacktriangle) $g_2 = -0.004$, $g_3 = -0.003$, $g_4 = -0.00027$, $\epsilon_c = 3.30$, $f_c = 3.41$, $t_m = 140$ fs at $T = 260$ K; (\circ) $g_2 = -0.004$, $g_3 = -0.003$, $g_4 = -0.00027$, $\epsilon_c = 2.90$, $f_c = 3.47$, $t_m = 3.9$ ps at $T = 235$ K; (\blacktriangledown) $g_2 = -0.001$, $g_3 = -0.0032$, $g_4 = -0.0003$, $\epsilon_c = 2.34$, $f_c = 3.36$, $t_m = 440$ ps at $T = 203$ K.

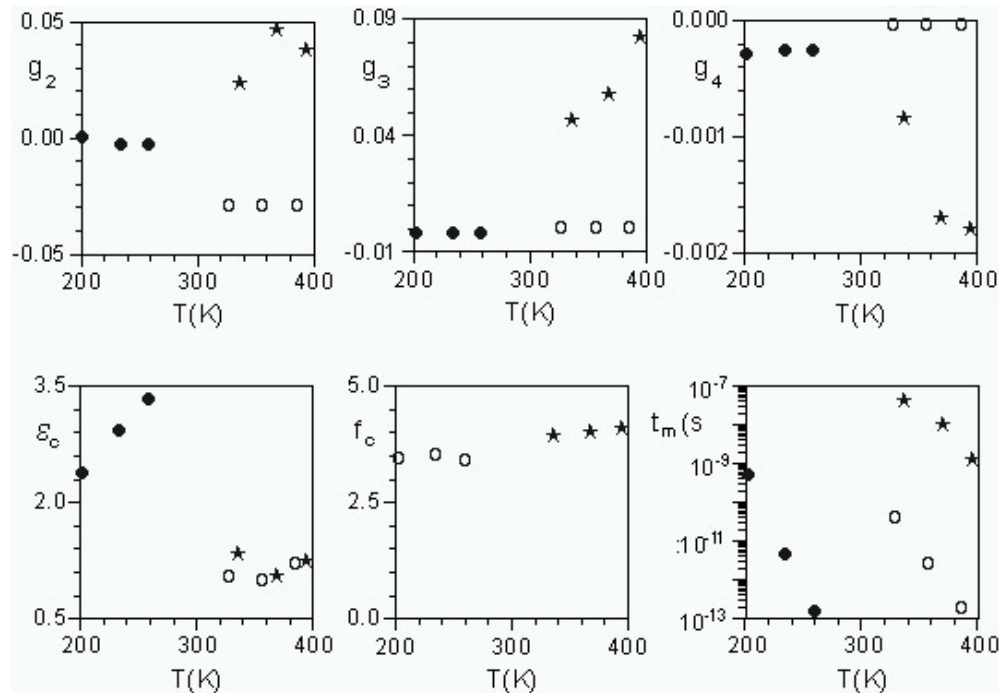


Figure 6. Temperature dependences of the various fit parameters listed in the text: *, dry polyglycine; ●, dry polyalanine; ○, polyalanine with 6% H₂O.

were not always available through the digitization of the figures from Wölfle and Stoll (ϵ' and ϵ'' being displayed with a logarithmic ordinate) and the inaccuracy in ϵ' might have prevented a successful fitting. (The interested reader may inspect the low-temperature ϵ' -data from figures 4–11 of [30].) The digitization errors for ϵ' were particularly large for nylon 3 and nylon 4 at the lower temperatures, since ϵ' exhibits a very weak frequency dependence (much less than a factor of 2 over a frequency window of eight decades). (2) Equations (4)–(6) represent asymptotic results for the A_4 -singularity, i.e. are valid only for parameter values ‘close’ to the critical surface. It is possible that for a given set of experimental data corrections to asymptotic results may come into play, since the distance from a MCT singularity is not known *a priori* for any given experiment. (3) It has been shown that hopping processes can cause drastic modifications of A_2 -spectra [31] and it is conceivable that they can have similar effects for higher-order singularity spectra. At this moment it is not clear whether or which of these possibilities cause the observed discrepancies.

One might argue that the previous data can also be fitted by polynomials. This is indeed the case. However, MCT explains why the independent variable should be $\log(\omega)$ rather than the frequency ω itself, thus deriving (rather than assuming) the stretching of the relaxation, while in the case of a polynomial fit the $\log(\omega)$ -dependence must be taken as an assumption. Moreover, the Kramers–Kronig relations impose an additional constraint which cannot be satisfied by polynomials, and no empirical formulae can account for the features in the data analysed here.

Of further concern might be the fact that some of the spectra analysed here correspond to temperatures smaller than T_g , and one might argue that MCT does not apply under these conditions. As can be seen from figures 1 and 2, the isothermal spectra for nylon

3 and nylon 4 at a given temperature in the range 266–383 K are almost identical in shape, although this temperature interval is below T_g for nylon 3, while it encompasses T_g for nylon 4, and there is no feature in the spectra which singles out T_g as a special temperature. Also, the range of validity for the predictions of MCT models is determined *a posteriori*, by experiment. The debate over the meaning of T_c and its connection with the liquid–glass transition and T_g is enlightening, and indicates how one ought to proceed when comparing MCT predictions with experiments. MCT provides functional relationships for the frequency dependence of susceptibility spectra, or for the variation of relaxation times with temperature, but no absolute values for temperatures or time-scales. As a starting point in testing MCT predictions, one must therefore find a range of experimental parameters over which predictions for a given model agree with the data, and there are no constraints in this search, other than that the values of the various experimentally determined parameters should have physically reasonable values. Moreover, the glass transition temperature T_g is a strictly empirically evolved concept, merely indicating that ‘something drastic’ has happened to the supercooled liquid (e.g. the dramatic increase in viscosity by many orders of magnitude), its value is determined by convention and it has no solid theoretical justification. Therefore it should not prevent a constructive dialogue between experiment and theory, as is attempted in the present work.

Besides the previously mentioned issues, several other points deserve attention and need discussing. Although neutron and light scattering experiments have provided substantial support for MCT and have detected many of the features that it predicts, there exists at present a debate regarding the applicability of MCT results to the electrical susceptibility of glass-forming materials. MCT considers the glass transition to be primarily a densification effect, and the simplest models involve only the density–density correlation function. The factorization *ansatz* for time and wave-vector dependencies in correlation functions leads to property-independent scaling laws in the α – β relaxation region for these models, i.e. various susceptibilities ought to exhibit the same shapes. In physical terms, all observable dynamics follows the dynamics of density fluctuations. This appears to be the case for relatively simple liquids like a concentrated aqueous LiCl solution and the molten salt $[\text{KNO}_3]_{0.6}[\text{Ca}(\text{NO}_3)_2]_{0.4}$ [35, 36]. However, Nagel and co-workers [37, 38] have shown that in some low-molecular-weight liquids (salol, glycerol, propylene glycol), the dielectric loss $\epsilon''(\omega)$ does not exhibit a minimum at frequencies where there is a minimum in susceptibility spectra $\chi''(\omega)$ as determined from light and neutron scattering. This suggests that the density–density correlation function may not always be relevant for dielectric relaxation, and raises the question of whether results derived for the density–density correlation function can be readily applied to susceptibilities derived from other correlation functions. In particular, one might argue that such an over-extension of MCT results happens precisely in the present article. Another problem is the huge difference between the characteristic time-scales for the β -relaxation as probed by light and neutron scattering and the time-scales derived from dielectric relaxation. In addressing these objections, I remind the readers that extensive studies by Johari and Goldstein have revealed the existence of both the primary (α -) and secondary (β -) relaxations in a large number of molecular liquids [39, 40]. Also, recent dielectric spectroscopy data on the molten salt $[\text{KNO}_3]_{0.6}[\text{Ca}(\text{NO}_3)_2]_{0.4}$ from Loidl, Böhmer and co-workers [41] provide evidence for the existence of a β -minimum, and show that the β -relaxation time-scale derived from dielectric relaxation is the same as that derived from light and neutron scattering experiments. This indicates that the findings of Nagel *et al.*, while interesting in themselves, could represent exceptions rather than the rule, even for liquids constituted of small molecules. An overall look at available dielectric relaxation data for glass-forming liquids suggests that small-molecule glass formers exhibit a distinct

behaviour, depending on whether they are ionic or constituted of polar molecules, and that for some molecular liquids dipolar reorientations couple only very weakly to density fluctuations. As far as the difference in typical time-scales seen in different experiments is concerned, I emphasize the fact that MCT models do not provide absolute values for time-scales, and that recent work by Götze and co-workers (see [42]) shows that a two-correlator MCT model can account for the observed differences in relaxation dynamics, and one may therefore conclude that MCT is able to reconcile the observed differences in relaxation dynamics.

Regarding the objection that the results of MCT, which has been developed for simple (monatomic) liquids, are not valid for systems as complicated as polymers, recent Monte Carlo simulations indicate that MCT is able to describe quantitatively the relaxation dynamics in supercooled polymers [43]. Furthermore, it is worth noting that the existence of multiple relaxations in polymers is a well established fact [44]. In light of the accumulated experimental evidence, it was first suggested by Williams [45] that the relaxation behaviour in polymeric glasses be interpreted in a way which transcends the details of molecular motion and does not require material-specific models, given the similarities between the relaxations exhibited by glasses made from both polymeric and molecular liquids. This represents an almost universally accepted view at present. MCT provides an explanation for the α - and β -relaxations in precisely such a generic fashion, devoid of chemical specificity. Götze, Sjögren and co-workers [1, 2, 27, 28] have shown that MCT results offer descriptions for dielectric relaxation in many polymeric glass formers, where one would expect to find that the motion of dipoles is more closely linked to the motion of the polymer chains as a whole, and thus to the dynamics of density fluctuations. This conjecture is supported by multi-dimensional NMR results from Spiess and co-workers (see [46]), who have shown that main-chain motion must occur in polymers during the reorientation of a side-group. If we were to take our clues from the interpretation of the β -relaxation, which was explained for many years through *ad hoc* material-specific models, it may well be the case that the higher-order singularities (A_3 , A_4), so far observed only in polymers, represent new classes of generic relaxation behaviour in disordered systems.

A problem which might be worth addressing is the fact that relaxation patterns which can be described through MCT A_3 - and A_4 -scenarios have been observed so far only in polymeric systems exhibiting some degree of crystallinity (polyethylene terephthalate [27], polyethylene oxybenzoate [27], polychloro-trifluoro ethylene [27, 28], polyoxymethylene [28], nylon 610 [28], polyalanine, polyglycine, nylon 3 and nylon 4), and it is not clear whether completely disordered systems can exhibit a relaxation behaviour which matches A_3 - or A_4 -singularity signatures. Accounting for the relaxation dynamics in semicrystalline materials, either with (Monte Carlo or molecular dynamics) computer simulations or analytical models represents a daunting, if not intractable, theoretical problem. Additional experimental investigation of various glass-forming materials may help to clarify this issue and provide clues for theoretical model building.

One might also ask the following question: how can higher-order MCT singularities be explored experimentally in a systematic fashion? The data analysed in the present article indicate a possible way: starting with a material whose relaxation pattern matches the A_2 -scenario, one must vary additional parameters besides temperature. It was suggested that pressure [27] ought to provide the additional experimental 'knob to tweak'. High-pressure experiments are notoriously difficult, requiring very specialized equipment, and present problems of accurate calibration, especially when one has to vary the temperature over a wide range as well. A more easily accessible parameter would be composition, for binary or multi-component glass formers. In the case of polymers, chain length and tacticity are

two parameters which spring to mind immediately, as well as the addition of plasticizers (or anti-plasticizers) and the systematic chemical variation of the monomer repeat unit.

The current analysis indicates that a thorough testing of MCT predictions and a search for higher-order glass transition singularities necessitates data covering an exceptionally wide frequency interval, well exceeding five decades. As illustrated in figures 1, 2 and 4, data covering 4–6 decades in frequency can be accounted for quite easily with equations (1) and (2). In cases where the material under investigation exhibits a relaxation behaviour which can be successfully described within the A_2 -scenario, an exhaustive testing of MCT predictions is possible with experiments involving the change in temperature over a wide range and a limited experimental frequency window of 4–5 decades, as was shown by Cummins and co-workers [15–17], since there exist more results for the A_2 -singularity than those listed in equations (1)–(3). (This restriction was made for the purpose of the present analysis.) In cases where some predictions for a given MCT model fail, while others still obtain, a limited frequency window is insufficient for a blanket rejection of all MCT models, and it becomes imperative that the data cover as wide a frequency window as possible. Even in cases where data are collected over a sufficiently wide frequency window and exhibit agreement with some predictions for a MCT model, but disagree with others (as is the case with the A_2 -singularity and the data from [47]), the observed discrepancies might well be due to distortions of lower-order singularity patterns in the vicinity of a higher-order singularity, and rejection of MCT claims can be complete only if higher-order scenarios also fail to account for the observed behaviour.

MCT models focused so far on those properties of glassy relaxation which are shared by various systems, i.e. on universal results. In order to construct more realistic models for the glass transition, one needs a microscopic understanding of these systems. The nylons analysed here represent the simplest possible nylons. The origin of the dielectric relaxation features in the various parts of the monomer repeat unit is well established for these materials [30], and the MCT scenario describing their dielectric relaxation was determined in the present work. This ought to provide an incentive for the construction of microscopic models, to illuminate the underpinnings of the behaviour predicted by MCT.

5. Conclusions

There exists agreement between MCT predictions and the dielectric relaxation data for the series of nylons discussed in the present article. The spectra exhibit all of the characteristic signatures of an A_4 -singularity: inflection points, linear regions in $\ln(\omega)$, $1/f$ noise regions, as well as some evidence for a double minimum. The presence of the higher-order (A_4 -) singularity causes a distortion of a lower-order (A_2 -) singularity pattern: (a) the predicted $\sqrt{|\Delta T|}$ -behaviour for the spectrum amplitude at the α - β crossover minimum breaks down for dry polyalanine, although the spectra can be described with the constrained α - β interpolation formula (equations (1) and (2)) over a remarkably wide frequency range; (b) the addition of water to polyalanine distorts the A_2 -spectra beyond the ability of the A_2 -formulae to account for the data and causes the appearance of an A_4 -signature at the lowest temperature. The A_4 -scenario can also account for the data in a quantitative fashion, as illustrated by several examples for polyglycine and polyalanine.

MCT catastrophe scenarios offer a coherent picture for relaxations in these complex systems and can describe complicated susceptibility data for which no competing analytical descriptions exist. A critic of the mode-coupling approach might argue that MCT-inspired data analyses are mere ‘curve-fitting exercises’. This is indeed, to some extent, the case at the moment. A minimal-number-of-parameters fit inspired by theory is nevertheless to

be preferred to empirical fits devoid of any justification other than that of a numerical agreement with data.

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