Dielektrische Spektroskopie an binären Polymermischungen

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1 Introduction

Polymeric materials have found a wide range of applications as industrial design materials for a large number of technological devices. This lies on the fact that their properties can be easily modified either chemically or mechanically. Polymer materials with well defined properties can be obtained for example by blending homopolymers, combining different monomers in random or block copolymers and by cross-linking. There has been an increasing interest on polymer mixtures and the research activities in this field are centered on both the need to produce advanced high performance materials based on well known products and the need of basic knowledge on the phase behaviour. This in turn offers an opportunity for morphology control during processing. Related to the question of the morphology control is the glass transition. Not only does the glass transition temperature determine the transformation of material property but also the rate at which the glass transition occurs influences the properties of the material. Flow and relaxation behaviour for example depend strongly on how far one is above the glass transition temperature ($T_g$).

Polymer blends are combinations of at least two polymer components that can either mix completely to form a homogeneous phase or form a heterogeneous two-phase mixture with sharp domain interfaces. Therefore with respect to their phase behaviour polymer blends can be characterized as being either miscible or immiscible.

The phase behaviour of polymer blends comprising two amorphous polymers is experimentally accessible in a window which is bounded at high temperatures by the thermal decomposition temperature of the pure components and at low temperatures by the glass temperature of the system. Below the glass transition temperature thermodynamic equilibrium can not be achieved and the phase behaviour can only be estimated.
Key to the complete characterisation of multicomponent systems is the knowledge about their structure and dynamics. Of particular interest is the understanding of the molecular dynamics in the vicinity of the glass transition temperature which still presents very intriguing questions. Among these is the question concerning the strong broadening of the glass transition dispersion and the broadening of the $\alpha$-relaxation process (dielectric, mechanical, NMR) observed in polymer mixtures as compared to the transitions in homopolymers. This effect, known for a long time now, has only been qualitatively associated with concentration fluctuations which are characteristic for multicomponent systems [She73, Wet78, Alex80, Kar82].

A more quantitative description of the dynamics in binary polymer mixtures within the glass transition was recently given by Fischer et. al [Fis 92, Zet 92]. They attributed the broadening of the dispersions to the existence of concentration fluctuations which lead to a distribution of $T_g$. For systems obeying WLF or VFT free volume scaling, a temperature dependent distribution of relaxation time can be calculated. By determining the fluctuation amplitudes one can relate the broadening in the glass and dielectric dispersions to thermodynamic variables. This model enables a fit of dielectric relaxation data for the $\alpha$-relaxation with an analytically calculated relaxation curve and as a result one obtains the variance $\langle (\delta\phi)^2 \rangle$ of the concentration distribution in the sample.

It is now generally accepted that glass transition is a co-operative phenomenon. Several models based on the concept of co-operative dynamics within the glass transition have been proposed, each having its own index that defines the extent of co-operativity. Ngai [Nga80] developed the coupling scheme which was used to describe dynamics and correlation in polymer mixtures [Rol91]. Similarly, this approach assumes the presence of concentration fluctuations which leads to a
distribution of chain segments environment. As a consequence there will be a
distribution of relaxation rates and coupling parameters. The variance of the
coupling parameter distribution measures the width of the glass or dielectric
dispersions. Although the Ngai coupling scheme has been successful in describing
the relaxation behaviour in some systems it is strictly developed for
thermorheologically simple systems which satisfy the time-temperature
superposition. Since the shape of the relaxation curves in mixtures usually strongly
depends on temperature, this condition is hardly met [Zet90 Kat92]. Thus there are
still many open and controversial questions and hence a need for alternative
approaches to a better understanding (quantitatively, and qualitatively) of the
various observed effects in polymer-polymer mixtures.

1.1 Aim of the current study:

The current study employs dielectric spectroscopy to study the molecular
dynamics within the glass transition in the one phase regime of compatible
polymer blends. Two systems have been investigated. Blends of polystyrene with
a statistical copolymer Poly (cyclohexylacrylate-butylmethacrylate) and blends of
bisphenol A and tetramethylbisphenol polycarbonate. The experimental data for
the first system is analysed using the concentration fluctuation model according
to Fischer et al [Fis92]. The values of \( < (\delta\phi)^2 > \) obtained from the dielectric data
are combined with SANS measurements [Hack93] to estimate the length scale of
cooperativity within the glass transition. Further the influence of blending solid
polymers on their glassy state is investigated via the sub-Tg \( \beta \)-relaxation. The
experimental results for the \( \beta \)-relaxation are analysed using theoretical models for
non co-operative relaxation processes [Star90].
2 THEORY

2.1 Thermodynamics of Polymer-Polymer Mixtures

Equilibrium properties of materials can be sufficiently predicted when their Gibbs free energy $G$ is known as a function of independent variables such as temperature, pressure, and composition. In the thermodynamics of mixtures the relevant quantity is the change in the Gibbs function due to the process of mixing defined as

$$
\Delta G_{\text{mix}} = G - \sum n_i G_i^0
$$

(2.1)

where $n_i$ is the number of moles of component $i$, $G_i^0$ is the molar Gibbs function (chemical potential $\mu_i^0$) of the pure component $i$. If the free energy of mixing can be calculated for all possible compositions of the mixture, then it is easy to calculate the values of temperature, pressure and composition at which the mixture will either form a single stable phase or phase separate.

There are several theoretical procedures for predicting $\Delta G_{\text{mix}}$. Among them, the more frequently used theories are the Flory-Huggins theory based on a lattice model [Flo41, Hug42], perturbation or excluded-volume theories [Lac76] which treat the spatial and energetic interaction of polymer segments, and the equation-of-state and phenomenological theories [Prig13] which consider aspects such as the volume changes on mixing and compressibility. In the following the basic thermodynamic principles of Polymer-Polymer mixtures will be treated according to the Flory-Huggins theory.

2.1.1 The Flory - Huggins Theory

According to the second law of thermodynamics the phase behaviour of Polymer mixtures is controlled by two thermodynamic factors, the entropy of mixing which consists of combinatorial and non-combinatorial contributions
and the enthalpy of mixing which is related to the interactions between the segments. The combinatorial part of the entropy of mixing supports miscibility whereas the enthalpy favours miscibility only for exothermic interactions.

The Flory-Huggins theory is based on splitting $\Delta G_{\text{mix}}$ into an enthalpy and entropy term as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

(2.2)

The entropy of mixing is assumed to be mainly combinatorial and can be computed from the number of possible arrangements of the molecules on a lattice using the Boltzmann relation

$$S_{\text{conf}} = k \ln W$$

(2.3)

The use of the Boltzmann relation assumes an ideal mixture where

$$W = (n_A + n_B)! / (n_A! \ n_B!)$$

is the number of different was of arranging $n_A$ and $n_B$ molecules of substance A or B on a regular lattice comprising $n = n_A + n_B$ cells and $k$ is the Boltzmann constant. This is valid for single segment materials only and the change of the entropy of mixing is given as

$$\Delta S_{\text{mix}} = -R \left( n_A \ln \phi_A + n_B \ln \phi_B \right)$$

(2.4)

where $\phi = \phi_B$ is defined as the volume fraction of component B and $\phi_A = 1 - \phi$ the fractional volume of component A

$$\phi = \phi_B = \frac{n_B N_B}{n_A N_A + n_B N_B}$$

(2.5)
where \( n_{A,B} \) is the number of molecules for polymer A and B with the degrees of polymerisation \( N_A \) and \( N_B \).

The enthalpy of mixing is calculated as a change of interaction energies among molecular surfaces during the process of mixing and can be expressed as

\[
\Delta H_{\text{mix}} = RT\phi_A \phi_B \chi_{12}
\]  
\[\text{(2.6)}\]

where \( \chi_{12} \) is a dimension-less energetic interaction parameter.

By substituting eq. 2.4 and 2.6 in eq. 2.2 one obtains the change of free energy upon mixing per unit lattice point for two equally sized components

\[
\Delta G_{\text{mix}} = RT\left( \phi_A \phi_B \chi_{12} + \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right)
\]  
\[\text{(2.7)}\]

In general, miscible blends display phase separation either at elevated temperatures or by cooling depending on the interplay between the entropy and the enthalpy of mixing to determine the free energy of the system. The conditions for phase stability in a binary mixture of composition \( \phi \) at a fixed temperature \( T \) and pressure \( P \) are

\[
\Delta G_{\text{mix}} < 0, \text{ and } \left. \frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi^2} \right|_{P,T} > 0
\]  
\[\text{(2.8)}\]

Employing the second condition in eq. (2.8) in (2.7) and assuming that \( \chi \) is independent of concentration, one gets

\[
\left. \frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi^2} \right|_{P,T} = \left( \frac{1}{N_A \phi_A} + \frac{1}{N_B \phi_B} - 2\chi \right)RT
\]  
\[\text{(2.9)}\]
From equations 2.7 and 2.9, the miscibility of two components can be conceived of as being dependent on the balance of the favourable entropy of mixing $\Delta S_{\text{mix}}$ and the changes of $\Delta G_{\text{mix}}$ due to local interactions. The combinatorial entropy of mixing stabilises the mixture and that $\chi < 0$ favours miscibility of the components, especially in the case of high molecular weight polymers when the combinatorial entropy of mixing tends to very small values.

Figure 2.1: Schematic diagram showing the variation of the Gibbs function with composition.
Figure 2.1 shows the variation of the Gibbs function $\Delta G$ as a function of composition $\phi$ for two different interaction parameters $\chi$ and the corresponding $(\phi, T)$ phase behaviour. The stability conditions (eq. 2.8) express the fact that for a given temperature and pressure the curve for $\Delta G(\phi)$ must be convex downward (Fig.2.1b) and in this case $\frac{\partial^2 \Delta G}{\partial \phi^2} > 0$ for the whole composition range.

If on the other hand the curve is of type (a) and convex upwards, a system having a composition between $\phi_1$ and $\phi_2$ is unstable with respect to the conjugate phases $\alpha$ and $\beta$ which have the lowest value of the Gibbs function. The system will therefore separate into the two phases in order to minimise its free energy.

The thermodynamic criterion for two phases to coexist at equilibrium is that the chemical potential $\mu$ of each component in the two phases be the same. In a binary mixture this can be expressed as

$$\frac{\partial \Delta G}{\partial \phi_1} = \frac{\partial \Delta G}{\partial \phi_2} \quad \text{or} \quad \mu_1 = \mu_1' \quad \mu_2 = \mu_2' \quad (2.10)$$

where the prime designates the second phase. The double tangent (Fig. 2.1b) defines the two equilibrium phase compositions and the locus of such conjugate phases form the binodal curve (Fig. 2.1c). Between points C and F, the system becomes very unstable against thermally induced concentration fluctuations. The two inflection points D and E where $\frac{\partial^2 G}{\partial \phi^2} = 0$ define the spinodal. At these points the composition fluctuation becomes infinity and the mixture is unstable. Between these two points $\frac{\partial^2 G}{\partial \phi^2} < 0$ and the homogeneous mixture is unstable to infinitesimal fluctuations and there is no thermodynamic barrier to phase growth. Thus, separation takes place by a continuous and spontaneous process occurring
by diffusion flux against the concentration gradient (spinodal decomposition). Between the spinodal and the binodal, the curvature is positive and the system is metastable. In this region small fluctuations tend to decay very fast, and hence phase separation can only proceed by overcoming a barrier with large composition fluctuation (nucleation and growth).

For studying phase relationships, it is customary to utilise the molar change in the Gibbs function of mixing $\Delta G_{\text{mix}}^m$ which at constant temperature $T$ and pressure $P$, is related to the chemical potentials of the various components [Stua53] as

$$\Delta G_{\text{mix}}^m = \frac{\Delta G_{\text{mix}}}{n} = \sum_{i} \phi_i \mu_i = \phi_A \mu_A + \phi_B \mu_B \quad (2.11)$$

Differentiating (2.10) with respect to $\phi$ gives

$$\mu_A = \Delta G_{\text{mix}}^m + (1 - \phi_A) \frac{\partial G_{\text{mix}}^m}{\partial \phi_A} \quad (2.12a)$$

$$\mu_B = \Delta G_{\text{mix}}^m + (1 - \phi_B) \frac{\partial G_{\text{mix}}^m}{\partial \phi_B} \quad (2.12b)$$

The spinodal conditions for a binary mixture are readily obtained by setting equation (2.9) equal to zero so that

$$\frac{1}{N_A (1 - \phi_B)} + \frac{1}{N_B \phi_B} - 2 \chi = 0 \quad (2.13)$$

This gives

$$\chi_s = \frac{1}{2} \left( \frac{1}{N_A (1 - \phi_B)} + \frac{1}{N_B \phi_B} \right) \quad (2.14)$$
and the second derivative of the free energy with respect to the composition is given by

$$\frac{\partial^2 \Delta G_{\text{mix}}}{\partial \phi^2} = 2kT(\chi_s - \chi)$$  \hspace{1cm} (2.15)

At the critical or consolute temperature $T_c$ where both the spinodal and the binodal have a common horizontal tangent,

$$\frac{\partial^2 G}{\partial \phi^2} = \frac{\partial^3 G}{\partial \phi^3} = 0, \quad \text{and} \quad \frac{\partial^4 G}{\partial \phi^4} > 0$$  \hspace{1cm} (2.16)

or

$$\frac{1}{N_A(1 - \phi_B)^2} - \frac{1}{N_B(\phi_B)^2} = 0$$  \hspace{1cm} (2.17)

Solving equations 2.16 and 2.17 leads to the result

$$\phi_B^c = \frac{\sqrt[4]{N_A}}{\sqrt[4]{N_A} + \sqrt[4]{N_B}} \quad \text{and} \quad 2\chi_C = \frac{\sqrt[4]{N_A} + \sqrt[4]{N_B}}{N_A N_B}$$

where $\phi_B^c$ and $\chi_C$ are respectively the composition and the interaction parameter at the critical point.

For a symmetric mixture $N_A = N_B$ and the above results simplify to

$$\phi_c = \frac{1}{2} \quad \text{and} \quad \chi_C N = 2$$  \hspace{1cm} (2.18)
It is worthy noting that equations (2.13) - (2.17) are only valid for mixtures of monodisperse polymers having repeat units of equal size. In addition, the binary interaction parameter must be independent of concentration, which in fact is a basic assumption of the Flory-Huggins theory [Flo41]. In practice many mixtures are asymmetrical and comprise polydisperse components. The restriction to monodisperse polymers can easily be removed as shown by Koningsveld and co-workers [Kon70]. Thus analogous to equation 2.9, the spinodal condition for a polydisperse system is

\[
\frac{1}{N_{wA}(1 - \phi_B)} + \frac{1}{N_{wB}\phi_B} + \frac{\partial^2(\chi\phi_A\phi_B)}{\partial\phi_B^2} = 0
\]  \hspace{1cm} (2.19)

where \(N_{wA}\) and \(N_{wB}\) are the weight-average number of lattice sites occupied by A and B respectively. According to the Flory-Huggins theory eq. 2.19 yields

\[
\chi_s = \frac{1}{2} \left( \frac{1}{N_{wA}\phi_A} + \frac{1}{N_{wB}\phi_B} \right)
\]  \hspace{1cm} (2.20)

Similarly the conditions (2.16) at the critical point hold. For a polydisperse mixture this is specified by

\[
\frac{N_{zA}}{N_{wA}\phi_A^2} - \frac{N_{zB}}{N_{wB}\phi_B^2} + \frac{\partial^3(\chi\phi_A\phi_B)}{\partial\phi_B^3} = 0
\]  \hspace{1cm} (2.21b)

which leads to a critical composition

\[
\phi_C^B = \left[ 1 + \frac{N_{wA}}{N_{wB}} \cdot \sqrt{\frac{N_{zB}}{N_{zA}}} \right]^{-1}
\]  \hspace{1cm} (2.21b)
where $N_{zA}$ and $N_{zB}$ is the z-average number of lattice sites occupied by A and B respectively. Thus if the appropriate moments of distribution of the chain lengths are known and identifying these with the number of lattice sites occupied by the two species, the effect of polydispersity on the thermodynamics of mixing can be treated.

From equation (2.18) it is implied that a miscibility gap occurs when
\[ \chi > \chi_c = \frac{2}{N} \] and for \[ \chi < \chi_c \] there is complete miscibility. By introducing a temperature dependence of the interaction parameter a phase diagram ($\chi, T$) can be constructed. Patterson [Pat78] used a Prigogine - Flory [Flo70] version of the equation-of-state theory and expressed the temperature dependence of $\chi(T)$ as a contribution of two effects.

\[
\chi(T) = \frac{\Delta H_{\text{mix}}}{RT} + \frac{C_p(T)\tau_{12}}{2R}
\]  

(2.22)

where $\tau_{12}$ is the free volume difference between two components in a system.

The first effect is associated with the contact energy difference between unlike and like segments where the enthalpy of mixing $\Delta H_{\text{mix}} < 0$ for exothermal mixtures. The second effect contained in the second term of equation (2.22) follows from the difference in thermal expansions or free volume difference between the two components in the system and $C_p(T)$ is the configurational heat capacity. It causes a reduction in the entropy. The temperature dependence of $\chi$, is shown schematically in figure 2.2, for both endothermal and exothermal mixtures. For exothermal systems only one miscibility gap will occur at high temperatures (typical for blends where a lower critical solution temperature LCST is visible, line b), whereas for endothermal systems, two miscibility gaps one at low temperatures (upper critical solution temperature UCST) and at higher temperatures curve a). In practice the observation of a theoretically anticipated
mixing or de-mixing is limited by the freezing in of structures at the glass transition temperature or by the degradation at high temperatures.

**Figure 2.2:** Schematic representation of the temperature variation of the interaction parameter $\chi_{12}$ (solid lines a and b). The dotted lines represent interactions due to: 1. dispersion forces, 2. free volume, 3. specific interactions. 1 and 2 are the interactions encountered mostly with upper and lower critical solution temperatures(a), 2 and 3 are typical for polymer mixtures where only a lower critical solution temperature is visible(b).
2.2. Concentration Fluctuations and Glass transition

The dynamics and structure in condensed matter are two interdependent properties. Dynamic changes may be facilitated by structure change or vice-versa. For example, configurational rearrangements or structural relaxation involving movements of small segments are known to be associated with the existence of density fluctuations present in single component bulky polymers [Ber76]. These fluctuations also cause fluctuations in the dielectric constant. In multicomponent systems, mutual diffusion arises due to concentration fluctuations [Wan93]. From these examples it is evident that for a complete characterisation of the properties of matter, information about both the structure and the dynamics is necessary. In the following, fundamental relations of the density and concentration fluctuations to experimentally accessible thermodynamic susceptibilities and variables obtained from scattering experiments are discussed. Via the pair distribution function $g(r)-1$ and the static structure factor, a "coarse graining volume " $v$ can be defined, which at the lowest resolution will be characterised by a unique glass transition temperature $T_g$. This volume will determine the extent of co-operativity in the vicinity of $T_g$ and in mixtures the characteristic $T_{g1}(\phi)$ for such volume elements is concentration dependent.

2.2.1 Concentration Fluctuations in thermal equilibrium

A macroscopic system under a given set of constraints (e.g. temperature, volume and composition) can exist in a large number of different microscopic states. According to classical thermodynamics [Lan79] the system in the state of highest probability is characterised by the lowest value of the Gibbs (G) or Helmholtz free energy (F). The system can however spontaneously change its energy such that the mean deviation $<\delta F>$ from the most probable state is given by

$$<\delta F> = \frac{kT}{2}$$ (2.23)
Other properties of the system fluctuate as well and the free energy as a function of any property of interest \(x\), for example the concentration, is always at a minimum for the most probable state for which \(x = \langle x \rangle\). The probability that a property \(x\) (density, concentration etc.) locally deviates from the mean \(\langle x \rangle\) by \(\delta x\) at a constant volume and energy is given by

\[
W(x)dx = \frac{\exp[-\Delta F(x)/kT]}{\int_0^\infty \exp[-\Delta F(x)/kT]dx}
\]  

(2.24)

where \(\Delta F(x)\) is the free energy connected with \(x\) and \(F = G - PV\). By a Taylor-series expansion of \(\Delta F(x)\) in terms of \(\langle x \rangle\) one obtains

\[
\Delta F(x) = \Delta F(\langle x \rangle) + \left(\frac{d\Delta F}{dx}\right)_{x=\langle x \rangle} (x - \langle x \rangle) + \frac{1}{2} \left(\frac{d^2\Delta F}{dx^2}\right)_{x=\langle x \rangle} (x - \langle x \rangle)^2 + \ldots
\]

In the equilibrium limit, \(\frac{d\Delta F}{dx} = 0\), and \(W(x)dx\) can be expressed as

\[
W(x)dx = \sqrt{\frac{a}{\pi}} \exp[-a(x - \langle x \rangle)^2]dx
\]

(2.25)

with

\[
a = \frac{1}{2kT} \left(\frac{d^2\Delta F}{dx^2}\right)_{x=\langle x \rangle}
\]

Equation (2.25) is a general relation which can be applied to determine the fluctuation of any variable that influences the free energy. To calculate the mean squared concentration fluctuations one applies this equation. Assuming that the time average of the concentration fluctuations is zero eq. (2.25) reduces to
\[
\langle (c - \langle c \rangle)^2 \rangle = \langle (\delta c)^2 \rangle = \frac{\int_0^\infty (\delta c)^2 W(c) d(\delta c)}{\int_0^\infty W(c) d(\delta c)} \quad (2.26)
\]

where \( W(c) \) is the probability that the concentration \( c \) lies between \( c \) and \( c + \delta c \), and this can be obtained by making a Gaussian approximation for the concentration fluctuations [Doi86]. Thus,

\[
W(c) dc = \sqrt{\frac{a}{\pi}} \exp\left[-a(c - \langle c \rangle)^2\right] d(\delta c) \quad (2.27)
\]

This is a Gaussian distribution for the concentration with \( a \) as defined before but here \( x = c \). From equation (2.27) it follows that

\[
\langle (\delta c)^2 \rangle = \frac{1}{2a} = \frac{kT}{(\delta^2 \Delta F / \bar{\delta c}^2)_{c=\langle c \rangle}} \quad (2.28)
\]

where \( \langle (\delta c)^2 \rangle \) is the fluctuation in a volume element of size \( \Delta V \) and \( \Delta F \) is the free energy change associated with the fluctuation. The change in free energy is in turn related to the change of the chemical potential \( \mu \). By defining \( c \) as a relative concentration given by \( c = \frac{n_B}{n_A} \) with \( n_i \) being the number of molecules of type \( i \), the mean squared concentration fluctuation can be expressed as [Dav62, Hill56]

\[
\langle (\delta c)^2 \rangle = \frac{kT}{c < N_B >} \left( \frac{\partial \mu_B}{\partial c} \right)^{-1}_{T,P} \quad (2.29)
\]
The Gaussian approximation for the concentration fluctuations is justified in concentrated solutions (liquid or solid). However this approximation is not applicable in the semi-dilute range of composition. In polymer mixtures and in the case of no interactions among the component segments, the mean squared fluctuations can be calculated as a sum of correlation functions of independent Gaussian chains [Doi86]

\[
<(\delta c)^2> = \frac{c}{V} S(q)
\]  

(2.30)

where \(S(q)\) is the scattering function of ideal polymers, \(V\) is the reference volume and \(c\) is the average concentration. The scattering function \(S(q)\) of a polymer mixture is given by de Gennes [deG79] random phase approximation (RPA) expression

\[
\frac{1}{S(q)} = \frac{1}{\phi_A N_A f_D(q^2R_{gA}^2)} + \frac{1}{\phi_B N_B f_D(q^2R_{gB}^2)} - 2\chi
\]  

(2.31)

\(N_i f_D(qR_{g_i})\) is the scattering function of an individual chain, and \(f_D\) denotes the Debye structure factor for ideal non-interacting chains. For monodisperse Gaussian chains

\[
f_D = \frac{2}{q^2R_g^2} \left( 1 - \frac{(1 - \exp(-q^2R_g^2))}{q^2R_g^2} \right)
\]  

(2.32)

and the term \(2\chi\) comes from the fact that the interactions in the system are considered to be of short range.

When the mixture comprises polydisperse polymer components, \(f_D\) is substituted by \(f_K\) given by an expression suggested by Kirste and Oberthür [Kir82]
\[ f_k(q^2 R_g^2) = \frac{2(1-Uy)^{-1/U} + y - 1}{(1+U)y^2} \]  

(2.33)

with \( y = \frac{R_g^2 q^2}{1+2U} \), \( U = \frac{M_w}{M_n} - 1 \)

or by assuming a Zimm-Schulz distribution [Sch39, Zim48], \( f_K \) takes the form

\[ f_k(q^2 R_g^2) = \frac{1}{q^2 <R_g^4>_n} \left[ q^2 <R_g^2>_n - 1 + \left( \frac{1}{1 + \frac{q^2 <R_g^2>_n}{k}} \right)^k \right] \]  

(2.34)

where \( <R_g>_n \) is the number average radius of gyration and \( k \equiv 1/U \) in equation (2.32) defines the polydispersity.

For small \( q \) values i.e \( q R_g \ll 1 \) the Zimm approximation [Mei92] can be used and for both \( f_D \) and \( f_K \) one obtains

\[ \lim_{qR_g \to 0} f_{D,K}(qR_g) = 1 - \frac{1}{3} q^2 R_g^2 \], \( f^{-1} \approx 1 + \frac{1}{3} q^2 R_g^2 \)  

(2.35)

Using the relation \( R_{gi}^2 = \frac{\sigma_i^2 N_i}{6} \), with \( \sigma_i \) being the segment length and by taking the average segment length \( \sigma^2 = \phi_A \sigma_A^2 + \phi_B \sigma_B^2 \) one gets for the scattering function

\[ \frac{1}{S(q)} = 2(\chi_s - \chi) + \frac{\sigma^2 q^2}{18\phi_A \phi_B} \]  

(2.36)

Equation (2.35) takes the standard Ornstein-Zernike form
\[ S(q) = \frac{S(0)}{1 + \xi^2 q^2} \]  

(2.37)

where \( S(0)^{-1} = 2(\chi_S - \chi) \) is the intensity scattered at \( q = 0 \), and \( \xi \), the correlation length of the fluctuations is defined as

\[ \xi^2 = \frac{R_g^2}{3 \left| \frac{\chi}{\chi_s - \chi} \right|} \]  

(2.38)

### 2.2.2 The Structure factor

The scattering function \( S(q) \) conveys structural information. For example, from this function one can calculate the pair and the radial distributions and the coordination number. In crystals \( S(q) \) gives the Bragg peaks. It also represents in general, the mean squared thermal fluctuations in particle number \( S_{NN}(0) \), concentration \( S_{cc}(0) \) and the correlation between these two fluctuations \( S_{NC}(0) \), which can be derived from the Fourier transforms of the local number density and concentration of a mixture [Fis87]. In the limit \( q \to 0 \), \( S(q) \) has direct connection on the one hand with fluctuations and on the other with thermodynamic quantities. Thus \( S(q) \) provides a direct link of the thermodynamics to an experimentally accessible quantity, the scattering intensity \( I(q) \) which is obtained in scattering experiments.

\[ \frac{1}{S(q)} = N |f_a|^2 \frac{1}{I(q)} \]  

(2.39)

where \( |f_a|^2 \) is a contrast factor which depends on the kind of experiment (SALS, SAXS, SANS). For the case of SANS, \( |f_a|^2 \) is the scattering amplitude. In a
mixture $|f_a|^2 = \left( \frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2$ with $b_A$, $b_B$ and $v_A$ and $v_B$ are the scattering lengths per mole and molar volumes for component A and B respectively.

For pure amorphous materials, the scattering intensity $I(q)$ is described in terms of radial distribution function $g(r)$ which can be derived as

$$g(r) - 1 = \frac{1}{(2\pi)^3 \rho V} \int \left( \frac{I(q)}{Nf^2(q)} - 1 \right) \frac{q \sin qr}{r} dq$$ (2.40)

where $f(q)$ is the particle scattering factor and $N$ is the number of scatterers in given volume. According to Ruland et al [Rul75] and Song et al [Son87] $I(q)$ is related to the density fluctuations $\psi(v)$ by

$$\psi(v) = \frac{1}{(2\pi)^3 \rho V} \int \frac{1}{v} I(q) [F(q)]^2 dq$$ (2.41)

where $V$ is the scattering volume of the sample and $F(q)$ is the Fourier transform of the form factor representing the reference volume $v$, and $\rho$ is the average density of the scatterers. Of particular interest are the fluctuations in the thermodynamic limit. In this case $v \to \infty$ and $F(q)$ becomes a delta function and equation (2.41) reduces to

$$\psi(\infty) = \lim_{q \to 0} \frac{I(q)}{\rho V} = \rho kT\beta(T)$$ (2.42)

where $\beta(T)$ is the isothermal compressibility. Equation (2.42) expresses the fact that the density fluctuations are driven by thermal energy of magnitude $kT$ but at the same time being opposed by the bulk modulus of magnitude $\beta(T)^{-1}$. 
Proceeding from Rulands equation Song et al [Son87] have shown that the density fluctuations as a function of volume $F_{\eta}(v)$ and the spatial correlations can be evaluated from the scattering intensity $I(q)$ as follows:

One considers a reference volume $v_1$ (of arbitrary shape and size) placed at distance $|\vec{r}|$ from another volume $v_2$ not necessarily of the same shape and size. If $n_1$ and $n_2$ are the number of particles in $v_1$ and $v_2$ respectively, the correlation function $\psi(v_1, v_2)$ of the fluctuations is defined as

$$\psi(v_1, v_2) = \frac{<(n_1 - <n_1>) <n_2 - <n_2>)>}{<n_1>^{1/2} <n_2>^{1/2}}$$  
(2.43)

For $n_1 = n_2$, this equation reduces to

$$\psi(v_1, v_2) = \frac{<(\delta n)^2>}{<n>}$$  
(2.44)

and for $v_1 = v_2 = v$ and $|\vec{r}|=0$, the density fluctuations $\psi(v)$ shown in equation (2.44) correspond to the self-correlation $\psi_0(v, v)$.

By defining $\eta(\vec{r}) = \rho(\vec{r}) - <\rho>$, where $\rho(\vec{r})$ is the density of particles at position $\vec{r}$, and a geometric factor $f_1(\vec{r})$ of the reference volume $v_1$, such that

$$f_1(\vec{r}) = \begin{cases} 1 & \text{in } V \\ 0 & \text{otherwise} \end{cases},$$

the deviation of the number $n_1$ of particles within the volume $V_1$ from its average $<n_1>$ can be expressed as

$$\delta N_1(\vec{r}) = \eta(\vec{r}) \otimes v_1(\vec{r})$$  
(2.45)
which is a convolution product of the density fluctuation and the volume $v_1$. The spatial correlation of the density fluctuations $<\delta n_1, \delta n_2>_R$ where $R$ is the distance between two points, is given by

$$<\delta n_1, \delta n_2>_R = \frac{1}{V(2\pi)^3} \int F\{\eta(\vec{r}) \otimes v_1(\vec{r})\} F^*\{\eta(\vec{r} + \vec{R}) \otimes v_2(\vec{r} + \vec{R})\} dq$$  \hspace{1cm} (2.46)

here $F\{\}$ denotes the Fourier transform and $F^*\{\}$ is its complex conjugate. By applying the convolution theorem equation (2.46) leads to

$$<\delta n_1, \delta n_2>_R = \frac{1}{V(2\pi)^3} \int e^{-iq\vec{R}}|F\{\eta(\vec{r})\}|^2 v_1(q)v_2^*(q)dq$$  \hspace{1cm} (2.47)

where $V$ is the volume of the sample and $v_1$ is the Fourier transform of the geometric factor of $\nu_1(\vec{r})$. The spatial correlation of the density fluctuations is given by

$$\psi_R(v_1, v_2) = \frac{1}{(2\pi)^3 V} \int e^{-iq\vec{r}} I(q) \frac{F_1(q)}{v_1^{1/2}} \cdot \frac{F_2^*(q)}{v_2^{1/2}} dq$$  \hspace{1cm} (2.48)

which reduces to equation (2.47) when $|\vec{R}| = 0$, and $v_1(\vec{r}) = v_2(\vec{r})$.

The physical meaning of the density correlation function can be seen in the sense that it provides a way of looking at the pair correlation on a more coarse scale. Thus at a reduced resolution, a "coarse graining volume" $v$ can be defined which equals to the reference volume. This volume is of great significance because as will be discussed later, it will be characterised by a unique glass transition temperature $T_g$ which in mixtures is a function of the composition. In the vicinity of glass transition the size of this volume will determine the scale of cooperative processes [Fis92]. Our main interest is to determine experimentally the
size of the volume \( v \) where co-operativity influences dynamic processes. If a sphere of radius \( r \) is taken as the reference volume, the Fourier transform of its form factor is given by

\[
\nu(q) = \frac{24v[\sin(qr) - qr \cos(qr)]}{(2rq)^3}
\]  

(2.49)

Analogous to the treatment for the density fluctuations for pure systems the concentration fluctuations as a function of volume can be derived as follows:

The concentration of component \( B \) as a volume fraction \((\phi)\) in the mixture is defined as in equation (2.5). By introducing the relative concentration \( c \) given by

\[
c = \frac{n_B}{n_A}, \text{[Dav60], eq. (2.5)}
\]

(2.5)

and

\[
\phi = \frac{cN_B}{N_A + cN_B} \quad \text{and} \quad 1 - \phi = \phi_A = \frac{N_A}{N_A + cN_B}
\]

(2.50)

By differentiating equation (2.50) with respect to \( c \) and rearranging terms leads to the relation for the variance of the concentration fluctuations

\[
< (\Delta \phi)^2 > \quad = \quad \frac{(N_A N_B)^2}{(N_A + cN_B)^2} \quad < (\Delta c)^2 >
\]

(2.51)

\[
= \phi^2 (1 - \phi)^2 \frac{< (\Delta c)^2 >}{c^2}
\]

The concentration fluctuations as a function of volume \( \phi(v) \) can defined similar to equation (2.44) where in the case of binary mixtures the voids leading to density fluctuations in pure polymers are filled by the molecular segments of the second component. Thus
\[
\psi_{\phi}(v) = \frac{\langle (\delta n_B N_B)^2 \rangle}{n_A N_A + n_B N_B} = \frac{\langle (\delta n_B)^2 \rangle}{n_B} \cdot \phi N_B
\]  

(2.52)

By assuming that the mixture is incompressible, i.e.

\[
\delta n_A N_A + \delta n_B N_B = 0
\]  

(2.53)

and since

\[
\delta c = \left( \frac{\partial c}{\partial n_A} \right)_{n_B} \delta n_A + \left( \frac{\partial c}{\partial n_B} \right)_{n_B} \delta n_B
\]  

(2.54)

one obtains by squaring eq.(2.54) and dividing by \( c^2 \)

\[
\frac{\langle (\delta c)^2 \rangle}{c^2} = \frac{\langle (\delta n_B)^2 \rangle}{n_B^2} \cdot \frac{1}{(1 - \phi)^2}
\]  

(2.55)

A comparison of equation (2.51) with (2.55) gives the relation

\[
\psi_{\phi}(v) = \langle (\delta \phi)^2 \rangle \cdot (n_A N_A + n_B N_B) = \langle (\delta \phi)^2 \rangle \cdot M
\]  

(2.56)

where \( M = n_A N_A + n_B N_B = V / a^3 \) with \( a^3 \) = volume of a lattice cell.

By substituting the Flory-Huggins expression for the Gibbs free energy (eq.2.7) in equation (2.12), the concentration fluctuations given by (2.30) can be expressed as

\[
\langle (\delta \phi)^2 \rangle = \frac{1}{(n_A N_A + n_B N_B) S_0^{-1}} = \frac{S_0}{M}
\]  

(2.57)
where \( S_0 \) is the scattering function in the long wavelength limit (\( q = 0 \)). This corresponds to the fluctuations in the thermodynamic limit when \( v \to \infty \). Equation (2.56) can be written as

\[
\psi_\phi(v \to \infty) = S(q = 0)
\]

(2.58)

The structure factor \( S(q) \) for mixtures can be obtained from scattering experiments (see chapter 2.2) [Mom89, Hack93]. Since \( S(q = 0) \) is experimentally not directly accessible, measurements are usually done in other \( q \)-ranges and extrapolated to \( q = 0 \).

Substitution of the structure factor for mixtures and the form factor of a spherical volume in eq.(2.41) gives

\[
\psi_\phi(v) = \frac{2r}{3\pi} \int_0^\infty \frac{\left( 3\sin qr - qr \cos qr \right) / (qr)^2}{\phi_A N_A f_D (q^2 R_{ga}^2) + \phi_B N_B f_D (q^2 R_{gb}^2)} - 2\chi \]  

(2.59)

Figure 2.3 shows a plot of \( \psi_\phi(v) \) as a function of the radius of \( r \) evaluated from equation (2.59) for the PS/P(CHA-BMA) (see Zet92 for the system PS/PVME).

In the thermodynamic limit (\( r \to \infty \)), \( \psi_\phi(v) = \) constant = \( S(q = 0) \)
Figure 2.3  \( \psi_\phi(v) \) as a function of the radius of a spherical reference volume. At the thermodynamic limit \( \psi_\phi(v) = \text{constant} = S(q = 0) \)

Solving equation (2.56) for a spherical volume yields for the concentration fluctuations

\[
<(\delta \phi)^2> = \frac{1}{2\pi^2} \frac{a^3}{r^2} \int_0^\infty S(q) \left[ \frac{3[\sin(qr) - qr \cos(qr)]}{(qr)^2} \right]^2 dq
\]

(2.60)

where \( S(q) \) is given by

\[
\frac{1}{S(q)} = \frac{1}{\phi_A N_A} + \frac{1}{\phi_B N_B} - 2\chi + \frac{1}{18} \left( \frac{\sigma_A^2}{\phi_A} + \frac{\sigma_B^2}{\phi_B} \right) q^2
\]

(2.61)

with \( \left( \frac{\sigma_A^2}{\phi_A} + \frac{\sigma_B^2}{\phi_B} \right) = \frac{a^2}{\phi(1-\phi)} \). \( a \) is the average segment length.

Equation (2.60) enables the evaluation of \( r \) when \( <(\delta \phi)^2> \) is known. Later \( r \) will be identified with the scale of co-operativity in the glass transition.

2.3  Glass transition and the \( \alpha \) - relaxation process
It is well established that a wide range of molecular systems which do not crystallise upon cooling from the liquid (rubbery) state undergo a distinct transformation of material property at the onset of the glass transition. Among these properties are the modulus, specific volume, enthalpy, entropy, specific heat, refractive index and the dielectric function. The glass transition usually is manifested as the temperature region where the thermal expansion coefficient $\alpha$ (also the heat capacity, and the compressibility) show discontinuity [Bue62]. In the temperature regime on either side of the glass transition temperature $T_g$ two or sometimes more well defined molecular relaxation processes are commonly observed. The process above $T_g$ (\textit{\(\alpha\)-process}) usually considered as the primary process is referred to as the dynamic glass transition. The process occurring below $T_g$ (\textit{\(\beta\)-process}) is thought of as a secondary process associated with the particular molecular system involved. A common feature related to the dynamic glass transition is that most polymeric and glass-forming systems exhibit an average relaxation time $\langle \tau \rangle$ for the $\alpha$-process (observed for example by mechanical, dielectric NMR spectroscopy etc.) which obeys the Vogel equation

$$\langle \tau \rangle = A \exp\left(\frac{B}{T - T_0}\right)$$

(2.62)

where A, B and $T_0$ are material constants and $T_0$ is typically 50 K below the experimental glass transition. Furthermore, many results obtained from relaxation and scattering techniques for glass forming systems in the $T_g$-range can be described by the stretched exponential relaxation function

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right)^\beta$$

(2.63)
where $\tau$ is an effective relaxation (or correlation) time which also obeys the Vogel equation, and $\beta$ is a parameter $0 < \beta \leq 1$, which increases with increasing sample temperature.

The glass transition has been a subject of intense experimental and theoretical work because of the key role it plays in influencing material property. In this section, some of the theoretical models and approaches developed to describe the glassy state and the glass transition are outlined. An overview of the glass transition behaviour in polymer blends is also given.

The theoretical models which describe molecular dynamics in the vicinity of the glass transition temperature can be classified mainly into two:

(a) Thermodynamic theories which treat the glass transition as a second order phase transition and

(b) Kinetic theories which treat the glass transition as a non-equilibrium process

### 2.3.1 Thermodynamic theories.

#### 2.3.1.1 Relations amongst thermodynamic quantities at $T_g$.

Many experimental results suggest that the glass transition phenomenon has the nature of a second order thermodynamic transition. A good test for this would be the application of the second order transition thermodynamic relations first formulated by Ehrenfest on the experimental results [Cal60]. The Ehrenfest relations were derived analogous to the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$  (2.64)
and for a second order phase transition the following relations result

\[
\frac{dP}{dT} = \frac{\Delta \alpha}{\Delta \kappa}\quad (2.65)
\]

and

\[
\frac{dP}{dT} = \frac{\Delta C_P}{TV\Delta \alpha}\quad (2.66)
\]

where $\Delta C_P$, $\Delta \kappa$, $\Delta \alpha$, are the changes in heat capacity, the compressibility and the thermal expansion coefficient, respectively, which occur at the second order transition temperature $T_2 = T_g$.

Combination of (2.65) and (2.66) gives for $T_g$

\[
T_g = \left[ \frac{\Delta \kappa \Delta C_P}{V(\Delta \alpha)^2} \right]_{T=T_g}
\]

(2.67)

where $\Delta C_P$, $\Delta \kappa$, $\Delta \alpha$, are the changes in heat capacity, the compressibility and the thermal expansion coefficient respectively which occur at the second order transition temperature $T_2 = T_g$.

Without invoking second order thermodynamic transitions, it can generally be shown that if a single ordering parameter determines the position of equilibrium in a relaxing system, the following relation holds [Prig54]

\[
\frac{\Delta \kappa \Delta C_P}{TV(\Delta \alpha)^2} = R = 1
\]

(2.68)

where $R$ is called the Prigogine - Defay ratio. If more than one ordering parameter is required, as it seems to be the case with glass - formers, then the
thermodynamic stability requires that $R > 1$. This requirement can be expressed as

$$\frac{\Delta \kappa}{\Delta \alpha} \geq \frac{TV \Delta \alpha}{\Delta C_P}$$

(2.69)

### 2.3.2 Theory of Gibbs and DiMarzio

The thermodynamic theory of the glass transition was first formulated for systems of chain polymers by Gibbs and DiMarzio [Gib58] based on lattice calculations. The theory predicts a true second order transition at a temperature $T_2 = T_g - 50$ K when a material finally reaches equilibrium albeit at infinitely long times. A basic premise of the theory is that, a given conformation by one molecule places restrictions on the conformations which could be taken by others, and this restriction of the total number of configurations increases with a decrease in temperature. The transition from one configuration to another is associated with an energy barrier $\Delta E$ and determines the transport or relaxation properties of a glass-forming material. Central to the Gibbs-DiMarzio theory is the determination of a configurational partition function $Q$, from which the expression for configurational entropy can be calculated. The application of the partition function assumes an equilibrium state. Accordingly the glass transition is predicted to occur when the configurational entropy $S_C$ reaches a critical small value. According to Meyer-Flory-Huggins lattice calculations [Flo53], $S_C$ becomes zero at a finite temperature $T_2$ at which a second order transition in the Ehrenfest [Cal60] sense occurs. At this temperature the number of accessible configurations, $W$, allowed by the amorphous phase partition function appropriate to higher temperatures tends to unity. Once the partition function $Q$ is formulated, the entropy can be calculated from statistical thermodynamics as
\[ S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,n} + k \ln Q \]  

(2.70)

from which all the necessary calculations can be made.

In infinitely slow experiments a glassy phase should eventually emerge where the entropy of the amorphous phase compares to that of the crystalline phase. This was the resolution of the Kauzmann [Kau48] paradox in which it was noted that, for most glass formers, an extrapolation of the super cooled entropy below \( T_g \) crosses the associated crystalline value at a non zero temperature \( T_K \) (the Kauzmann temperature). This would require that some changes in thermodynamic and inferentially relaxation properties of the equilibrium liquid must change in some way at or above \( T_K \) to avoid this paradoxial situation. \( T_K \) is identified as the equilibrium glass transition temperature.

Although the thermodynamic theories are successful in determining the quantitative correlations of the glass temperature with molecular weight [Gib59], random copolymer composition [DiM59] and diluents [DiM63] and with known chain stiffness parameters [DiM57], they do not provide the form of heat capacity temperature relation to be expected near \( T_g \) partly because of the difficulty in deciding the exact form of the partition function as \( W \rightarrow 1 \). Moreover, they suffer a great drawback in that a true equilibrium second order glass transition is experimentally yet to be observed. They also lack information about the kinetics involved in the transition region with which experimental observations can be compared.

2.3.3 Free volume theories

The glass transition exhibits certain kinetic characteristics in that it is strongly influenced by the rate of cooling or heating as well as the duration of loading and
frequency of an applied stress. In this respect, the glass state in polymers is thermodynamically a non-equilibrium state. In order to describe such a state an internal order parameter in addition to the usual variables of state is necessary. Fox and Flory [Fox50] proposed that this order parameter should be a free volume and they hypothesised that the glass transition results from the decrease of the free volume of the amorphous phase below some characteristic value. Consequently the molecular mobility at the glass transition is drastically reduced so that a non-equilibrium state would become frozen resulting to an iso-free volume state.

There are many theories [Turn60, Fer80, Shen66, Kov64] which require, as prerequisite of the glass transition, the existence of a free volume. These theories generally apply the lattice model [Flo56, Mey39] and base their arguments on the temperature dependence of molecular transport properties such as fluidity (\(\phi\)) (which is related to viscosity) and the self-diffusion constant \(D\) in the glass transition region. In this section a detailed outline of the free-volume theory of Sanchez [San74] is given.

Basing on the hole theory of the liquid state proposed by Erying [Ery36] and Frenkel [Fre46], Sanchez treats the liquid or polymer melt as a mixture of molecules and holes, with the molecules occupying some lattice sites while the other sites are empty. The holes are considered to be pseudo-particles with zero chemical potential (\(\mu = 0\)). The number \(N_0\) of the holes is temperature dependent and Sanchez’s theory calculates among others the energy change due to the introduction of new holes in a glass forming system. By assuming a random mixing of the holes and the molecules, the change in entropy is approximated by

\[
\Delta S = -R \left( N_0 \ln v_0 + N_1 \ln v_1 \right)
\]

(2.71)

where \(N_0\) and \(N_1\) are the numbers of holes and molecules respectively and \(v_0\) and \(v_1\) are the volume fractions of the holes and the molecules.
The total change of the Helmholtz free energy $\Delta F$ that is associated with the introduction of $N_0$ holes in a liquid initially free of holes is given by

$$\Delta F = v_1 N_0 E_h + RT (N_0 \ln v_0 + N_1 \ln v_1)$$  \hspace{0.5cm} (2.72)

where $E_h$ is the energy required to produce a hole and $R$ is the gas constant.

The equilibrium number of holes is determined by minimising the free energy functions with respect to $N_0$. This is satisfied by either

$$\frac{\partial \Delta F}{\partial N_0} = 0 \text{ or } \frac{\partial \Delta G}{\partial N_0} = 0$$ \hspace{0.5cm} (2.73)

where $\Delta G$, is the change in the Gibbs energy. Equation 2.73 is equivalent to the requirement that the chemical potential $\mu$ of the holes be zero and for a small hole fraction the minimisation of the free energy leads to

$$v_0 \approx \exp \left\{ 1 - \frac{1}{r} - \frac{E_h}{RT} \right\}$$ \hspace{0.5cm} (2.74)

where $r$ is a measure of the molecule size and is proportional to the molecular weight. To obtain a complete equation of state the hole volume fraction $v_0$ must be related to the macroscopic volume $V$. By using the lattice model, the following relations are obtained,

$$V = (r N_1 + N_0) V_h$$ \hspace{0.5cm} (2.75)

where $V_h$ is the hole volume and

$$N_0 = v_0 \left( \frac{r N_1}{1 - v_0} \right)$$ \hspace{0.5cm} (2.76)
Substitution of (eq 2.76) in (eq 2.75) yields

\[ \frac{1}{V} = \frac{1 - v_0}{V_0} = \frac{v_1}{V_0} \]  

(2.77)

with \( V_0 = (rN_1)V_h \) being the hard core volume of the \( N_1 \) molecules.

The thermal expansion coefficient for a glass forming liquid can be expressed as

\[ \alpha = \alpha_h + \alpha_0 \]  

(2.78)

where \( \alpha_h \) is the thermal expansion of the liquid associated with the changes in the hole concentration and \( \alpha_0 \) is the contribution due to the thermal expansion of the occupied volume. It is in fact assumed that below \( T_g \), the thermal expansion of the glass is equal to \( \alpha_0 \) and above \( T_g \), \( \alpha = \alpha_h + \alpha_0 \). This assumption is justified by the fact that below \( T_g \) the holes are frozen in the glass matrix, whereas above \( T_g \) changes in the hole concentration will occur. Since the hard core volume \( V_0 \) and \( \alpha_0 \) are considered to be independent of temperature and pressure, it follows from equation 2.77 that

\[ \alpha_h = \left. \frac{\partial \ln V}{\partial T} \right|_P = \left. \frac{\partial v_0}{\partial T} \right|_P \cdot \frac{1}{1 - v_0} \]  

(2.79)

Substitution of (2.74) in (2.79) leads to

\[ T \alpha_h = \frac{E_h}{RT} \cdot \frac{1}{\exp\left\{ 1 - \frac{1}{r} + \frac{E_h}{RT} \right\} - 1} \]  

(2.80)

For polymeric liquids \( \frac{1}{r} \approx 0 \), and \( T \alpha_h \) is mainly a function of \( \frac{E_h}{RT} \).

The change in the thermal expansion coefficient \( \Delta \alpha \) occurring in the glass transition can thus be identified with \( \alpha_h \) and at \( T_g \).
\[ T_{g\alpha_h} = T_{g\Delta\alpha} \] (2.81)

Sanchez has shown that \( T_{g\Delta\alpha} \) has a maximum value of 0.159 corresponding to \( \frac{E_h}{RT} = 0.841 \).

By utilising the viscosity theory of Cohen and Turnbull [Coh59] in which it is required that a critical volume \( v^* \) must be available to a molecule before a diffusive motion can occur, and the temperature dependence of the viscosity given by the Doolittle [Doo51] equation

\[ \ln \eta = \ln A + \frac{B}{T + T_0} \] (2.82)

the viscosity \( \eta \) can be expressed explicitly as a function of free volume

\[ \eta = A \exp \left[ \frac{B v^*}{v_f} \right] \] (2.83)

where \( B = 2.303C_1C_2 \) and \( C_2 = T_g - T_0 \) and \( C_1, C_2 \) are the WLF constants [Wil65]

The total probability of finding a hole of size exceeding \( v^* \) is

\[ p(v > v^*) = \exp \left( -\gamma \frac{v^*}{v_f} \right) \] (2.84)

where \( v_f \) is the average free volume associated with a molecule, \( v \) is the volume of the hole, and \( 0.5 < \gamma < 1 \).

The viscosity expression obtained by relating the viscosity and diffusion is

\[ \ln \eta = \ln \eta_0 + \gamma \frac{v^*}{v_f} \] (2.85)
Defining \( N \) as the number of diffusive segments in a polymeric molecule of size \( r \), and \( r_m \) as the size of the mobile segment such that

\[
N = \frac{rN_1}{r_m} = \frac{V_0}{v_m}
\]  

(2.86)

where \( v_m \) is the hard core volume of the mobile segment and further using the definition of the average free volume \( v_f \) according to Gibbs and DiMarzio [Gib58], Sanchez obtained an expression for the average free volume by postulating that the temperature \( T_2 \) where the viscosity should become infinity is equivalent to the Vogel temperature \( T_0 \).

\[
v_f = v_m \left( \frac{V - V_\infty}{V_0} \right)
\]  

(2.87)

\( V_\infty \) is the macroscopic volume of the liquid at \( T_0 \). Substituting (2.87) into (2.85) gives

\[
\ln \eta = \ln \eta_0 + \left( \frac{\gamma v^*}{v_m} \right) \cdot \left( \frac{V_0}{V - V_\infty} \right)
\]  

(2.88)

or from (2.77)

\[
\ln \eta = \ln \eta_0 + \left( \frac{\gamma v^*}{v_m} \right) \cdot \left( \frac{[1 - v_0(T)] [1 - v_0(T_0)]}{v_0(T) - v_0(T_0)} \right)
\]  

(2.89)

Equation (2.88) is significant because it shows that the fundamental relaxation time associated with diffusive motions is determined by the excess volume
(V₀ - V∞) above T₀. This is a postulate similar to the one of Adams and Gibbs[Ada65] except that they argued that the relaxation time is governed by the excess configurational entropy above T₂ or T₀.

Expanding (2.88) in a Taylor series about T₀ one obtains

\[ \ln \frac{\eta}{\eta_0} \approx \gamma \frac{v^*}{v_m} \frac{V_0}{\alpha_\infty V_\infty} \frac{1}{T-T_0} \]  

(2.90)

where \( \alpha_\infty = \alpha_h(T_0) \).

With \( E_h = 2RT_0 \), the higher terms in the Taylor series go to zero and equation (2.88) compares with the Vogel equation to give for the parameters

\[ A = \ln \eta_0, \quad B = \gamma \frac{v^*}{v_m} \frac{V_0}{\alpha_\infty V_\infty} \]  

(2.91)

and the Cohen Turnbull parameter

\[ \gamma \frac{v^*}{v_m} = \frac{0.254C_1C_2}{T_0} = \frac{1.01C_1C_2}{E_h} \]  

(2.92)

The hole energy \( E_h \) thus completely characterises the volume-temperature behaviour of the polymer. Assuming that the relaxation times associated with mechanical or dielectric relaxation processes are proportional to the viscosity, then the relation

\[ \eta \propto \zeta \propto \tau \]  

(2.93)

holds where \( \zeta \) is the coefficient of friction. This relation follows directly from the Rouse [Rou53] model and has been experimentally shown to hold for a number of polymer melts [Mer65].

Further comparison with the Vogel equation gives for the activation parameter
According to Ferry, [Fer80]

\[
C_1^g = \frac{1}{2.303 f_g} \quad \text{and} \quad C_2^g = \frac{f_g}{\Delta \alpha}
\]

Knowing the free volume fraction at \( T_g \), the change of the thermal expansion can be determined. Sanchez obtained expressions for the volume fraction of the holes at \( T_g \) and the change of the thermal expansion coefficient as

\[
v_0(T_g) = \exp \left(1 + \frac{2T_0}{T_g}\right)
\]

(2.95)

and

\[
\alpha_h(T_g) = \Delta \alpha = \frac{2(T_0/T_g)}{\exp(1+2T_0/T_g) - 1}
\]

(2.96)

### 2.3.4 Relaxation Behaviour of the Glass-Formers near the glass transition: the Concept of Co-operativity.

The peculiar slowing down of the relaxation processes at \( T_g \) in under-cooled liquids is a characteristic behaviour of most glass formers within the glass transition region. This effect has been identified as being due to a co-operative phenomenon such that the inter-atomic and spatial correlations in the glass state are determined by the extent of co-operative molecular rearrangements. One of the problems which has become of primary interest in the recent times, for both experimental and theoretical work, is to determine the length scale of the spatial correlations leading to co-operativity.
The concept of co-operativity was first used by Adam and Gibbs [Ada65] to interpret relaxation and viscosity properties of glass forming liquids. These authors derived an expression for the probability of the co-operative rearrangement involved in the relaxation or viscous flow process by finding the minimum size of a molecular group (CRR) capable of independent rearrangement at a given temperature. The temperature dependence of the relaxation behaviour is governed by the temperature variation of the size of the co-operatively rearranging region. This co-operatively rearranging region is defined to be the smallest unit that can undergo a transition to a new configuration without simultaneous configurational change on or outside its boundary (no interaction). The main idea of AG is that the number of units that co-operatively rearrange increases with decreasing temperature, and the potential energy barrier for the transition is proportional to this number $z$

$$E_a = z \Delta \mu$$

(2.97)

where $\Delta \mu$ is the potential energy per molecule hindering rearrangement and is independent of $z$ and $T$. The rearrangement probability and hence the size of each CRR could be expressed as a function of the total configurational entropy $S_c$ given by

$$W(T) = A \exp \left( \frac{-C}{TS_c} \right)$$

(2.98)
\[ z^*(T) = \frac{N_A s^*}{S_c(T)} \]  

(2.99)

where in (2.90) C is a constant containing the term \( \Delta \mu \) and in (2.91) \( z^*(T) \) is the minimum size of a co-operative unit. \( s^* \) is the entropy of the smallest CRR. and \( N_A \) is the Avogadro number. \( S_c \) is a function of the change \( \Delta C_P \) of heat capacity given by

\[
S_c = \int_{T_0}^{T} \Delta C_P d \log T
\]

(2.100)

where \( T_0 \) is the temperature at which \( S_c = 0 \).

A general relationship between the relaxation time, the temperature and heat capacity change can be obtained since \( \Delta C_P \) can be measured at \( T_g \). Assuming that \( \Delta C_P \) is entirely configurational [Hog91, Ang91], \( \Delta C_P \) can be approximated as \( \Delta C_P(T) \approx c / T \), where \( c \) is a constant. This approximation leads to a relaxation time \( \tau \) given by

\[
\tau = \tau_0 \left( \frac{D T_0}{T - T_0} \right)
\]

(2.101)

Equation (2.101) is equivalent to the Vogel equation with the parameter \( D \) determining the Fragility of a glass former.

Using similar thermodynamic and molecular arguments (isomeric-state theory) Matsuoka [Mat90] has derived a relation of the size of the domain of co-operatively relaxing dipoles with temperature as
where $T^*$ is the temperature at which co-operativity starts to set in. According to Matsuoka this temperature should be universal for most glass formers and should be approximately equal to 500°C which however is questionable. Miller et. al [Mil68] have applied the Adams-Gibbs and free-volume theories of polymer melt viscosity to Polymethylene chain and obtained $z^* = 5$ as the number of monomer segments (-CH$_2$-) in a co-operative unit at $T_g$.

2.3.5 The thermokinetic fluctuation theory

The thermokinetic fluctuation theory of the glass transition proposed by Donth [Don92] bases on the higher intermolecular correlations at $T_g$ which lead to sizes of co-operatively rearranging regions large enough that thermodynamic analysis can be applied. By applying thermodynamic fluctuation theory [Lan69], Donth derived an expression for the volume of a CRR taking temperature as the thermodynamic activity.

$$V_a(T_g) = \frac{kT_g^2 \Delta C_P^{-1}}{\rho \delta T^2}$$  \hspace{1cm} (2.103)

where $\rho$ is the density of the bulk material and $(\Delta C_P)^{-1}$ is the relaxation strength of the reciprocal specific heat at constant pressure. Considering $V_a$ as a sphere with radius $\xi$, the characteristic length scale of the glass transition is obtained from

$$\xi = (3V_a / 4\pi)^{1/3}$$  \hspace{1cm} (2.104)
Different thermodynamic activities such as pressure and concentration should yield different characteristic lengths however their temperature dependence should be the same since according to Donth all activities are guided by the same WLF scaling. For example the volume of co-operativity is related to fluctuation of concentration as

\[ \langle \delta \phi^2 \rangle = \frac{kT}{v(V_a)} \Delta \left( \frac{\partial^2 G}{\partial \phi^2} \right)^{-1} \]  

(2.105)

The temperature dependence of \( V_a \) is given by

\[ V_a \propto N_a \propto (T - T_0)^{-2} \]  

(2.106)

Therefore the characteristic length should scale with temperature as

\[ \xi_a \propto (T - T_0)^{-\nu} \]  

(2.107)

with exponent \( \nu = 2/3 \) (or \( 2/d \) for any dimension \( d \geq 1 \) [Fis92, Don92]

2.3.6 The coupling Scheme

In order to describe segmental relaxation and glass transition behaviour of polymers, Ngai [Nga80, 88] developed the coupling scheme which bases on the fact that relaxation processes in complex systems are co-operative. The essence of the model is that conformational relaxation of a single chain in bulk is unobserved because this primitive relaxation is retarded by inter-chain interactions and correlations among the elements comprising the system. The coupling among the primary species provides a time-dependent effect on the relaxation rate. The theoretical context of a time dependent relaxation rate is
based on classic Liouville dynamics [Gold80] supplemented by an extension of the Dirac constraint theory to time dependent constraints [Dir64]. At times longer than time $t_c = 1/W_c$ characteristic of the strength of intermolecular coupling, the initially constant relaxation rate $W_0$ slows down. For thermorheologically simple systems, the effect of the coupling in the relaxation rate is given by

$$W(t) = W_0 f(t)$$  \hspace{1cm} (2.108)

where $f(t) = \begin{cases} 1 & \text{if } W_c t < 1 \\ (W_c t)^{-n} & \text{if } W_c t > 1 \end{cases}$ and $0 < n < 1$ \hspace{1cm} (2.109)

In these expressions, $(w_c)^{-1}$ is the time characteristic of the system and $n$ is a parameter characterising the coupling strength between the primary species. This same parameter also measures the extent of co-operativity. If the time-temperature correspondence holds, the evolution of the normalised relaxation function $\phi(t)$ for a single relaxation mechanism can be written as

$$\frac{d\phi}{dt} = -W_0 f(t) \phi$$ \hspace{1cm} (2.110)

For polymers around the dynamic glass transition and above, intermolecular coupling or co-operativity is important so that

$$\frac{d\phi(t)}{dt} = -W_0 (W_c t)^{-n} \phi$$ \hspace{1cm} (2.111)

From equation, the KWW equation is obtained

$$\phi(t) = \exp(-t/\tau^*)^{1-n}$$ \hspace{1cm} (2.112)
with \[ \tau^* = \left[ (1 - n)(wc)^n \tau_0 \right]^{1/(1-n)} \]

where \( \tau^* \) is the effective relaxation time of a complex system, and \( \tau_0 = (w_0)^{-1} \) is the primitive relaxation time.

The predictions of the coupling model for relaxation times in dielectric, mechanical, and density fluctuations [Nga88] variables are given by

\[ \tau_i^* = \left[ (1 - n_i)(W_c)^{n_i} (W_{0i})^{-1} \right]^{1/(1-n_i)} \quad (2.113) \]

where \( i \) stands for the type of variable used. Since the friction coefficient near \( T_g \) varies rapidly with temperature and as was shown in eq.(2.93), \( (W_{0i})^{-1} \) are proportional to friction coefficient \( \zeta \), with

\[ \zeta \approx \exp \left[ \frac{B_0}{T - T_0} \right] \quad (2.114) \]

so that (eq. 2.113) becomes

\[ \tau_i^* \approx \exp \left\{ \frac{B_0}{(1 - n_i)(T - T_0)} \right\} \quad (2.115) \]

where \( i \) represents dielectric, mechanical, and density fluctuation relaxations respectively. Since \( \tau_i^* \) is related to the mean relaxation time \( \tau_i \) by [Nga88]

\[ \tau_i = \int_0^\infty \exp \left[ -t \frac{s}{\tau_i^*} \right] dt = \frac{\tau_i^*}{1 - n_i} \Gamma \left( \frac{1}{1-n_i} \right) \quad (2.116) \]

where \( \Gamma \) is the gamma function, and \( \tau \) is given by the Vogel equation
\[ \tau = \tau_0 \exp \left[ \frac{B}{\alpha(T - T_0)} \right] \quad (2.117) \]

where \( \alpha \) is the coefficient of thermal expansion.

Substituting (2.117) in (2.116) one obtains for the activation parameter \( B \) from the three relaxation processes,

\[ B_{\text{die}} = \frac{B_0}{1 - n_{\text{die}}} \]
\[ B_{\text{mech}} = \frac{B_0}{1 - n_{\text{mech}}} \]
\[ B_{\text{dens}} = \frac{B_0}{1 - n_{\text{dens}}} \quad (2.118) \]

leading to the invariance relation

\[ (1 - n_{\text{die}})B_{\text{die}} = (1 - n_{\text{mech}})B_{\text{mech}} = (1 - n_{\text{dens}})B_{\text{dens}} = B_0 \quad (2.119) \]

which allows for comparison of data obtained using different techniques. \( B_0 \) can for example be determined using Brillouin-Scattering [Wyn92].

Ngai et al [Nga92] have applied this model to describe relaxation behaviour in polymer mixtures. As will be discussed later in chapter 4, the conclusions drawn from this model are based on the requirement that the system in question should be thermorheologically simple so that the time-temperature superposition holds. This requirement is however not satisfied in most polymer mixtures.

### 2.4 Glass transition behaviour in miscible polymer blends
A simple and commonly used method to analyse the miscibility of polymer blends, is the determination of their glass transition temperatures \( T_g \) as a function of composition. It is well known [Ola79, Chan88, Lin88] that a single-phase homogeneous blend will have only one glass transition while a multiphase, partially miscible or immiscible blend will exhibit two transitions. Numerous equations have been proposed to correlate the dependence of the \( T_g \) of a miscible blend and its composition. These equations are usually derived from free volume theories or thermodynamic arguments [Gor77, Woo58]. The thermodynamic approach is based on the characteristic continuity of extensive thermodynamic variables and the discontinuity of their derivatives at the glass transition temperature \( T_g \). Based on the thermodynamic arguments and assuming continuity of the configurational entropy at \( T_g \), Couchmann - Karasz and Couchmann [Cou78] obtained relations to predict the \( T_g \) composition dependence of binary mixtures. For a blend the molar entropy \( s \) is expressed as

\[
S = \phi_A S_A + \phi_B S_B + \Delta S_{mix} \tag{2.120}
\]

where the excess entropy of mixing \( \Delta S_{mix} \) includes all excess entropy changes (conformational, thermal etc.).

For small molecular mixtures \( \Delta S_m \) would be solely configurational while for mixed high polymers it would be conformational. Assuming the excess entropy of mixing to be continuous at \( T_g \), a general relation results giving \( T_g \) as a function of the pure component properties:

\[
\ln T_g = \frac{w_1 \Delta C_{p_1} \ln T_{g_1} + w_1 \Delta C_{p_2} \ln T_{g_2}}{w_1 \Delta C_{p_1} + w_2 \Delta C_{p_2}} \tag{2.121}
\]
where $T_g$ is the glass transition of the blend, $w_i$ is the weight fraction of component $i$ and $\Delta C_{p,i}$ is the difference in the specific heat capacity between the liquid and the glassy state at $T_g$. Proceeding in a similar manner but using volume continuity condition at $T_g$ leads to the relation

$$T_g = \frac{\phi_1 \Delta \alpha_1 T_{g_1} + \phi_2 \Delta \alpha_2 T_{g_2}}{\phi_1 \Delta \alpha_1 + \phi_2 \Delta \alpha_2}$$

(2.122)

where $\phi_1$ and $\phi_2$ are molar volumes and $\Delta \alpha_1, \Delta \alpha_2$ are the isobaric volume expansivity increments derived from $\alpha_i = \frac{1}{V_i} \left( \frac{\partial V}{\partial T} \right)_P$.

In the case where $\Delta C_{p1} = \Delta C_{p2}$ and applying the logarithm expansion in equation (2.121) leads to the Fox equation [Fox56]

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

(2.123)

It is notable however that the thermodynamic theories of glass transition are equilibrium theories that successfully predict the location of the glass transition temperature but do not predict the kinetic properties.

Another outstanding feature of the glass transition in miscible blends is the broadened temperature range of the transition as compared to the pure components. A similar effect has been observed in polymer-plasticizer systems and the width of the transition can be used as a measure of the strength of interactions between the blend components [Fe86, Kim89].

The broadening of the glass transition is attributed to concentration fluctuations in the mixture which are in excess of the normal thermal fluctuations in density observed in pure components. These fluctuations become frozen into the glassy state on cooling and influence the range of temperatures over which molecular motions become active on subsequent heating. The magnitude of the fluctuations
increases as the affinity of the components of the mixture for each other decreases. At the extreme limit of phase instability these fluctuations become macroscopic. Weaker interactions are expected to permit larger equilibrium fluctuations in composition. However for a given composition, the variation of $T_g$ in the mixture will be larger the greater the difference $T_{gB} - T_{gA}$. This difference plays an important role in determining the temperature dependence of the relaxation time distribution in the mixtures as will be shown later.

To assess the relative magnitude of composition fluctuations from thermal data, it is necessary to normalise the observed glass transition width $\Gamma$ for the difference in $T_g$s of the components. Pomposo et al [Pom93] have used for the corrected width $\Gamma_c$, the expression:

$$\Gamma_c = \frac{\Delta \Gamma}{\Delta \Gamma_{\text{max}}}$$

(2.124)

where $\Delta \Gamma$ is the difference between the experimental width and the width of the additive component and $\Delta \Gamma_{\text{max}}$ represents the potential width minus the additive breath (fig. 2.4). The potential width is the difference between the end point of the transition region for the higher $T_g$ component and the onset temperature for the lower $T_g$ component as shown schematically in Figure 2.4.
Figure 2.4. Schematic presentation of the glass transition behaviour in pure components compared to blends. Curve $D$ stands for a blend which would show a maximum broadened glass transition.

![Graph showing the glass transition behaviour](image)

Figure 2.5 Normalised width of the glass transition region as a function of composition for blends of PS/ $P(CHA\text{-}BMA)$

Figure 2.5 shows the corrected widths of the glass transition for CHA-BMA / PS blends, which shows a maximum between $\phi_{PS} = 0.3$ and 0.4.

It follows from eq.(2.124) that if the experimental width is equal to the additive width, $\Gamma_c = 0$ and if the experimental width is equal to the maximum potential width, $\Gamma_c = 1$. The fact that $\Gamma_c$ is very much less than 1, implies that very small concentration fluctuations will be present in these blends. It is however notable that the transition width analysis gives only a qualitative picture of the extent of the influence of the concentration fluctuations. An obvious goal would be to seek for a quantitative determination of the level of the concentration fluctuations present in the mixtures.
2.5 Concluding Remarks

A thermodynamic theory to describe the phase behaviour of polymer-polymer mixtures based on the Flory-Huggins lattice model has been presented. By use of equilibrium fluctuation theory, the concentration fluctuations in mixtures are related to structural parameters and to important experimentally accessible variables. Theories describing the glass transition process in single component systems have also been outlined and extended to describe the composition dependence of the glass transition temperature in mixtures.
3. Relaxation in the Linear Response Regime.

3.1 Linear relations

Systems whose responses can be described by relations linear in the external forces imposed on them are called linear systems. Denoting the displacement of a system at time $t$ by $R(t)$ and the corresponding external action by $A(t)$ the linear relation for an isotropic system can be expressed in the form

$$R_\mu(t) - <R_\mu> = L_{\mu\mu}A_\mu(t)$$

(3.1)

where $\mu$ distinguishes the kinds of vector or tensor components and $<R_\mu>_0$ is the equilibrium value in the absence of external forces.

In the case in which various processes coexist, the effect of the various kinds of forces is obtained by using the Boltzmann superposition principle [Bolt76]

$$R_\mu(t) - <R_\mu> = \sum_\nu L_{\mu\nu}A_\nu(t)$$

(3.2)

with $L_{\mu\nu}$ being identified as the kinetic coefficients[Ons31, Sch89]. Relation (3.2) is however only applicable to slowly varying linear irreversible processes with an instantaneous response to the forces. When the response lags the forces, all aftereffects due to forces prior to time $t$ must be superposed. This follows from the principle of causality, according to which the present state results from the past cause. The system in question becomes non-Markovian [Eva82] and equation (3.2) takes the form

$$R_\mu(t) - <R_\mu> = \sum_\nu \int_{-\infty}^{t} dr' \sum_\nu \Phi_{\mu\nu}(t-t')A_\nu(t')$$

(3.3)
The first term on the right-hand side denotes a contribution whose delay can be neglected whereas the delay of the second term cannot be neglected. Macroscopic systems with a large number of degrees of freedom lose memory of the effect of the past values of the forces with time so that

$$\lim_{t \to \infty} \Phi_{\mu \nu} (t - t') = 0$$  \hspace{1cm} (3.4)$$

For the case where the temporal variation of the forces are so slow that the forces may be regarded constant during a time interval \( \tau \) above which the convergence to zero in (3.4) holds, the following expression is obtained

$$R_\mu (t) - \langle A_\mu \rangle_0 = 4 \sum_{\nu} \chi_{\mu \nu} A_\nu (t) + \int_0^\infty ds \sum_{\nu} \Phi_{\mu \nu}(s) A_\nu (t - s)$$  \hspace{1cm} (3.5)$$

where \( s = t - t' \) is the integration parameter in the second term of equation (3.3). The main contribution to the integral comes from range of \( s < \tau \). By considering the action to be instantaneous in a given time scale, the time dependence of the force may be expressed by the Dirac \( \delta \) function (Fig. 3.1)

$$A_\nu (t) = \delta_{\mu z} \delta (t - t_1)$$  \hspace{1cm} (3.6)$$

where \( z \) denotes the direction of action of the external force. Substituting eq. (3.6) into (3.3) and introducing a step function external force

$$A_0(t) = \theta (t_1 - t)$$  \hspace{1cm} (3.7)$$

with \( \theta \) being the Heavyside unit step function defined as
\[ \theta(x) = \int_{-\infty}^{x} dx' \delta(x') = \begin{cases} 1 & (x > 0) \\ 0 & (x < 0) \end{cases} \] (3.8)

leads to

\[ R_{\mu}(t) - \langle R_{\mu} \rangle_0 = \chi^{\infty}_{\mu \xi} \delta(t-t_1) + \Phi_{\mu z}(t-t_1) \theta(t-t_1) \] (3.9)

\( R(t) = \langle R_{\mu} \rangle \) (at \( t < t_1 \)). The first term in (3.9) represents the instantaneous response to the pulsed force, while the second is the effect of the pulsed force remaining after time \( t_1 \): \( R(t) - \langle R \rangle = \Phi_{\mu z}(t-t_1) \) (\( t > t_1 \))

From equation (3.4) the system will return to thermal equilibrium in long time \( t_1 \) (Fig. 3.1). The function \( \Phi \) is called the **aftereffect** (Nachwirkungsfunktion) or the **linear response function**.

**Figure 3.1:** Response to a pulsed force
3.2 Relaxation

Relaxation means the time-dependent return to equilibrium of a system that has been perturbed by a change in an applied constant field. Among the common fields are mechanical, thermal as well as electrical and magnetic stresses, for each of which a given system will exhibit a characteristic frequency-dependent response.

The integral of the response function $\Phi(t)$ gives a relaxation function $\psi(t)$

$$\psi_{\mu\nu}(t) = \int ds \Phi_{\mu\nu}(s)$$  \hspace{1cm} (3.10)

The inverse gives the response function as

$$\Phi_{\mu\nu}(t) = -\frac{d\psi_{\mu\nu}(t)}{dt}$$  \hspace{1cm} (3.11)

When the convergence of the response function is sufficiently rapid and the integral in (3.10) converges then

$$\lim_{t \to \infty} \psi_{\mu\nu}(t) = 0$$  \hspace{1cm} (3.12)

which means that $R_\mu(t)$ converges towards $<R_\mu^0>$.

Response due to a harmonically oscillating force can be described by a superposition of harmonic oscillations.

$$A_{\nu}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} A_{\nu, \omega}$$  \hspace{1cm} (3.13)
3 Relaxation in the linear response regime

\( R_\mu(t) - <R_\mu> = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} R_{\mu,\omega} \)  \hspace{1cm} (3.14)

with

\[ A_{\nu,\omega} = \int_{-\infty}^{\infty} dt e^{i\omega t} A_{\nu}(t) \hspace{1cm} (3.15) \]

\[ R_{\mu,\omega} = \int_{-\infty}^{\infty} dt e^{i\omega t} \{ R_{\mu}(t) - <R_\mu> \} \hspace{1cm} (3.16) \]

Substituting (3.5) in (3.16) and (3.13) into the right hand side of eq. (3.5) gives the Fourier transform of the linear relation

\[ R_{\mu,\omega} = \sum_\nu \chi_{\mu\nu}(\omega) A_{\nu,\omega} \hspace{1cm} (3.17) \]

where the formula for the Dirac \( \delta \)-function was used

\[ \delta(x) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{i\omega x} \hspace{1cm} (3.18) \]

and

\[ \chi_{\mu\nu}(\omega) = \chi_{\mu\nu}^{\infty} + \int_{0}^{\infty} dt e^{i\omega t} \Phi_{\mu\nu}(t) \hspace{1cm} (3.19) \]

is the complex admittance.
The characteristic relaxation frequencies are of particular importance because unlike resonance frequencies, they are highly temperature dependent. Experimentally it is easier to measure either the relaxation function or the response to harmonic forces by measuring the complex admittance. In particular the part of the complex admittance related to energy dissipation is of great interest because the energy dissipation in relaxation processes is associated with long-range irreversible motion of particles. Thus, the relaxation spectra provide a means of studying mass transport and configurational rearrangements mechanisms, occurring during the glass transition, of the molecular constituents of glass-forming materials induced by the external fields. Many different techniques may be applied in the study of system responses to each of the various stresses referred to above and the choice of a particular technique will usually depend on the frequency range being investigated (Fig. 3.2).

*Figure 3.2:* Range of frequency accessible to some techniques for studying responses of systems to external exciting external stresses. FI stands for free induction decay and SE for solid echo.
3.1 Dielectric Relaxation.

When the constraint that undergoes a change is an electric field, the observable quantity that varies with time is the polarisation (P) giving rise to dielectric relaxation. Among the contributions to the total polarisation, orientation polarisation is most important because it depends directly on the internal structure of the molecules of the dielectric.

The application of a constant electric field $\mathbf{E}$ to a dielectric results into the development of an electric displacement $\mathbf{D}$ that increases with time until a constant value is reached at sufficiently long time (Fig. 3.3).

![Figure 3.3](image)

*Figure 3.3*  
Relaxation after removal of the external field

After the removal of the electric field, the electric displacement returns with time to zero. For sufficiently small electric displacements $\varepsilon = \mathbf{D}/\mathbf{E}$ the system
Relaxation in the linear response regime can be treated as linear and consequently conforms to the superposition principle. The electric displacement can be expressed as a function of the applied field as

\[ \mathbf{D}(t) = [\varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\Phi(t)]\mathbf{E}(t) \]  

(3.20)

where \( \Phi(t) \) is a built-up normalised dielectric function (Fig. 3.4) whose extreme values are

\[ \Phi(t) = 1 - \phi(t) = 0, \text{ for } t = 0 \]  

(3.21a)

and

\[ \Phi(t) = 1 - \phi(t) = 1, \text{ for } t = \infty \]  

(3.21b)

\[ \phi(t) \] is the normalised decay or response function of the polarisation when a steady macroscopic electric field is removed from the medium.

If an electric field is applied at time \( t = 0 \) and it increases by an infinitesimal amount \( d\mathbf{E} \), at \( t = t' \ (0 < t' < t) \), the increase in electric displacement at time \( t \) is given by

\[ \mathbf{D}(t) = [\varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\Phi(t)]\mathbf{E}(t) \]  

(3.20)
3  Relaxation in the linear response regime

\[ \text{dD} = \varepsilon_\infty \text{dE} + (\varepsilon_0 - \varepsilon_\infty)\Phi(t - t')\text{dE} \]  
\[ (3.22) \]

In linear systems, the total displacement at a time \( t \) caused by a variable electric field \( \text{E}(t') \) is the result of superposition of all the increments, \( \text{dD} \) and

\[ D(t) = \varepsilon_0 \text{E}(t) + (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{t} \frac{d\text{E}(t')}{dt'} \Phi(t - t')dt' \]  
\[ (3.23) \]

By making the substitution \( t - t' = u \) and integrating by parts, one finds

\[ D(t) = \varepsilon_\infty \text{E}(t) + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{d\Phi(u)}{du} E(t - u)du \]  
\[ (3.24) \]

For an alternating field, \( \text{E} = E_0\exp(i\omega t) \) and equation (3.24) leads to

\[ \varepsilon^*(\omega) = \frac{D(t)}{E(t)} = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \exp(i\omega u) \left[ -\frac{d\Phi(u)}{du} \right] du \]  
\[ (3.25) \]

where

\[ -\frac{d\Phi(u)}{du} = \frac{d\Phi(u)}{du} \]

and

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \]
is the complex dielectric permittivity

Rearrangement of terms of equation (3.25) leads to

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \left( -\frac{d\phi}{dt} \right) \exp(-i\omega t) dt = L\left( -\frac{d\phi}{dt} \right)$$  \hspace{1cm} (3.26)

The first term of equation (3.26) is related to $-d\phi/dt$ through a Laplace transform. Thus by one-sided Fourier transformation of the time derivative of the decay or time correlation function $\phi(t)$ into the frequency domain one obtains the complex permittivity $\varepsilon^*$ of the system. This enables the direct comparison of dielectric spectroscopy and photon correlation data where the correlation function can directly be measured [Boe 90].

The real part $\varepsilon'$ and the imaginary part $\varepsilon''$ of the complex permittivity are connected by the Kramers-Kronig dispersion relations

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \int_0^\infty \frac{\omega x \varepsilon''(x)}{x^2 - \omega^2} dx$$  \hspace{1cm} (3.27)

$$\varepsilon''(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon'(x)}{x^2 - \omega^2} dx$$  \hspace{1cm} (3.28)

which shows that one of these quantities may be determined from the other if data over a sufficiently wide range of frequencies are available. Here $x$ indicates taking the Cauchy principal value [Kubo91].
These relations apply only for pure relaxation processes. If the dielectric is lossy, conductivity contributions at frequencies lower compared to the relaxation processes have to be subtracted [Gra78]. This will be illustrated in chapter 5.

In order to solve the integral equation (3.25) one requires to know the decay function over the entire relaxation range. For an ideal relaxation, the rate of return to equilibrium value of an observable quantity \( P \) is dependent on the deviation from the equilibrium value \( P_{\text{eq}} \) and for small fluctuations the response may be described by a linear first order approximation with the solution

\[
P - P_{\infty} \approx \exp(-t/\tau). \tag{3.29}\]

\( \tau \) is the relaxation time, which may be defined as the time in which the observable quantity is reduced to \( 1/e \) times the original value. For a dielectric relaxation involving a single relaxation time (Debye process),

\[
\phi(t) = \exp(-t/\tau) \tag{3.30}
\]

and equation (3.26) becomes

\[
\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{1 + i\omega\tau} \tag{3.31}
\]

from which the real \( \varepsilon'(\omega) \) and loss \( \varepsilon''(\omega) \) components of \( \varepsilon^* \) are given by

\[
\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2\tau^2} \tag{3.32}
\]
\( \varepsilon''(\omega) = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \) \hspace{1cm} (3.33)

In the limit of low and high frequencies, eqs. (3.31) and (3.32) lead to

\[ \lim_{\omega \to 0} \varepsilon''(\omega) = \varepsilon_0 \] \hspace{1cm} (3.34a)

and

\[ \lim_{\omega \to \infty} \varepsilon''(\omega) = \varepsilon_\infty \] \hspace{1cm} (3.34b)

---

**Fig. 3.5.** Variation of the real \( \varepsilon' \) and \( \varepsilon'' \) components of the complex dielectric constant \( \varepsilon^* \) with frequency for an ideal dielectric with a single relaxation time.
It can be seen (Fig. 3.5) that $\varepsilon'$ is a continuously decreasing function of frequency and $\varepsilon''$ approaches zero both for small and for large values of frequency, reaching a maximum at $\omega \tau = 1$.

The ratio $\varepsilon'/\varepsilon'$ is defined as the loss tangent $\tan \delta$.

Although very simple liquids obey the above equations, in polymers, the dispersion usually occurs over a wider frequency range than predicted by equation (3.10). This behaviour is commonly interpreted to be a result of many relaxation mechanisms involved in the relaxation with a different relaxation time $\tau_i$. Accordingly, $\phi(t)$ should be expressed as a weighted sum of exponential decay functions [Wil72]

$$
\phi(t) = \sum n_i \exp(-t/\tau_i) \tag{3.35}
$$

where $\Sigma n_i = 1$

This leads to the integral involving a normalised continuous distribution of relaxation times [McC67] $g[\ln(\tau)]$, so that

$$
\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{\infty} g[\ln(\tau)] d[\ln(\tau)] \frac{1}{1 + \omega^2 \tau^2} \tag{3.36}
$$

and

$$
\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_{-\infty}^{\infty} g[\ln(\tau)] \omega \tau d[\ln(\tau)] \frac{1}{1 + \omega^2 \tau^2} \tag{3.37}
$$
Knowledge of the relaxation function is paramount to interpret the dielectric behaviour of most polar systems including macromolecules.

From equation (3.26) the real and the imaginary parts of the normalised complex dielectric constant are given by

\[ \frac{\mathcal{E}'(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] \cos \omega t \, dt \]  
(3.38)

\[ \frac{\mathcal{E}''(\omega)}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[ -\frac{d\phi(t)}{dt} \right] \sin \omega t \, dt \]  
(3.39)

Equations (3.38) and (3.39) may be inverted giving

\[ \frac{d\phi(t)}{dt} = \frac{2}{\pi} \int_0^\infty \frac{\mathcal{E}'(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \cos \omega t \, d\omega \]

\[ = \frac{2}{\pi} \int_0^\infty \frac{\mathcal{E}''(\omega)}{\epsilon_0 - \epsilon_\infty} \sin \omega t \, d\omega \]  
(3.40)

Thus if one of the components of the complex dielectric function is known over the entire relaxation range, the relaxation function \( \phi(t) \) can be determined.

Integration of eq (3.39) gives

\[ \phi(t) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon_\infty - \mathcal{E}(\omega)}{\epsilon_0 - \epsilon_\infty} \sin \omega t \, d(\ln \omega) \]
3 Relaxation in the linear response regime

\[ 3.41 \]
\[ \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} \cos \omega t \, d(\ln \omega) \]

Since the normalised decay function is unity at \( t = 0 \), the relaxation strength \( \Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty \) is related to the loss permittivity by the expression

\[ 3.42 \]
\[ \Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty = \frac{2}{\pi} \int_{-\infty}^{\infty} \varepsilon''(\omega) \cos \omega t \, d(\ln \omega) \]

Several relaxation functions have been proposed to fit experimental data for real systems whose dispersions and absorption cannot be described by a single relaxation function. Among the most important are the Cole-Cole [Col41], Davidson-Cole [Dav51] and the Williams-Watts [Wil70] functions. A more generalised relaxation function was proposed by Havriliak and Negami [Hav 66] and formulated as a combination of the Cole-Cole and the Davidson-Cole equations. This function reads as

\[ 3.43 \]
\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + (i\omega \alpha)^\gamma)} \]

with \( 0 < \alpha \leq 1 \) and \( 0 < \alpha \gamma \leq 1 \)

When \( \gamma = 1 \) and \( 0 < \alpha \leq 1 \), equation (3.43) reduces to a Cole-Cole equation and when \( \alpha = 1 \) and \( 0 < \gamma \leq 1 \), it leads to the Davidson - Cole equation. When both \( \alpha \), \( \gamma = 1 \), the single time relaxation function is obtained whereas the KWW stretched exponential function is gained numerically as a Fourier transform of equation (3.43) in the time domain [Colm93].
3 Relaxation in the linear response regime

The Cole-Cole equation describes data well, where the relaxation behaviour is symmetrical about the logarithm of the maximum loss. For non symmetrical processes the Davidson-Cole, the Havriliak Negami and the KWW functions represent the experimental data well.

The real and imaginary parts of the HN function are given by

\[ \varepsilon'_{HN}(\omega) = \varepsilon_x + (\varepsilon_0 - \varepsilon_x) \frac{\cos(\gamma \varphi)}{\left(1 + 2(\omega \tau_0)^\alpha \cos \frac{\pi \alpha}{2} + (\omega \tau_0)^{2\alpha}\right)^{\frac{\gamma}{2}}} \]

(3.44)

\[ \varepsilon''_{HN}(\omega) = (\varepsilon_0 - \varepsilon_x) \frac{\sin(\gamma \varphi)}{\left(1 + 2(\omega \tau_0)^\alpha \cos \frac{\pi \alpha}{2} + (\omega \tau_0)^{2\alpha}\right)^{\frac{\gamma}{2}}} \]

(3.45)

with

\[ \varphi = \arctan \frac{(\omega \tau_0)^\alpha \sin \frac{\pi \alpha}{2}}{1 + (\omega \tau_0)^\alpha \cos \frac{\pi \alpha}{2}} \]

The parameters \( \alpha, \gamma \) and \( \tau \) can be determined at a given temperature either from a complex-plane plot as proposed by Cole [Col41] or directly by fitting experimental data.

3.3 Distribution of Relaxation times

As already pointed out, the decay functions in real systems are not simple exponential and \( \varepsilon''(\omega) \) is usually broader in frequency than given by equation (3.20) and is also skewed to high frequencies. In such cases \( \varepsilon'' \) must be described by the inclusion of a distribution function \( g(\tau) \) or \( g(\tau/\tau_0) \) for the relaxation times such that
\[
\frac{\varepsilon^*(i\omega \tau_0) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_{-\infty}^{\infty} \frac{g(\tau/\tau_0)}{1 + i\omega \tau} d\ln(\tau/\tau_0)
\]

(3.46)

with

\[
\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{g(\tau/\tau_0)}{1 + \omega^2 \tau^2} d\ln(\tau/\tau_0)
\]

(3.47)

\[
\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \int_{0}^{\infty} \frac{g(\tau/\tau_0) \omega \tau}{1 + \omega^2 \tau^2} d\ln(\tau/\tau_0)
\]

(3.48)

Key to relaxation spectroscopy on polymers is the determination of the functions \(g(\tau)\) or \(g(\tau/\tau_0)\) and examining their relationships to the glass transition, the liquid or glass structure and the molecular interaction potentials therein. By solving equation (3.46) for \(g(\tau/\tau_0)\), Davidson and Cole [Dav51] obtained the expression

\[
g(y) = \frac{1}{2\pi i(\varepsilon_0 - \varepsilon_\infty)} \left[ \varepsilon^* \left( \frac{1}{ye^{i\pi}} \right) - \varepsilon^* \left( \frac{1}{ye^{-i\pi}} \right) \right]
\]

(3.49)

where \(y = \tau/\tau_0\)

Havriliak and Negami[Hav67] substituted for iy, \(ye^{\pm i\pi}\) and obtained

\[
\varepsilon^* \left( \frac{1}{ye^{\pm i\pi}} \right) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \left( \frac{1}{ye^{\pm i\pi}} \right)^\alpha}
\]

(3.50)
with the solution

\[ g(\tau/\tau_0) = \frac{(\tau/\tau_0)^{\alpha\gamma} \sin(\gamma \theta)}{\pi \left[ (\tau/\tau_0)^{2\alpha} + 2(\tau/\tau_0)\alpha \cos(\pi \alpha) + 1 \right]^{\frac{\gamma}{2}}} \]  

(3.51)

where

\[ \theta = \arctan \left( \frac{\sin(\pi \alpha)}{(\tau/\tau_0)\alpha + \cos(\pi \alpha)} \right) \]  

(3.52)

When \( \alpha = 1 \), equation (3.50) leads the Davidson-Cole distribution function

\[ g(\tau/\tau_0) = 1 \sin \pi \gamma \left( \frac{\tau}{\tau - \tau_0} \right)^\gamma \]  

for \( \tau < \tau_0 \)  

(3.53)

and

\[ g(\tau/\tau_0) = 0 \]  

for \( \tau > \tau_0 \)

For \( \gamma = 1 \), equation (3.50) yields the Cole-Cole time distribution function

\[ g(\tau/\tau_0) = \frac{1}{2\pi} \sin \pi \alpha \{ \cosh[\alpha \ln(\tau/\tau_0)] - \cos \pi \alpha \}^{-1} \]  

(3.54)

Figure 3.6 shows the three normalised distribution functions evaluated for the parameters \( \gamma = 0.5, \alpha = 0.5 \) and \( \tau_0 = 10^3 \) s.
Normalised relaxation time distributions corresponding to (1) the Havriliak-Negami, (2) the Davidson-Cole and (3) the Cole-Cole relaxation functions evaluated for the parameters $\gamma = 0.5$, $\alpha = 0.5$ and $\tau_0 = 10^3 s$.

The two parameters $\alpha$ and $\gamma$ therefore uniquely represent the distribution of relaxation times with $\alpha$ determining the width while $\gamma$ reflects the skewness of the distribution.

An important quantity which characterises a dielectric relaxation process is its relaxation time. The determination of the mean relaxation time has recently received close attention [Zet92, Hof93] with respect to the question as to which of the averages physically represents the relaxation processes. This follows from the realisation that no unique $\tau$, independent of the method of evaluation, can be obtained from the empirical relaxation functions for real
systems. For example, in the case of the Havriliak-Negami function, the maxima for \( \varepsilon''_{HN}(\omega) \) and the corresponding \( g(\tau) \) do not coincide (\( \omega_{\text{max}} \neq \frac{1}{\tau_{\text{max}}} \)).

Although it is commonly found in the literature [Köh91, Hay92], that the characteristic time for a dielectric process is obtained from fitting the data using the Havriliak-Negami function this value should rather be identified as being the characteristic time for this relaxation function. A different \( \tau \) is obtained by taking the value at the peak maximum[Hof93]. From the relaxation time distribution function one can obtain the time averages \( <\tau> \) or \( <\log \tau> \). These two averages do not exist for the Havriliak-Negami function. The only physical meaningful averages are obtained when one works in the logarithmic scale[Zet92] leading to

\[
<\tau>_{\log \tau} = 2 \int_{-\infty}^{\infty} \tau \, g(\log \tau) \, d \log \tau \tag{3.55}
\]

\[
<\log \tau>_{\log \tau} = 2 \int_{-\infty}^{\infty} \log \tau \, g(\log \tau) \, d \log \tau \tag{3.56}
\]

A feature which reflects molecular interactions and correlation is the temperature dependence of the relaxation time distribution. A temperature dependence of the distribution will be determined by either a temperature dependence of both \( \alpha,\gamma \) or a by temperature dependencies of the parameters which are opposite in sense. It will be shown later that polymer mixtures exhibit a much stronger temperature dependence of the shape parameters compared to pure components. A procedure for describing the relaxation time distribution taking into account mixing effects will be discussed in detail for binary systems in chapter 7.
There are other models which have been used to interpret broad dispersions and absorptions. One approach relates the dispersion to the fluctuation of the free energy of a system [Sca89]. According to this approach the spectral energy associated with the fluctuation is essentially the integral of the loss tangent versus logarithm of frequency curve.

\[
<F(M^2)> - F(0) = \frac{3kT}{\pi} \int_0^\infty \frac{p''(\omega)}{p'(\omega)} d\omega 
\]

where \(\frac{p''(\omega)}{p'(\omega)}\) is the loss tangent and \(p\) stands for the polarisation.

### 3.4 Chain Dynamics

Polymers in solution and in the melt continuously change their shape and position randomly by thermal agitation. Therefore the macroscopic theory outlined in the previous section should be related to the microscopic structure of the system. This is achieved by considering the fluctuations of the dipole moment \(<M>\) which arise due to conformational changes resulting from thermal agitation. Usually such agitation lead to a Brownian motion which is known to dominate various time-dependent phenomena such as viscoelasticity, birefringence, polarity and light scattering [Ber76]. This motion is characterised by a time-correlation function \(\Phi(t)\). By considering a variable \(A\) for example the position \(r\) or the dipole moment \(\mu\), the time auto-correlation function \(C_{AA}(t)\) is given by

\[
C_{AA}(t) = <A(0) \cdot A(t)> = \iiint A(p, q, u) \cdot A(p, q, t + u) f(p, q) dp dq 
\]

where \(A(t + u)\) is the value for a molecule at time \(t + u\), given that it was \(A(u)\) at time \(u\), \(f(p, q)\) is the equilibrium-phase space-distribution function, and \(f(p,
q)dpdq is the probability that a molecule has the conjugated momenta p and coordinates q in the intervals p to p + dp and q to q + dq. For t = 0,

\[ C_{AA}(0) = \langle A^2(0) \rangle = \iint A^2(p, q, u) \cdot f(p, q) dpdq \]  \hspace{1cm} (3.60)

which is the mean square value of A in the equilibrium state that can be evaluated from time independent statistical mechanics. For large values of t, the correlation between A(u) and A(t + u) vanishes and \( C_{AA}(t) = \langle A(u) \rangle^2 \). In complex polymer systems cross-correlation between different molecules play an important role. The time cross-correlation function is defined as

\[ C_{AiAj}(t) = \langle A_i(0)A_j(t) \rangle \]  \hspace{1cm} (3.61)

where

\( A_i \) and \( A_j \) are the dynamic variable A of molecules i and j ( i \( \neq \) j )

According to Fröhlich-Kirkwood[Frö48, Böt73], the static dielectric permittivity \( \varepsilon_0 \) for an ensemble of dipolar chain molecules and the constituent dipole moments of a polymer system are related by the expression

\[ \varepsilon_0 - \varepsilon_\infty = \frac{4\pi}{3k_B T} \cdot \frac{3\varepsilon_0(2\varepsilon_0 - \varepsilon_\infty)}{(2\varepsilon_0 + 1)^2} \frac{\langle M(0) \cdot M(0) \rangle}{V} \]  \hspace{1cm} (3.62)

where M(0) is the instantaneous dipole moment of a microscopic sphere of volume V embedded in the system, and \( \langle M(0) \cdot M(0) \rangle \) is the mean-square dipole moment deduced in the absence of an applied field and evaluated over all the configurations of the ensemble contained in the sphere.

The time correlation function is define as
\begin{equation}
\Phi(t) = \frac{< M(0) \cdot M(t) >}{< M(0) \cdot M(0) >} = \frac{< \mu_0(t) \cdot \mu_j(t) > + \sum_{j \neq k} < \mu_j(0) \cdot \mu_k(t) >}{\mu^2 + \sum_{j \neq k} < \mu_j(0) \cdot \mu_k(0) >}
\end{equation}

(3.63)

where \(\mu_j(t)\) denotes the elementary dipole moment in the chain at time \(t\).

If \(t\) is very small so that very little change takes place in this interval, then \(M(t) \approx M(0)\) and the correlation function is close to unity. If, however, \(t\) is so large that considerable fluctuation takes place, then there will be little correlation between \(M(t)\) and \(M(0)\) and the correlation function approaches zero as \(t \to \infty\). Hence the correlation function contains all temporal information of the system and is therefore related to the frequency dependence of the permittivity.

For non-associated systems, the complex dielectric constant \(\varepsilon^*(\omega)\) is related to the decay function

\[
\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} \cdot \rho(\omega) = L \left( -\frac{d \Phi_0}{dt} \right)
\]

(3.64)

with

\[
\Phi_0(t) = \frac{< \mu(0) \cdot \mu(t) >}{< \mu(0) \cdot \mu(0) >},
\]

and \(\rho(\omega)\) is an internal field factor [Cook70, Wil79]. In this case the cross-correlation is zero. It follows from the correlation function, that the differences in the dielectric behaviour of polymers and simple substances arise from the cross-correlation terms appearing in equation (3.65).

3.5 Typical Dielectric Spectra
In solid polymers the relaxation function shows abrupt changes in its real and imaginary parts at frequencies which may be related to the different molecular motions of the dipolar groups. The dielectric spectra obtained can be represented by either plotting isochronous permittivities as a function of temperature, or by defining a relaxation-time distribution as a function of temperature. The shape of the distribution curve gives information about the dipole-dipole interactions. Figure 3.7 shows schematically some typical dielectric transitions.

![Figure 3.7: Typical dielectric relaxation processes.](image)

Three transitions are shown: the primary ($\alpha$-relaxation) which is a slow transition occurring at high temperatures, and two secondary transitions, the $\beta$- and the $\gamma$-
relaxation which are fast transitions. In amorphous polymers the \( \alpha \)-relaxation is associated with large-scale Brownian motion involving many chain segments. In the temperature scale the \( \alpha \)-process corresponds to the glass transition. The \( \beta \)-transition generally represents localised relaxation processes in the glassy state.

3.6 Temperature Dependence of Dielectric Relaxations

In the case of subglass relaxations, the relaxation time associated with the maximum of the absorption \( \tau = \frac{1}{\omega_{\text{max}}} \) exhibits an Arrhenius behaviour

\[
\tau = \tau_0 \exp \left( \frac{E_a}{RT} \right)
\]  

(3.65)

where \( E_a \) is the activation energy of the process.

On the contrary, the relaxation times associated with the dynamic glass transition (\( \alpha \)-relaxation) are in most systems dependent on the free volume, so that the time \( \tau \) is related to the free volume fraction \( v_f \) by the Doolittle equation [Doo57]

\[
\tau = \tau_0 \exp \left( \frac{B}{v_f} \right)
\]  

(3.66)

with \( B \) given by the Cohen-Turnbull expression [Coh54]

\[
B = \xi \frac{v^*}{v_m}
\]  

(3.67)

Where \( v^* \) is the minimum required volume for a relaxation process to take place, \( v_m \) is the mean volume of the relaxing polymer segment and
0.5 < \xi < 1. By assuming that \( v_f \) is a linear function of temperature 
\( v_f = \alpha (T - T_0) \), equation (3.66) becomes the Vogel-Fulcher-Tamman equation 
[Vog21]

\[
\tau = \tau_0 \exp \left[ \frac{B}{\alpha (T - T_0)} \right]
\]  (3.68)

\( \alpha \) is the expansion coefficient, and \( T_0 \) (commonly referred to as the Vogel 
temperature) is the temperature at which the free volume would be zero, were it 
not for the formation of the glassy state. The relative free volume corresponding 
to \( T_g \), \( \frac{v_g}{B} \) is given by

\[
\frac{v_g}{B} = \frac{\alpha (T_g - T_0)}{B \alpha}
\]  (3.69)

The parameter \( B \) is related to the minimum volume necessary for a relaxation 
process to take place. By plotting \(-\log \tau \) vs \( \frac{1}{T - T_0} \) or \( \frac{1}{\log (f_{0,VFT} / f_{\text{max}})} \) against 
temperature \( T \), (Fig. 3.4) the parameters in equation (3.68) can be determined. It 
is known for many systems, that at a characteristic temperature \( T_A \) the relaxation 
behaviour changes from the Vogel-type to an Arrhenius behaviour. This 
temperature has been identified as the temperature which marks the beginning of 
co-operativity discussed in Chap 2.

Equation (3.48) is equivalent to the William Landel Ferry (WLF) which follows 
from the free volume theory of glass transition [Hed77, McC67].

\[
\log \left( \frac{\tau}{\tau_0} \right) = -\frac{C_1 (T - T_g)}{C_2 + T - T_g}
\]  (3.70)
with

\[ C_1 \equiv \frac{B}{T_g - T_0}, \quad \log \tau_g = A + C_1 \]

\[ C_2 \equiv T_g - T_0, \quad B = C_1 C_2 \]

where the constant A results from transforming the Vogel equation in the logarithmic scale.

*Figure 3.8: Plot for determining the Vogel parameters.*

### 3.7 Concluding Remarks
Relaxation spectroscopy theory in the linear response regime has been outlined. This theory has been extended in detail to the macroscopic relations relevant in dielectric spectroscopy. A relationship between the macroscopic theory and the microscopic structural behaviour in polymers is given by a time correlation function which characterises Brownian-like motions. The influence of temperature on typical dielectric transitions is also discussed.
4 Theoretical Models to describing the $\alpha$-relaxation Behaviour in Polymer Mixtures near the Glass Transition Temperature and sub - $T_g$ $\beta$ - relaxation Process

4.1 Introduction

The $\alpha$-relaxation in polymer mixtures in the temperature window defined by $T_g \leq T < T_g + 100$ K in which the WLF temperature dependence of the relaxation time holds and the glass transition are governed by their phase behaviour which can well be described within the framework of the Flory-Huggins theory (see chapter 2). In the one phase, binary mixtures exhibit a single $T_g$ intermediate between the glass transition temperatures of the pure components, whereas phase separated samples show two or more transitions. For blend components with distinctly different $T_g$’s, the single glass transition temperature can be used as a basis for assessing miscibility. Although a necessary condition for miscibility, a single $T_g$ is however not sufficient to demonstrate thermodynamic miscibility. It is commonly observed that the temperature range of the glass transition is broader in mixtures than in the pure components (Fig. 2.4). This broadening effect is also reflected in $\alpha$-relaxation (dynamic glass transition) where the dielectric spectra (also dynamic mechanical and NMR measured spectra) are broader in mixtures than the corresponding pure component relaxation spectra[Chi92]. The same effect has been observed in super-cooled binary liquid mixtures [Wil72] and in plasticised polymers [Hed77]. For polymer-polymer mixtures the broadening strongly depends on the interaction between the two polymers (which is measured by $\chi(T)$) and on the glass transition temperatures of the pure components. The effect is more pronounced the closer the system is to $T_g$ and is observable if the glass transition temperatures of the pure components vary by at least 20 K. For components
with almost equal $T_g$'s, the broadening is not strong and in case the shape parameters of the relaxation curves do not depend on temperature, the time - temperature superposition principle applies both in the pure components and in the mixtures [Alex80, Aleg93].

Until recently, broadening of the $\alpha$ - relaxation and glass transition dispersions in mixtures have only qualitatively been attributed to the presence of concentration fluctuations which are characteristic for mixed systems [She73]. Since the fluctuations are related to the free energy of mixing, this assertion offers an opportunity to link the broadening with thermodynamic variables and hence relate dynamics with structure effects that can be defined by a structure factor [deG79]. It is generally accepted that glass transition is characterised by co-operative dynamics [Don92, Fis92, Mat90]. The determination of the length scale of co-operativity that governs the glass transition has become of key interest in many works concerned with the glass transition phenomena [Shö93].

In this chapter, two theoretical models that have been developed to describe the broad dispersions and absorption in mixtures are outlined. It will be shown that by relating the glass transition dynamics with the pair correlation function of concentration fluctuations in mixtures, the size of co-operatively relaxing domains can be estimated. Further, models based on non co-operative dynamics are presented which will be used to describe the $\beta$-relaxation process.

### 4.2 The Concentration Fluctuation Model

The concentration fluctuation model was first developed by Fischer and Zetsche [Fis92] to give a quantitative analysis of the dielectric $\alpha$-relaxation in polymer-polymer and polymer-plasticiser mixtures. The physical basis of the model lies on the description of broad relaxation processes in mixtures by the inclusion of a relaxation time distribution $n_V(\tau)$ (see section 3.3). The shape of this distribution
in mixtures is strongly dependent on temperature and within the temperature window defined by $T_g(\phi)$ and the decomposition temperatures for the pure components, this distribution determines the shape of the relaxation curves. The broad dispersions are assumed to be caused by microscopic heterogeneity due to the presence of concentration fluctuations. Thus properties which are concentration dependent will fluctuate as well. If the variable is a response to an external field (e.g. electric), it will show a spread corresponding to the distribution of concentration. The mean square deviation of such concentration dependent variable $R(\phi)$ is given by

$$< (\delta R)^2 >_{(\phi)} = \left[ \left( \frac{dR}{d\phi} \right)^2 \right]_{\phi = <\phi>} < (\delta \phi)^2 >$$  \hspace{1cm} (4.1)$$

Equation (4.1) expresses the fact that if for a mixture comprising components with distinct properties $R$, the function $R(\phi)$ is known, the spread of the property $R$ can be determined if $< (\delta \phi)^2 >$ is known. This applies only for very small fluctuations. Thus as an example, the spread of the glass transition temperature distribution is given by

$$< (\delta T_g)^2 >_{(\phi)} = \left[ \left( \frac{dT_g}{d\phi} \right)^2 \right]_{\phi = <\phi>} < (\delta \phi)^2 >$$  \hspace{1cm} (4.2)$$

If $R$ is concentration independent then $\frac{dR}{d\phi} = 0$ and $< (\delta R)^2 > = 0$. In order to determine $< (\delta R)^2 >$ one requires to know both the function $R(\phi)$ and $< (\delta \phi)^2 >$ of the concentration distribution.

Based on the above principles, the model was formulated as follows:
The presence of local concentration fluctuations enables the sample to be divided into \( i \) sub-cells of size \( V \) each of which has a concentration \( \phi_i \). A "coarse-graining" volume \( V_a \) is introduced and one has to determine the size of this volume for which a unique glass transition temperature \( T_g^{i}(\phi_i) \) can be defined for the \( i \)th sub-cell.

The concentration distribution \( p(\phi_i) \) in the sample is assumed to be Gaussian with a variance \( \langle (\delta\phi)^2 \rangle \).

\[
p(\phi_i) \approx \frac{(\phi_i - \phi_0)^2}{2 \langle (\delta\phi)^2 \rangle}
\]

This approximation is justified in concentrated solutions where density fluctuations are very small but does not apply in the semi-dilute regions. With the Gaussian approximation for the concentration fluctuations, the free energy can be expressed as in equation (2.28).

For non interacting polymers where excluded volume interactions cancel out the pair correlation function for the concentration fluctuations is given by [Doi86]

\[
\langle (\delta\phi)^2 \rangle = \frac{\phi}{V_a} S(q = 0)
\]

where \( S(q) \) is the scattering function of an ideal polymer which may given by the random phase approximation (see chapter 2.2.1) and

\[
\delta\phi(q) = \frac{1}{V} \int_{V} \delta\phi(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d\mathbf{r}
\]
Identifying the volume $V_a$ with the reference volume in scattering experiments, its size can be calculated using equation 2.60.

The system is assumed to be incompressible which is equivalent to the requirement that the density fluctuations should be small.

Within the measurement time, the concentration fluctuations are considered to be stationary i.e.

$$\delta \phi (\vec{r}, t_0) = \delta \phi (\vec{r}, t_1)$$

(4.6)

This assumption enables the assignment of a unique $< (\delta \phi)^2 >$ to every relaxation curve at different temperatures since the relaxation times of the concentration fluctuations are much longer than those of the $\alpha$-relaxation.

The glass transition temperature of the macroscopic sample is concentration dependent and the same concentration dependence $T_g(\phi_i)$ is assumed to apply in every sub-cell.

The relaxation time distribution of the mixture is obtained by using either the WLF or VFT equations which relate the measurement temperature with a characteristic relaxation time $\tau$. The reference temperature is taken as the average $T_g(\phi_i)$. Thus from

$$\log \tau = \log \tau_g - \frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

(4.7)

a relaxation time $\tau_i(\phi_i, T)$ can be defined for each sub-cell i. The distribution of the relaxation time is given by
\[ G(\tau, T) = \int p(\phi)n_v(\tau, T, \phi)\, d\phi \]  

(4.8)

where \( n_v(\tau, T, \phi) \) is the relaxation time spectrum in a reference volume \( V \).

From the WLF equation it follows that for a given temperature \( T \),

\[
<\left(\delta \log\left(\frac{\tau}{\tau_g}\right)\right)^2> = \left(\frac{d\log\left(\frac{\tau}{\tau_g}\right)}{dT_g}\right)^2_{T_g<T_g>} \cdot <\delta T_g^2>
\]

(4.9)

\[
= \left\{ \frac{C_1 C_2 + 2C_1 (T - T_g)}{(C_2 + T - T_g)^2} \right\}^2_{T_g<T_g>}
\]

From equation (4.9) the deciding variable for the mean square deviation

\[
<\left(\log\left(\frac{\tau}{\tau_g}\right)\right)^2> \text{ is the interval } T - T_g. \text{ It is apparent from the WLF behaviour,}

that if \( \frac{dT_g}{d\phi} \approx \text{constant} \) then for very large intervals \( T - T_g \),

\[
\frac{d\log\left(\frac{\tau}{\tau_g}\right)}{dT_g} \to 0, \text{ and for a given } <(\delta T_g)^2> \text{ which is associated with the variance of the concentration distribution, the distribution of relaxation time becomes narrower at higher temperatures almost acquiring a constant value (Fig. 4.1)}
\]
Figure 4.1: WLF behaviour for the pure components PS and P(CHA-MBA) and a (50/50) mixture. The temperature dependence of the width of the time distribution is shown for a constant concentration fluctuation $<(\delta \phi)^2> = 0.001$

Starting from the concentration dependence of the glass transition temperature one obtains

$$<\left(\delta \log \left(\frac{\tau}{\tau_g}\right)\right)^2> = \left(\frac{d\log \left(\frac{\tau}{\tau_g}\right)}{dT_g}\right)_{T_g = T_g}^2 \left(\frac{dT_g}{d\phi_B}\right)_{\phi = \phi_B}^2 <(\delta \phi)^2>$$  \hspace{1cm} (4.10)
It is known that the fluctuations in temperature and concentration are statistically independent [Lan79]. i.e. $\langle \delta T \delta \phi \rangle = 0$. Since $\log ( \tau / \tau_g )$ is a function of both $\phi$ and $T$ one of these variables can be fixed and the effect of the other on the relaxation behaviour should be determined. This is easily achieved in dielectric measurements which are performed at quasi-thermal equilibrium conditions at constant pressure such that $T$ is the same for all volume elements.

### 4.2.1 Evaluation of the glass transition temperature and time distributions for the system $P$(CHA-BMA)/PS

The composition dependence of the glass transition temperature for the mixtures PS/$P$(CHA-BMA) is given by the Fox equation (2.123) from which an inverse relation is obtained

$$\phi(T_g) = \frac{T_{gb}}{T_{ga} - T_g} \left( \frac{T_{gb}}{T_g} - 1 \right)$$  \hspace{1cm} (4.11)

This expression is substituted into the expression for the Gaussian concentration distribution leading to the transformation $n(\phi) \rightarrow n_v(T_g)$ (see Fig 4.2a)

Similarly from the WLF relation one obtains the inverse relation

$$T - T_g (\tau) = -\frac{C_2 + \log(\tau / \tau_g)}{C_1 + \log(\tau / \tau_g)}$$  \hspace{1cm} (4.12)

leading finally to $n(\phi) \rightarrow n(\tau, T - T_g)$ (Fig 4.2b)
Figure 4.2: Distributions of (a): glass transition temperature calculated for various P(CHA-BMA)/PS mixtures with a constant concentration fluctuation $\sigma = 0.05$ and (b) relaxation times for a mixture with a mean concentration $\phi_{PS} = 0.5$ evaluated at various temperature intervals $T - T_g$. 
William et al [Wil55] have shown that $\tau / \tau_g$ expressed as a function of $T - T_{ref}$ ($T_{ref} = T_g$) is identical for a wide range of polymers and solutions, and within an average range $T - T_g \leq 50$ K, can lie on a master curve. This allows for a comparison of the widths of the relaxation curves at equal $T - T_g$ and in the same frequency window.

Figure 4.3 shows the distribution of relaxation times evaluated for various mixtures with a constant concentration fluctuation $\sigma = 0.05$ at the same temperature interval $T - T_g = 20$ K. As expected all the distribution curves lie within the same frequency window defined by $-6 < \log (\tau/\tau_g) < -1$. The half widths of the normalised time distributions $\log (\tau/\tau_g)$ for the mixtures show a temperature dependence

$$\left( \delta \log \left( \frac{\tau}{\tau_g} \right) \right)^{-\frac{1}{2}} \propto T - T_g$$

(4.13)

Extrapolation of the curves shows (see insert in Fig 4.4), that the widths of the distribution curves diverge at a value $T - T_g = -60$ K which is equal to the WLF parameter $C_2$
Figure 4.3: Relaxation time distribution evaluated at $T - T_g = 20 \text{ K}$ for mixtures $PS / P(CHA-BMA)$ with $\phi_{PS} = 0.2, 0.3, 0.4,$ and $0.5$

Figure 4.4: The half widths of the relaxation time distributions corresponding to various mixtures with same $\sigma = 0.05$. The widths scale with temperature as $(\delta \log(\tau / \tau_g))^{-1/2} \propto T - T_g$
4.2.2 The dielectric $\alpha$-relaxation function for a mixture.

This is evaluated for a mixture in which the relaxation behaviour is dominated by one component. It is assumed that within each sub-volume the shape of the dielectric function $\varepsilon_A^{*}(\omega)$ for the polar component is the same as that in the pure state and can be described by a relaxation function, e.g. the Havriliak-Negami function with the shape parameters $\alpha$ and $\gamma$ (eq. 3.43). The dielectric loss $\varepsilon_M''(\omega)$ of the mixture results from the summation over all sub-volumes:

$$\varepsilon_M''(\omega) = \sum_i \varepsilon_i''(\omega \tau_i) = \int_0^\infty n_v(\tau_i) \varepsilon_A''(\omega \tau) d\tau$$  \hspace{1cm} (4.14)

with $\varepsilon_A''(\omega \tau) \equiv$ imaginary part for the Havriliak-Negami function of the polar component (eq. 3.43). Transformation of equation (4.14) on the logarithmic scale yields

$$\varepsilon_M''(\log \omega) = \int_{-\infty}^\infty L(\log \tau) \varepsilon_A''(\log \omega + \log \tau) d\log \tau$$  \hspace{1cm} (4.15)

with $L(\log \tau) = \tau n_v(\tau)$

This is a convolution integral of the distribution function $L(\log \tau)$ of the mixture with the dielectric function of the polar component. By this procedure Fischer et al. [Fis92, Zet92] showed that relaxation curves with the same temperature and frequency dependence typical for polymer mixtures could analytically be obtained if the relevant parameters for a given system are known. This model was so far tested on the mixture of Polystyrene and Polyvinylmethylene (PS/PVME) which has a lower critical solution temperature (LCST). A further application of this
model on the dielectric $\alpha$-relaxation in mixtures of polystyrene and a statistical copolymer Poly(cyclohexylacrylate-stat-butylmethacrylate) will be presented in chapter 7.

### 4.3 The Coupling Model for Mixtures

The coupling model extended onto mixtures by Roland et al. [Rol92] stems from Ngai coupling scheme originally formulated for homopolymers [Nga80]. The basic argument of this model is that, the fundamental interchain conformational transition as described by a Hall-Helfand type expression [Hall82] acquires a time dependence when interactions among neighbouring segments build up to a degree sufficient to retard the relaxation. In a mixture it is assumed that the local environment will vary among segments due to concentration fluctuations. Interchain interactions and correlation are expected to fluctuate in accordance with the local composition heterogeneity. This results to a distribution of effective relaxation times and couplings of segmental movements and consequently a distribution of the coupling parameters of the pure homopolymers. Both these distributions can be modelled by assuming a gaussian approximation for the concentration fluctuations. Hence one can determine the range of distribution of the coupling parameters for each blend component.

It is assumed that the relaxation behaviour of the pure homopolymers can be described in terms of the a KWW or Havriliak-Negami function. In this case the dynamically response of the mixture $\chi_i(t)$ is analytically given by

$$\chi_i(t) = \chi_i(0) \int_0^1 \exp\left(-a_i(n-n_i)^2\right) \exp\left(-\frac{t}{\tau^*(n)}\right)^{1-n} \, dn$$

(4.16)
where

\[ \tau^*_i(n) = \left( [1-n] w_i^n \tau_{0i} \right)^{1/(1-n)} \]  

(4.17)

\( \tau^* \) is the apparent relaxation time with \( n \) being the average value of the coupling parameter for component \( i \) and \( a_i \) is the variance of its distribution. \( n \) is related to the degree of intermolecular co-operativity associated with the relaxation process, and therefore provides a measure of the increase in the spectral or "effective distribution" of material response times, over that of a linear exponential decay.

For the dielectric relaxation in the absence of local fields and when one component dominates the relaxation behaviour, the loss curve for the mixture is given by

\[
\varepsilon''_M(\omega) = \text{Im} \int_0^1 \Delta \varepsilon \frac{1}{d} \left\{ \exp \left[ -a(n-\bar{n})^2 \right] \exp \left[ -\left( \frac{t}{\tau^*(\tau_0,n)} \right)^{1-n} \right] \right\} \exp \left[ -i \omega t \right] dt dn
\]  

(4.18)

where \( \bar{n} \) is the average coupling parameter for the mixture. The experimental loss curves are fitted using equation 4.17 giving as result the value \( n \) at given frequencies.

According to this approach, \( n \) is a function of the local composition and varies across the spectrum. It can be obtained for a given frequency and hence at a fixed temperature one obtains a distribution of \( n \). This distribution reflects the distribution in the degree of intermolecular coupling and of the relaxation time due to the variation of local environment. This model was also applied to analyse the dielectric \( \alpha \)-relaxation in PS/PVME mixtures. Since the shape of the relaxation curves in the mixtures varied strongly with temperature, the time-temperature superposition did not hold. This is however a strong requirement for
this model and perhaps explains the poor agreement with the experimental results [Rol92]. In this work, the data is fully analysed within the framework of the concentration fluctuation model.

4.4 Analysis of the sub-$T_g$ $\beta$-relaxation

The $\beta$-relaxation which is attributed to localised motions of small molecular segments is often much broader on a time or frequency scale than the glass transitions which are highly co-operative and are characterised by large activation enthalpies and entropy [McC67]. In case of polymers without flexible side groups, it has been shown by computer simulations that the subglass relaxation processes are the result of co-operative motions of a small number of bonds which do not introduce a significant displacement of the chain tails [Helf84]. For polymers with flexible side groups the relaxation involves conformational changes in the side groups.

As noted earlier, broad dispersions can be expressed by using a distribution of relaxation times or a stretched exponential function [Koh47, Wil70]. A distribution of relaxation times reflects a distribution of activation energies, a distribution of pre-exponential factors or both. Conformational changes that involve crossing energy barriers between two states of a configurational space may be described by the Arrhenius equation

$$\tau = \tau_0 \exp \left[ \frac{E_a}{RT} \right]$$

(4.19)

where $\tau$ and $E_a$ are, respectively, the relaxation time and the activation energy or barrier height for the process and $\tau_0$ has in many cases a value of $10^{-12.77}$ s.

4.4.1 Erying - Starkweather Analysis
The distribution of activation energies can be explained by using the theory of absolute reaction rates to interpret the potential barrier that governs the β-relaxation. According to this theory [Dav92] the relaxation rate is given by

\[ f = \frac{kT}{2\pi\hbar} \exp\left(-\frac{\Delta H^*}{kT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \]  \hspace{1cm} (4.20)

The activation Gibbs free energy \( \Delta G^* \) is related to the activation enthalpy \( \Delta H^* \) and the activation entropy \( \Delta S^* \) by the equation

\[ \Delta G^* = \Delta H^* - T\Delta S^* \]  \hspace{1cm} (4.21)

Equation (4.20) can be rewritten to give

\[ \Delta G^* = RT \ln\left(\frac{kT}{2\pi\hbar f}\right) \]  \hspace{1cm} (4.22)

The activation energy \( E_a \) is related to \( \Delta H^* \) by

\[ E_a = \Delta H^* + RT \]  \hspace{1cm} (4.23)

thus

\[ E_a = RT \left(1 + \ln\left(\frac{kT}{2\pi\hbar f}\right)\right) + T\Delta S^* \]  \hspace{1cm} (4.24a)

Starkweather [Star81,88,89,90] has shown that for many relaxation processes, the value of \( E_a \) obtained by an Arrhenius analysis is in good agreement with
where T' is the absolute temperature of the loss maximum at 1 Hz. This suggests that the entropy of activation is close to 0. Relaxation processes having this property have been identified as being simple or non-co-operative [Star91]. In this case the motions involved are localised and independent from each other.

To obtain a distribution of free energy of activation, the relaxation spectrum Φ is estimated by

\[ \Phi \approx \frac{2\varepsilon''}{\pi \Delta \varepsilon} \]  (4.25)

and the values of Φ are plotted versus ΔG*. The width of the distribution in frequency (δlnf) is related to the corresponding width in the activation enthalpy δΔH* by

\[ \delta \ln f = -\frac{\delta \Delta H^*}{RT} \]  (4.26)

Both the Arrhenius and Erying - Starkweather analysis will be applied to sub-Tg β - relaxation in BPA-PC and TMBPA-PC homopolymers and in their mixtures.

4.5 Concluding Remarks
Theoretical models to describe broad glass dispersions and the $\alpha$-relaxation in mixtures have been outlined. By assuming a gaussian concentration distribution in the sample the concentration fluctuation model can be used to determine the variance of the concentration distribution. Further a coarse-graining volume can be defined which may be associated with the scale of co-operativity characterising the glass transition dynamics. The coupling model based on the same requirement of the existence of concentration fluctuations in the mixture yields a distribution of a coupling parameter. The Arrhenius and Erying analysis of the subglass $\beta$ - relaxation in polymers are briefly discussed.
5 Experimental

5.1 Materials

<table>
<thead>
<tr>
<th>Structures and Abbreviations</th>
<th>$M_W$ [g/mol]</th>
<th>$\frac{M_W}{M_n}$</th>
<th>$T_g$ [K]</th>
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<tr>
<td>CHA (39%) BMA (61%)</td>
<td>415000</td>
<td>1.88</td>
<td>291</td>
</tr>
<tr>
<td>PS</td>
<td>198000</td>
<td>1.04</td>
<td>379</td>
</tr>
<tr>
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<td>421</td>
</tr>
<tr>
<td>TMBPA-PC</td>
<td>30000</td>
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<td>471</td>
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Table 5.1: Properties of the materials used in this study
5.2 Sample Preparation and Characterisation

The polymers used were a statistical copolymer, Poly (cyclohexylacrylate-butylmethacrylate) P(CHA-BMA) provided by Röhm, Polystyrene obtained from Service PSS in Mainz, bisphenol A (BPA-PC) and tetramethylbisphenol A polycarbonate (TMBPA-PC) which were both provided by Bayer Leverkusen. The composition of the copolymer was determined by using $^1$H-NMR spectroscopy. Figure 5.1 shows the NMR spectrum for P(CHA-BMA) with the corresponding signal assignment. The composition is obtained by integrating the signals for CHA (4.65 ppm) and for BMA (3.9 ppm). The content of one monomer is evaluated using the formula

$$mol\%\text{BMA} = \frac{I(3.9 \text{ ppm})}{I(3.9 \text{ ppm}) + 2 \times I(4.65 \text{ ppm})} \times 100$$  \hspace{1cm} (5.1)$$

The copolymer used contained 39% CHA and 61% BMA.

Figure 5.1: $^1$H-NMR spectrum for P(CHA-BMA)
Mixtures PS/P(CHA-BMA) and BPA-PC/TMBPA-PC were prepared by dissolving a pair of the desired polymers at a 10% level (g/ml) of the total polymer in a solvent. The solvent was tetrahydrofuran (THF) for PS/P(CHA-BMA) and methylene chloride (CH$_2$Cl$_2$) for the BPA-PC / TMBPA-PC mixtures. Films for the mixtures as well as for the pure components were solution casted using the same co-solvent. For non self-supporting films, the solution was poured directly on a gold plated steel electrode which was held tightly in a special prepared teflon ring. The electrodes were covered with aluminium cups in order to minimise the rate of solvent evaporation. In the case where samples phase separated when dried at room temperature, the solutions were placed in an excator with silica jelly and freeze dried. After the solvent was evaporated, the films were first air dried for two days at 296 K and then for a further five days under vacuum using a selected drying program which raised the temperature at 1 K steps until the sample acquired a temperature T$_g$+ 20 K. The sample was then cooled at the same rate to room temperature. The resultant films for the dielectric measurements were 0.2 ± 0.01 mm thick. Extra thin films (100 µm) were prepared in petri-dishes for the determination of the cloud point temperature. Differential scanning calorimetry (DSC) was used to examine the miscibility in the mixtures. The glass transition temperatures of the mixtures and the mixture components were determined using a Mettler DSC30 at scanning rate of 10 K/min. Several runs were made to ensure a uniform thermal history. This was done until reproducible scans were obtained (usually the third ), and all glass transition temperatures T$_g$ were taken as the temperature corresponding to half of the heat capacity change. Figure 5.2 shows the cloud point determined from light scattering and the glass transition temperature as a function of composition for the system PS / P(CHA-BMA). The composition dependence of the glass transition temperature for this system is well described by the Fox equation (2.122). The polymers BPA-PC and TMBPA-PC were miscible in the temperature range investigated and no phase separation was observed. The glass transition temperature varies proportionally to the blend composition (Fig. 5.3).
Figure 5.2: Phase diagram and concentration dependence of the glass transition temperature for the mixtures PS / P(CHA-BMA). The glass transition data is well described by the Fox equation for mixtures.
Figure 5.3: Glass transition temperature as a function of composition for BPA-PC / TMBPA-PC mixtures.

The densities of the pure components and their mixtures were determined by using a gradient column composed of isopropanol, distilled water and calcium nitrate at 296 K. Specific volumes of the pure polymers BPA-PC and TMBPA-PC were measured in a GNOMIX PVT machine by heating the samples to temperatures between 473 K and 503K and cooling them at 1K/min. Table 5.1 gives a summary for the density values for the two systems.
Table 5.1: Density values for a) homopolymers BPA-PC and TMBPA-PC and their mixtures, b) pure polymers PS and P(CHA-BMA) and their mixtures.

Table 5.2 χ parameter values for some BPA-PC/TMBPA-PC mixtures. O-Z stands for Ornstein-Zernike and v₀ is the segment volume.
For the PS / P(CHA-BMA) (Figure 5.3), the $\chi$ - parameter, in the concentration range $0.1 \leq \phi_{PS} \leq 0.5$, is almost concentration independent. Therefore in this composition range the Flory-Huggins mean field theory is applicable. The BPA-PC / TMBPA-PC have $\chi$ - parameters which for all compositions favour miscibility of the homopolymers over a wide range of temperature [Hel92]. By using the random phase approximation (RPA) the structure factor $S (q = 0)$ was calculated for the PS/P(CHA-BMA) mixtures at the temperatures corresponding
to those at which the dielectric $\alpha$ - relaxation was measured. Using the Ornstein-Zernike formula (eq. 2.37),
the correlation length $\xi$ for the concentration fluctuations was estimated. For all
the mixtures the values of $\xi$ obtained in the temperature of the dielectric
measurements were on average between 2-3 nm. Table 5.3 summarises the $\xi$
values as a function of temperature for different mixtures. Figure 5.4 shows the
evaluated $S(\mathbf{q}=0)$ plotted as a function of $T - T_g$ for various compositions.

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Table 5.3 The correlation length of the concentration fluctuations estimated using the Ornstein-Zernike equation for various PS/P(CHA-BMA) mixtures. The temperatures correspond to those at which the dielectric $\alpha$-relaxation was measured.
Figure 5.5: Structure factor $S(q = 0)$ evaluated as a function of $T - T_g$ for various mixtures.

5.3 Dielectric Spectroscopy

5.3.1 Determination of the complex Permittivity.

For frequencies lying in the range $10^{-4}$ to $10^8$ Hz, the experimental techniques used in dielectric experiments are based on the measurement of the equivalent capacitance and resistance at a given frequency [McC67]. Therefore, a polymer sample may be considered as being electrically equivalent to a capacitance $C_X$ in parallel with a resistance $R_X$ as shown in figure 5.6.
Figure 5.6: Parallel and series equivalent circuits to polymer samples.

Under the effect of a voltage \( V(t) = V_0 \exp(i\omega t) \), the admittance \( Y_x \) of the circuit is given by

\[
Y_x = \frac{1}{Z_x} = i\omega C_x + \frac{1}{R_x}
\]  \hspace{1cm} (5.2)

where \( Z_x \) is the impedance of the circuit. The total current \( I \) is given by

\[
I(t) = \frac{V(t)}{Z_x}
\]  \hspace{1cm} (5.3)

The components \( I_C \) and \( I_X \) of the current \( I \) are

\[
I_c(t) = \omega C_x V(t)
\]  \hspace{1cm} (5.4a)

\[
I_x(t) = \frac{V(t)}{R_x}
\]  \hspace{1cm} (5.4b)
For solid polymer samples and high-viscosity liquids, the dielectric measurements are performed by placing the samples between parallel-plate capacitor. Concentric cylindrical capacitors are used in the case of low-viscosity liquids.

![Figure 5.7 Schematic representation of a parallel-plate condenser](image)

The capacitance for a vacuum-filled parallel-plate capacitor is given by

\[
C_0 = \frac{\varepsilon_0 A}{d} \quad (5.5)
\]

where \( A \) is the area of each plate and \( d \) is the distance between them, \( \varepsilon_0 \) is the permeability in vacuum. For a cylindrical capacitor in vacuum, the capacitance is

\[
C_0 = 2\pi\varepsilon_0 \frac{1}{\ln(b/a)} \quad (5.6)
\]

Replacement of the vacuum by a dielectric gives rise to a complex capacitance \( C^* \) related to \( C_0 \) by

\[
C^* = C_0 \varepsilon^* \quad (5.7)
\]

where \( \varepsilon^* = \varepsilon' - \varepsilon'' \) is the complex permittivity.

The total current \( I(t) \) passing through a capacitor can be expressed as

\[
I(t) = \frac{dq(t)}{dt} = \frac{d[C^*V(t)]}{dt} \quad (5.8)
\]
Substituting equation (5.7) in (5.8), one obtains

\[ I(t) = (i\omega' + \varepsilon''\omega)C_0V(t) \]  

(5.9)

with

\[ I_c = \varepsilon'\omega C_0V(t) \]  

(5.10a)

\[ I_x = \varepsilon''\omega C_0V(t) \]  

(5.10b)

From equations 5.10 it follows that

\[ \varepsilon' = \frac{C_x}{C_0} \]  

(5.11a)

\[ \varepsilon'' = \frac{1}{R_x\omega C_0} \]  

(5.11b)

and the loss tangent \( \tan \delta \)

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{R_x C_x \omega} \]  

(5.12)

If the measurements correspond to the measurement of an equivalent series capacitance and resistance of the sample, the impedance of the circuit \( Z_S \) is given by

\[ Z_s = R_s - \frac{i}{\omega C_s} \]  

(5.13)
The total current $I(t)$ in the circuit can be written as

$$I(t) = \frac{V(t)}{Z_s} = \left( \frac{\omega^2 C_s R_s}{1 + R_s^2 \omega^2 C_s^2} + \frac{i\omega}{1 + R_s^2 \omega^2 C_s^2} \right)V(t) \quad (5.14)$$

The expressions obtained for $\varepsilon'$ and $\varepsilon''$ from eqs. (5.8) and (5.13) are

$$\varepsilon' = \frac{C_s}{C_0 (1 + R_s^2 \omega^2 C_s^2)} \quad (5.15)$$

$$\varepsilon'' = \frac{R_s \omega C_s^2}{C_0 (1 + R_s^2 \omega^2 C_s^2)} \quad (5.16)$$

and $\tan \delta = R_s \omega C_s \quad (5.17)$

![Vector diagram of the a) parallel and b) series equivalent circuits.](image)
When the sample is considered to be equivalent to a resistance in parallel with a capacitance, the resistance can be assumed to be made of two contributions $R_0$ and $R_1$. The first contribution arises from dc conductivity of the specimen and the second from the non-dc resistance. Accordingly $R_0$ is independent of frequency.

Since $R_0$ and $R_1$ are parallel, the resistance $R_x$ is given by

$$\frac{1}{R_x} = \frac{1}{R_1} + \frac{1}{R_0}$$

and

$$\varepsilon''(\omega) = \frac{1}{R_0 \omega C_0} + \frac{1}{R_1 \omega C_0} = \varepsilon''_0(\omega) + \varepsilon''_1(\omega)$$  \hspace{1cm} (5.18)

where $\varepsilon''_0(\omega)$ represents the dc contribution to the loss. To obtain $\varepsilon''_1(\omega)$ due to non-conductivity effects, $\varepsilon''_0(\omega)$ must be subtracted from $\varepsilon''(\omega)$ as will be illustrated in section (5.6).

### 5.3.2 Measurement Systems:

The methods used in this work for the determination of the complex dielectric function were all frequency domain techniques where a sinusoidal field is applied to the sample and the resulting current is detected. Because of the broad dielectric spectrum bands displayed by polymer materials, the angular frequency ($\omega$) of the field should be variable in the largest range as possible. The response of the sample is expressed in terms of the complex admittance, the real and imaginary parts of which are expressed as

$$Y' = \omega C_0 \varepsilon'' + C_0 \frac{\sigma}{\varepsilon_0}$$  \hspace{1cm} (5.19)

$$Y'' = \omega C_0 \varepsilon'$$  \hspace{1cm} (5.20)

and

$$\varepsilon^* = \frac{Y^*}{i \omega C_0}$$  \hspace{1cm} (5.21)
where \( C_0 \) is the capacitance of the empty sample holder, and \( \sigma \) is the conductivity. The real part of the admittance is proportional to the current component that is in phase with voltage, while the imaginary part is 90° out of phase with the field. These two components can be separated easily by a phase-sensitive detector and hence the admittance components can be measured. Details of the systems used are given below.

5.3.3 The Frequency Response Analyser

Measurements of the complex dielectric function were made in the frequency range \( 10^{-2} \) to \( 10^6 \) Hz using a frequency response analyser (Solartron-Schlumberger FRA 1260) with high impedance preamplifier variable gain. The principle of this system is the measurement of the correlation between the exciting sinusoidal voltage \( V(t) \) and the resulting current \( I(t) \). As illustrated in figure 5.9, the generator applies a digitally synthesised sine-wave signal to the dielectric sample (or a reference capacitor). The correlator multiplies the measured signal \( I(t) \) by two reference signals, an in phase signal \( V(t) = V_0 \sin(\omega t) \) and a 90° out of phase signal \( V_0 \cos(\omega t) \) and integrates the products over a defined number of periods. By this digital integration technique, the signal is analysed using an on line Fourier analysis. For linear systems, this procedure yields the coefficients \( A_1 \) and \( B_1 \) of

\[
A_n = \frac{2}{N T} \int_0^{N T} I(t') V_0 \sin(n \omega t') dt'
\]  

(5.22)

\[
B_n = \frac{2}{N T} \int_0^{N T} I(t') V_0 \cos(n \omega t') dt'
\]  

(5.23)

where \( N T \) is the integration time of the period \( T \) over \( N \) cycles, and \( n = 1,2,3,\ldots \).
$A_1 = V_0 I_0 \cos \varphi$ and $B_1 = V_0 I_0 \sin \varphi$ where $\varphi$ is the phase shift between the current and the voltage. The impedance is obtained as

$$Z = \frac{V_0^2}{A_1} + i \frac{V_0^2}{B_1}$$

(5.24)

The correlator has a low input resistance ($10^6 \, \Omega$) and to be able to measure low-loss polymer materials, one requires an impedance transformer. This is realised in this system by a Chelsea - Dielectric - Interface developed by Pugh and Ryan [Puh, Rya]. Figure 5.8 shows a schematic diagram of the frequency response analyser and the Chelsea -Dielectric -Interface.

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**Figure 5.9**: A schematic diagram of the frequency response analyser Solartron-Schlumberger FRA 1260 and the Chelsea -Dielectric -Interface
An Operational amplifier [Burr, Brown3582] with a high input resistance ($10^{11} \Omega$) and a variable gain, is set through switching a total of 34 separate resistors $R_m$ ranging from $10 \Omega$ to $10^{12} \Omega$ and similarly 4 measurements capacitors (100 pF to 0.1 $\mu$F), such that the input signal at the correlator is always maintained between 3 an 10 V. By so doing, errors that may arise due to exchange of the measurement range at the correlator are eliminated. The measurement of the complex admittance is facilitated as follows:

Firstly, the potentials at the point $x$ and $y$ are measured [Kre89]. The correlator measures directly the in phase voltage $V_x$ and the $90^\circ$ out of phase component $V_y$ of the voltage using a digital integration technique as described above. From the measured complex voltages $V_x^*$ and $V_y^*$ the complex admittance is calculated as

$$Y_s^* = \frac{Y_m^*}{(V_x^*/V_y^*)-1}$$  \hspace{1cm} (5.25)

$$Y_s^* = G_s + i\omega C_s$$  \hspace{1cm} (5.26)
\[ Y_m^* = \frac{1}{R_m} + i\omega C_m \]  

(5.27)

where \( Y_s^* \) = Admittance of the Sample

\[ Y_m^* \] = Admittance of the measuring circuit

\[ G_S \] = Conductance of the Sample

\[ R_m \] = Resistance, \( C_S \) = Capacitance of the sample, and \( C_m \) - Capacitor.

In order to improve the accuracy of the measurement, the admittance of a precision low-loss air capacitor used as a reference is compared with the admittance of the sample for every frequency. The capacitance of the sample is determined as follows:

(1) The operational amplifier is switched to \( y' \) and the measurement of \( V_Y \) is carried out at a constant value \( Y_m^* \). Then \( V_x^* \) is measured and analogous to equation (5.25)

\[ Y_r^* = \frac{Y_m^*}{[(V_x^*/V_y^*)-1]} \]  

(5.28)

where \( Y_r^* = G_r + i\omega C_r \). Combining equations (5.25) (5.26) and (5.27) yields for the admittance of the sample \( Y_s^* \)

\[ Y_s^* = \frac{Y_r^*[V_x^*/V_y^*]-1}{[V_x^*/V_y^*]-1} \]  

(5.29)

Thus the conductance of the measuring circuit \( Y_m^* \) is eliminated.
At low frequencies there may be a conductivity contribution which for polymers arises mainly from ionic impurities. This overlaps the relaxation part of the dielectric loss in the frequency $\omega < 1$. There has been great improvements done on the measuring programs used in the MPI dielectric spectroscopy laboratory which have taken into account the conductivity contribution from the measuring system. This has enabled the correct choice of the reference capacitor and measurements can now be carried out up to $10^{-3}$ Hz without much overlap of the relaxation and conductivity parts of dielectric loss. Although a very plausible improvement, measurements at these frequencies usually cost a lot of time. All measurement functions e.g. the switching from the sample capacitor to the reference capacitor and the selection of the suitable measurement resistance $R_m$ and capacitor combinations are fully automatic. From the calculated admittance, the values of $\varepsilon'$, $\varepsilon''$ and $\tan \delta$ for every frequency sweep at a given temperature are saved in a disk.

5.3.4 The Low-Frequency Bridge.

The Hewlett-Packard impedance analyser (HP4192A) uses a bridge technique to measure the complex impedance.

![Block diagram for the low frequency Bridge (HP4192A)](image-url)

*Figure 5.11: Block diagram for the low frequency Bridge (HP4192A)*
The Generator voltage $V_g^*$ causes a current $I_s$ that flows through the sample capacitor and the resistor $R_f$. A variable amplitude -phase oscillator sets a voltage $V_r^*$ with the same frequency as $V_g^*$ on the resistance $R_f$ until $I_d = I_s - I_f = 0$. At the Zero adjustment, $I_S = I_R$, and hence

$$I_s = \frac{dq}{dt} = i\omega C^*(\omega)V_g^*$$  \hspace{1cm} (5.30)

and

$$I_r = Y^*V(t)$$  \hspace{1cm} (5.31)

The complex impedance of the sample $Z_s^*$ is

$$Z_s^* = \frac{R_v V_g^*}{V_r}$$  \hspace{1cm} (5.32)

The Impedance analyser is specified for the frequency range from 5 Hz to 13 MHz. For polymer materials with low dielectric loss, the range between 1 kHz and 3 MHz is used because of the poor resolution of the bridge outside this range. Above 3 MHz, the bridge is influenced by resonance effects.

### 5.4 Temperature Control

The stability of the temperature at which a dielectric measurement is taken is very important in order to keep the sample in quasi-thermal equilibrium conditions. In all the measurement systems used in this work, the sample temperature was adjusted using a gas temperature system which was developed by Böhme, Kremer and Zak [Boe88, Kre89]. Below 450 K the temperature was controlled by a nitrogen gas heating system with a temperature stability within 0.2 K. The gas was produced by mounting a heater in a liquid nitrogen container.
For higher temperatures, the same system was used with either piped nitrogen gas or air. The sample cell was mounted in a home-made vacuum cryostat which was designed for a temperature range of 90 to 573 K. The temperature of the sample was measured with a platinum resistor (PT 100), which was inserted in one of the electrodes (Diameter of PT100 = 1.8 mm, and thickness of electrode = 4 mm). The resolution of the temperature measurement was 0.01 k using a Keithly Multimeter (195 A). Figure 5.12 shows a schematic diagram of the nitrogen gas temperature control system.
5.5 Analysis of the Relaxation Measurements.

The analysis of the dielectric spectra is carried out as summarised in the following scheme

\[
\varepsilon'' \propto \omega^{s-1}
\]  

(5.33)

with \(0.5 \leq s \leq 1\)

Due to the strongly differing functional form of the relaxation process and the conductivity contribution, the two can easily be separated as illustrated in figure 5.14 and 5.15. After the subtraction of the conductivity, half widths of the \(\alpha\)-loss
curves were determined. The accuracy of the values obtained depends very much on how well the low frequency conductivity is subtracted and on the higher frequency side, by the frequency window. In the case where both $\alpha$ and $\beta$-relaxation occurred, a twofold Havriliak - Negami function was fitted and the parameters $\alpha$, $\gamma$, $\tau$ and $\Delta\varepsilon$ for the relaxation peaks were obtained. Further, the temperature behaviour $\tau (T)$ and the temperature dependence of the shape parameters ($\alpha, \gamma$) could be analysed. A detailed analysis and the results from the mixtures are presented and discussed in the following chapters.

Figure 5.14a: A double logarithm plot showing the different functional forms of an $\alpha$ - relaxation process and the low frequency conductivity contribution measured in PS/PH (CHA-stat-BMA) mixtures at 333.2 K. A twofold Havriliak – Negami function plus a conductivity contribution was used to fit the data. The parameters are ($\alpha$ -process) $\Delta\varepsilon =1.2$, $\alpha =0.38$, $\gamma =0.8$, $\tau =0.0008\text{s}$. ($\beta$ -process) $\Delta\varepsilon =0.115$, $\alpha =0.54$, $\gamma =0.54$, $\tau =5.03 \times 10^{-7}\text{s}$. The parameter $s =1$ (eq. 5.33).
Figure 5.15: Subtraction of Conductivity contribution from a dielectric loss curve

5.6 Concluding Remarks

The materials and experimental techniques used in this work have been presented. A detailed account on the physical principles underlying the determination of the complex dielectric function is given. The measuring systems used in this study and the scheme of analysis for dielectric data are presented.
6 Experimental Results

6.1 Introduction
The dielectric data for the two systems studied were obtained mainly using the frequency response analyser which has a resolution of $5 \times 10^{-5}$ in the loss tangent $\tan \delta$, and is therefore also suitable for studying the weak $\beta$-relaxation. The impedance analyser with a resolution of only $10^{-3}$ was used to measure much stronger $\alpha$-relaxation. The highest temperature of measurement in the one phase region for the mixtures PS / P(CHA-BMA) was about 10 K below the binodal curve.

The resulting spectra measured at different temperatures and for various compositions were fitted with the Havriliak-Negami function and the parameters $\alpha$, $\gamma$, $\tau$, $\Delta \varepsilon$ were obtained. The half widths of the $\alpha$-relaxation were determined after the conductivity and high frequency $\beta$-relaxation were subtracted. ( P(CHA-BMA has a high frequency $\beta$-relaxation which is much weaker than the $\alpha$-relaxation [Kat92] ). For an accurate determination of the half widths, especially for the strongly broadened curves in the mixtures, it was important that almost the full relaxation curve appeared in the frequency window of the equipment. The sub-$T_g \beta$-relaxation curves in the BPA-PC / TMBPA-PC mixtures were fitted using the same procedure and the relaxation strengths obtained were corrected for density effects. In this chapter the experimental results are presented under the subheadings BPA-PC / TMBPA-PC and PS / P(CHA-MBA) mixtures.

6.2 Mixtures of BPA-PC / TMBPA-PC [Kat93]

6.2.1 $\alpha$-Relaxation
Figure 6.1, shows a plot of the dielectric loss $\varepsilon''$ against the logarithm of frequency for the $\alpha$-relaxation in the homopolymers and the mixture with $\Phi_{\text{TMBPA-PC}} = 0.1$. 
Figure 6.1: Dielectric loss $\varepsilon''(\omega)$ as a function of frequency for (a) BPA-PC, (b) blend with $\Phi_{\text{TMBPA-PC}} = 0.1$, and (c) TMBPA-PC at various temperatures. The symbols denote the experimental data, and the solid lines are fits according to the Havriliak-Negami function (eq. 3.43)
By comparison of the dielectric absorption in the homopolymers (Fig. 6.1a, c) with that of the mixture two features are evident. Firstly, the mixture exhibits a single but broadened $\alpha$-peak, and secondly, the peak is shifted in the frequency position as compared to the pure components. For TMBPA-PC both $\alpha$- and $\beta$-relaxation appear in the frequency window between $10^{-1}$ and $10^6$ Hz. Figure 6.2, shows the composition dependence of the half width of the relaxation frequency distribution. The homopolymers BPA-PC and TMBPA-PC have almost equal widths which are larger than the Debye-width of 1.14 decades. The half width of the relaxation curves were evaluated at the same distances from $T_g$ which is a function of composition. They acquire a maximum at intermediate composition between the pure polymers and are larger, the lower the temperature difference with respect to $T_g$. This is in agreement with what is expected from the relaxation time distributions (Figure 4.2).

**Figure 6.2:** Half widths $\delta_{1/2}\log \omega$ as a function of $\Phi_{\text{TMBPA-PC}}$ for the $\alpha$-peak plotted at $T - T_g = 20$ and 40 K.
6.2.2 $\beta$ - Relaxation

Both BPA-PC and TMBPA-PC show a sub-$T_g$ $\beta$-relaxation. Because these polymers have no side chains, the $\beta$-relaxation maxima are suppressible according to Heijboer classification [Hei76]. Figure 6.3 shows the frequency dependent loss curves of the $\beta$-relaxation for both the homopolymers and their mixtures.

Figure 6.3a: Dielectric loss $\varepsilon''(\omega)$ for the BPA-PC $\beta$-relaxation in the homopolymer and in a mixture with $\Phi_{TMBPA-PC} = 0.22$ at various temperatures. The temperatures are 166.4 K, 194.3 K, 203.7 K.
Experimental Results

K, 213.4 K, 223.0 K, 232.3 K (BPA-PC) and 185.3 K, 194.8 K, 203.8 K

215.2 K for the mixtures.

Figure 6.3b: Dielectric loss $\varepsilon''(\omega)$ for TMBPA-PC $\beta$-relaxation in the homopolymer and in a mixture with $\Phi_{\text{TMBPA-PC}} = 0.68$ at various temperatures. The temperatures corresponding to the curves are 334.4 K, 342.4 K, 350.3 K, 360.8 K, 369.1 K, 377.3 K, 385.7 K (TMBPA-PC) and 336.6 K, 345.0 K, 369.0 K, 378.3 K, 386.7 K, 395.1 K (mixture)
In the mixtures (Figs. 6.3 and 6.4) the β-relaxation appear in the same temperature range as for the pure components. Figure 6.4, shows an isochronal plot (10 Hz) for the loss factor $\varepsilon'' + (\omega)$ of the β-relaxation in the mixtures.

The β-relaxation of both homopolymers could be detected down to concentration levels of 10%. Contrary to dynamic mechanical results on the same system, reported by Jho et al., [Jho92] a critical TMBPA-PC concentration of 75% above which the BPA-PC β-peak is completely suppressed was not observed. It can be seen in Figure 6.4 that the TMBPA-PC β-peaks in the mixtures have curve forms.
similar to that of the homopolymer. The temperatures for the maxima are close to that of the homopolymers and shift very slightly to lower temperatures with increasing BPA-PC concentration. The BPA-PC \( \beta \)-peak is shifted more with increasing BMBPA-PC composition.

Figure 6.5: Activation plot for various BPA-PC / TMBPA-PC mixtures showing the temperature dependence of the relaxation time for both \( \alpha \)- and \( \beta \)-processes. The symbols correspond to mixtures with TMBPA-PC volume fraction: \( \nabla = 0 \), \( = 0.11, \star = 0.22, * = 0.38, \bullet = 0.68, \bigcirc = 0.82, \Delta = 1 \).

Figure 6.5 shows an activation plot summarising the dynamics of the \( \alpha \)- and \( \beta \)-processes in the mixtures. The temperature dependence of the \( \beta \)-relaxation shows an Arrhenius behaviour with the activation energies for BPA-PC and TMBPA-PC equal to 54 ± 2 and 79 ± 2 kJ / mol which are comparable with the values obtained from dynamic mechanical spectroscopy [Jho92] and those obtained by
13C solid-state NMR [Roy86] and dielectric measurements [Zet92]. The activation energy of TMBPA-PC is nearly constant throughout the full composition range whereas the activation energy of BPA-PC decreases with increasing TMBPA-PC concentration (Table 6.1).

The α - relaxation in the mixtures is dynamically situated within the frequency and temperature window marked by the pure components. The β-relaxation shows a distribution of the pre-exponential factors of the Arrhenius equation. The size τ0 for βTMBPA-PC decreases from 10^{-13.6} s for pure TMBPA-PC to 10^{-15.6} s for the mixture with 80% BPA-PC. In comparison, τ0 for βBPA-PC increases from 10^{-17} s for pure BPA-PC to maximum of 10^{-14.5} s with increasing concentration of TMBPA-PC (Table 6.1).

<table>
<thead>
<tr>
<th>Volume fraction (ΦTMBPA-PC)</th>
<th>E_a (βBPA-PC) kJ / mol ± 2</th>
<th>E_a (βTMBPA-PC) kJ / mol ± 2</th>
<th>-log τ0 (βBPA-PC)</th>
<th>-log τ0 (βTMBPA-PC)</th>
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<td>0.00</td>
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<tr>
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<td>95.0</td>
<td></td>
<td>15.5</td>
</tr>
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<td>95.1</td>
<td></td>
<td>*</td>
</tr>
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<td>1.00</td>
<td></td>
<td>79.0</td>
<td></td>
<td>13.6</td>
</tr>
</tbody>
</table>

Table 6.1 The activation energies (E_a) and the pre-exponential factor (-log τ_0) for BPA-PC and TMBPA-PC β-relaxation at various mixture compositions.

6.3 Mixtures of PS / P(CHA-BMA)

6.3.1 α-Relaxation
The system PS / P(CHA-BMA) has an upper miscibility gap (Fig. 5.2). The dielectric measurements were performed in the one-phase region (280 K - 380 K) and the \(\alpha\)-relaxation curves obtained for the pure components and for mixtures with \(\Phi_{PS} = 0.3\) and 0.5 are shown in Figure 6.6.
Figure 6.6: Comparison of dielectric loss curves $\varepsilon''(\omega)$ in pure $P(\text{CHA-BMA})$ (a.), and in mixtures with $\Phi_{PS} = 0.3$ (b.) and 0.5 (c.). Fits were performed using the Havriliak-Negami function (eq. 3.43).

Figure 6.7: Temperature dependence of the characteristic relaxation time $\tau_{HN}$ calculated from HN-fits for the pure polymers and a mixture $PS/P(\text{CHA-MBA})$ with concentration $\Phi_{PS} = 0.5$

Figure 6.7 shows that the dynamics of the $\alpha$-relaxation which are characterised by the temperature dependence of the mean relaxation times for the pure components and the mixtures. The WLF parameters $C_1$, $C_2$ and $f_0$ for the PS and the P (CHA-BMA) obtained by fitting the data are respectively 13.0, 64.5 K, 10^{-0.5} Hz and 15.6, 60 K, 10^{-3} Hz.
6.3.2 Shape Parameters and Half Widths

The glass transition temperatures for PS and P(CHA-BMA) vary by 90 K which is almost twice that between BPA-PC and TMBPA-PC. This system shows much broadening of the $\alpha$-relaxation in the mixtures than in the pure components. The shapes of the curves are strongly temperature dependent (Fig 6.6b, c). The curves become more symmetrical with increasing PS concentration. Figure 6.8 shows the concentration dependence of the parameters $\alpha$ and $\alpha\gamma$ compared at $T - T_g = 20$. 

![Graph showing HN-parameters vs $\Phi_{PS}$]
Figure 6.8: Havriliak-Negami shape parameters \( \alpha, \alpha\gamma \) (\( \PhiPS \)) as a function of composition taken at \( T - T_g = 20 \text{ K} \).

Figure 6.9 shows the half widths \( \delta_{1/2} \log \omega \) of the frequency dependent loss curves plotted as function of \( T - T_g \) for various mixtures. A comparison of the temperature dependence of the half widths of the calculated time distribution curves with that of the frequency distribution shows that \( \delta_{1/2}\log \omega \) diverges at the same value \( |T - T_g| = C_2 \), when the reciprocal of the width( 1/width) is plotted against \( T - T_g \) (Fig. 6.10a, b).
Figure 6.9: Half widths of the measured frequency distribution as a function of $T - T_g$ for various mixtures.
Thus $\delta_{1/2} \log \omega$ scales with temperature as

$$\left(\delta_{1/2} \log \omega\right)^{-1} \propto \left(T - T_g\right) \quad (6.1)$$

Since

$$\left(\delta_{1/2} \log \tau/\tau_g\right)^{1/2} \propto \left(T - T_g\right)$$

it follows from comparison of the two distributions that for a given constant concentration fluctuation.

$$\left(\delta_{1/2} \log \omega\right)^2 \propto \left(\delta_{1/2} \log \left(\tau/\tau_g\right)\right) \quad (6.2)$$

**Figure 6.10:** Comparison of the temperature dependence of the half widths of the frequency (a) and relaxation time (b) distributions of various mixtures.
Figure 6.11: Comparison of dielectric loss curves measured at $T - T_g = 20$ in mixtures with different compositions.

Figure 6.12: Relaxation time distribution evaluated at $T - T_g = 20$ corresponding to the mixtures in Figure 6.10 with variance $<(\delta \phi)^2> = 0.0035$ of the concentration distribution.
The temperature dependence of the half widths of the relaxation time distribution can be drawn directly from equation (4.10). In the case that $\frac{dT_g}{d\phi} \approx$ constant and for a constant $\delta\phi$,

$$< (\log(\tau/\tau_g))^2 > \propto \left( \frac{d \log(\tau/\tau_0)}{dT_g} \right)^2_{T_g = \langle T_g \rangle}$$  \hspace{1cm} (6.3)

From the Vogel equation (3.68),

$$\frac{d \log(\tau/\tau_g)}{dT_g} = \frac{B}{(T - T_0)^2}$$  \hspace{1cm} (6.4)

and substituting (6.4) in (6.3) leads to the observed relationship between $(\delta\gamma^2 \log \tau)$ and $(T - T_g)$. By using the WLF or the VFT scaling Donth has shown that the broadness of a spectrum $\delta\log \omega$ is related to the Vogel temperature $T_0$ by $(\delta \log \omega)^{-1} \sim T - T_0$ [Don92].

### 6.4 Concluding Remarks

On the basis of the presented experimental results the temperature behaviour of the distribution of relaxation times caused by concentration fluctuations for the $\alpha$-relaxation in mixtures is related to the temperature dependence of the measured relaxation frequency distribution. This is in support of the assertion that the broadening of the glass transition and dielectric dispersions in mixtures results from the fluctuation in composition. Although only one $\alpha$-relaxation is observed in the BPA-PC / TMBPA-PC mixtures, two $\beta$-relaxation processes are observed in the temperature range of the $\beta$-relaxation corresponding to the pure polymers
in their glassy state. A detailed analysis of the $\alpha$-relaxation using the concentration fluctuation model and the effect of blending on the $\beta$-relaxation strength for the two components in BPA-PC / TMBPA-PC mixtures will be presented and discussed in the following chapter.
7 Analysis of Results

7.1 Application of the Concentration Fluctuation Model to PS / P(CHA-BMA)

Polystyrene has negligible relaxation strength compared to the P(CHA-BMA) therefore this system satisfies the requirement for the analysis using the concentration fluctuation model. The parameters required for the analysis using this model are:

1. A function describing the variation of the glass transition temperature with concentration $T_g(\phi)$.
2. The WLF parameters $C_1$, $C_2$, and the glass transition temperatures for the pure components $T_{g_A}$ and $T_{g_B}$.
3. The Havriliak - Negami shape parameters $\alpha$, $\gamma$ as a function of $T - T_g$ for the component dominating the relaxation behaviour of the mixture.

The calculation is carried out as follows:

a) The $T_g$ for the mixture is calculated using the Fox equation as

$$T_{g_{\text{mix}}} = \frac{T_{g_A} \times T_{g_B}}{T_{g_B} + \phi_B \left( T_{g_A} - T_{g_B} \right)} \quad (7.1)$$

b) The glass transition temperature values of the pure components are obtained from the best fit of the data obtained using DSC (Figure 7.1)
Figure 7.1: Glass transition temperature as a function of composition. The solid line shows the fit using the Fox equation for mixtures.

The WLF parameters for the polar component are obtained taking the $T_g$ as reference. The values are $C_1 = 14.8$  $C_2 = 57.8$ and $f_g = 1.4 \times 10^{-3}$ Hz.

c) Since it is assumed in the model that the relaxation behaviour of the mixture is dominated by the polar component which retains its shape parameters in the mixture as in the pure state, the $\alpha$, and $\gamma$ (HN) for the mixtures are taken to be those at equal temperature intervals from $T_g$ with the pure component (Fig. 7.2)
By using the WLF parameters obtained in (b) a distribution function for the relaxation time arising due to concentration fluctuations is determined from $T_g$ ($\phi$) and the WLF equation (see Figure 4.2). This function is then folded with the loss function of the polar component characterised by the shape parameters $\alpha$, and $\gamma$ (HN) yielding a dielectric loss spectrum of the mixture which is of the form

$$
\varepsilon''_{\text{mix}}(\omega) = \int_0^\infty n_v(\tau) \cdot \varepsilon''_A(\omega \tau) d\tau
$$

(7.2)

By fitting the experimental relaxation curves with the product (7.2) the variance $< (\delta\phi)^2 >$ which is contained as the variable parameter in the relaxation time

Figure 7.2: The Havriliak-Negami shape parameters $\alpha$, $\gamma$ plotted against $T - T_g$ for the polar P(CHA-BMA)
distribution function $n_v(\tau_i)$ is obtained. The temperature dependence of the relaxation curves gives a direct relation of the calculated concentration fluctuations with temperature (Figure 7.4). Figure 7.3 shows the measured dielectric loss curves for various mixtures. The solid lines are the fits using equation (7.2) of the concentration fluctuation model. The same temperature dependence of the shape of the relaxation curves in the mixtures are well reproduced. Thus without invoking the validity of temperature-time superposition principle, this model reproduces the loss curves characteristic for mixtures. From the obtained results it follows that the Gaussian approximation made for the concentration fluctuations is justified. By a direct deconvolution of measured relaxation functions in mixtures of Polystyrene and Polyvinyl methyl ether (PS / PVME), similar relaxation distributions were obtained by Alvarez [Alv93, Alleg93]. His analysis applied a modified Contin-program and it was shown that the concentration distributions obtained from the dielectric measurements were nearly gaussian with the variances being in the same order of magnitude as those obtained using the concentration fluctuation model.
Figure 7.3: Measured dielectric loss curves for the PS / P(CHA-BMA) mixtures with $\Phi_{PS} = 0.2$ (a.) and 0.3 (b.) fitted with equation 7.2 of the concentration fluctuation model.
Figure 7.3: Measured dielectric loss curves for the PS / P(CHA-BMA) mixtures with $\Phi_{PS} = 0.5$ (c.) and 0.6 (d.) fitted with equation 7.2 of the concentration fluctuation model.
Figure 7.4: Concentration fluctuations as obtained from the fits in Fig. 7.2. The temperature dependence of the fluctuations is guided by the factors which determine the relaxation behaviour.

The concentration fluctuations plotted against $T - T_g$ fall onto a master curve in the composition range 0.2 to 0.5. This observation is specific for this system since $< (\delta \phi)^2 >$ values obtained earlier for PS/PVME [Zet92] do not show this behaviour (Figure 7.5). It reflects the temperature and composition dependence of the half widths shown in figure 6.10. In the miscibility range, the concentration and temperature dependence of the concentration fluctuations is determined by the static structure factor which also yields the temperature and concentration dependence of the interaction parameter ($\chi$). SANS measurements on PS/P(CHA-MBA) reveal a concentration independence of $\chi(T)$ in the composition range between $\Phi_{PS} = 0.2$ and 0.5. (see Figure 5.4). In contrast $\chi$ in PS/PVME strongly depends on composition [Had84, Shi85]. Since the $\alpha$-relaxation is governed by the volume of co-operativity which is itself a
function of \([T - T_g(\phi)]\), the concentration and temperature dependence of the concentration fluctuations will depend on the balance between the thermodynamic effects, \(S(q=0)\) and the dynamics \(V(T-T_g(\phi))\).

![Figure 7.5: Concentration fluctuations evaluated for mixtures PS / PVME plotted as a function of \(T - T_g\). The data was obtained from the Ph.D Dissertation of Aline Zetsche [Zet92]](image)

The assumption that the temperature dependence of the relaxation time in the mixtures is the same as in pure polar component allows for a check of the self-consistency of the model.
It is expected that the relaxation (HN) of P(CHA-BMA) components should be independent on composition and show the same WLF-parameters as the pure P(CHA-BMA). The results obtained for PS/P(CHA-BMA) confirm this assumption well up to 50% of polystyrene composition (Fig. 7.6). A similar consistency of the model was shown for the system PVME / PS [Fis92]. At higher PS compositions ($\Phi_{PS} > 0.5$), the shape parameters are strongly influenced by PS such that the curves cannot be fitted by $\alpha, \gamma (T - T_g)$ taken from the polar component.

Figure 7.6: Temperature dependence of the relaxation time of P(CHA-BMA) segments in the mixtures showing similar WLF behaviour as the pure polymer.
7.2 Size of Co-operatively relaxing Units.

It was pointed out in section (2.4) that within the glass transition the $\alpha$-relaxation is strongly governed by the volume of co-operatively relaxing domains. Requiring statistical independence of these domains a "coarse graining" volume $V_a$ can be introduced which will determine the extent of correlation of the concentration fluctuations in the mixtures. Thus apart from the interaction between the mixture components, the pair correlation function of the concentration fluctuations will depend on both $\chi(T)$ and the size of $V_a$. as the comparison of the results for PS/PVME and PS/P(CHA-BMA) seems to suggest.

In the thermodynamic limit (long wavelength limit) $< (\delta \phi)^2 >$ is inversely proportional to $V_a$. This will hold only for the case that $V_a >> $ $\xi^3$. It should be mentioned that $\xi$ is composition dependent and in fact in PS/P(CHA-BMA) which at a constant $T - T_g$ the level of concentration fluctuations was the same for various compositions, $\xi$ decreased with increasing PS composition.

Using an ansatz developed for density fluctuations [Rul75], the variance of the concentration fluctuations $< (\delta \phi)^2 >$ can similarly be related to the static structure factor $S(q)$ and the form factor $F(qr)$ of the co-operatively relaxing domain here identified as $V_a$. The structure factor of the PS / P(CHA-BMA) is known from small angle neutron scattering (SANS) measurements [Hack93]. By assuming a certain form for $V_a$ (for example a sphere for case of isotropic samples) the radius $r$ of the co-operatively relaxing domains can calculated from

$$< (\delta \phi)^2 > = \frac{\sigma^3}{(2\pi)^3} \int_0^\infty S(q)F^2(qr) \cdot 4\pi q^2 dq$$  \hspace{1cm} (7.3)$$

where $\sigma$ is the length of a statistical segment, $S(q)$ is the structure factor in the Random-Phase-Approximation and $F(qr)$ is the form factor of the co-operatively relaxing sphere of radius $r$. Figure 7.7 shows the length scale of co-operatively relaxing dipoles as function of temperature for various mixtures.
Figure 7.7: Temperature dependence of the volume of co-operativity obtained from fits curves in Fig. 7.3 and estimated for a sphere.
Figure 7.8: Log(r) vs Log (T - T₀) showing the temperature dependence

\[ r \propto (T - T₀)^v \] with \(-0.64 \leq v \leq 0.67\)

The temperature range in which the α-relaxation in miscible blends is measured lies in the region where the VFT scaling \((T < T_A)\) is obeyed. As is typical for polymers, the cross-over temperature \(T_A\), which marks the transition from VFT to an Arrhenius behaviour does not show up. An observation of this temperature is in mixtures further limited by the position of the coexistence curve. The α-relaxation in mixtures as is characteristic for the relaxation-processes in the VFT-range \(T << T_A\), is governed by co-operative dynamics, involving simultaneous and correlated changes of degrees of freedom of many segments in an extended region as opposed to independent motion of individual units typical in the Arrhenius range.

The assumption of co-operative dynamics implies the existence of "co-operatively rearranging domains [CRD] with a characteristic life time of the order of the relaxation time \(\tau_\alpha\) of the α-relaxation. In mixtures it is expected that the size of the domains will be influenced by composition, especially when
the components strongly vary in structure. This is in line with the observation by Ngai, that the degree of intermolecular coupling associated with the relaxation of a given segment will vary according to the composition of the local environment [Nga92].

The concentration fluctuation model enables the experimental determination of the size of the domains of co-operativity [Fis92, 93] in mixtures. Figure 7.7 shows the temperature dependence of the radius of a spherical domain of co-operativity in various mixtures. The mean domain radius $r$ increases as the temperature decreases which is in agreement with theoretical predictions.[Gib58, Don92, Fis92,] In the treatment of Adam and Gibbs, it was assumed that the apparent activation energy is proportional to the size of the unit that must move co-operatively. A similar assumption was made by Matsuoka [Mat90]. Figure 7.9 shows a double logarithmic plot of the variation of the apparent activation $E_a$ with temperature obtained from the WLF relation

$$E_a = \frac{R T^2 C_1 C_2}{[C_1 + (T - T_0)]^2} \quad (7.4)$$

where the WLF parameters are assumed to be equal to those of the polar component. $R$ is the gas constant and $T_0(\phi)$ is the Vogel temperature which is also composition dependent.
The apparent activation energy evaluated for the $\alpha$-relaxation in the mixtures varies inversely proportionally with $T - T_0$ leading to the relation between the activation energy and the volume of co-operativity, $E_a \propto V_a^{1/2}$. This follows from Figure 7.4 which shows that $V_a \propto (T - T)^{-2}$. The scale of co-operativity at $T_g$ can be estimated from DSC thermograms by using the Donth fluctuation formula

$$V_a = \frac{kT_g^2 \Delta C_p}{\rho(\delta T)^2}$$

(7.5)
where $\delta T$ is the half widths of the glass transition range $\frac{\Gamma T_g}{2}$. Table 7.3 shows the values of $r$ calculated for the homopolymers and the mixtures from DSC and the values obtained using the concentration fluctuation model (CFM) are shown for comparison.

<table>
<thead>
<tr>
<th>Mixture with PS concentration $\Phi_{PS}$</th>
<th>Radius $r \pm 0.5$ [nm] (DSC)</th>
<th>$r \pm 0.5$ [nm] (CFM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(CHA-BMA)</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>4.5</td>
<td></td>
</tr>
</tbody>
</table>

*Table 7.3:* The scale of co-operativity $r$ at $T_g$ estimated from temperature fluctuations and from dielectric measurements.

The values of $r$ obtained from both methods are composition dependent with those from DSC being smaller than those obtained using the concentration fluctuation model. However, the values compare well within the experimental errors involved in both methods.

Due to the fact that the $\alpha$-relaxation in the homopolymers and the mixtures are non-Arrhenius a comparison of the effect of temperature on the measured relaxation times in different mixtures can be compared by adapting the normalisation scheme proposed by Angell [Ang91] which employs $T_g$-scaled Arrhenius plots. These are normally referred to as the fragility plots for low molecular weight glass formers. For polymers, it has been suggested that the term
co-operativity plot should be more appropriate [Nga93]. Figure 7.10 shows a co-operativity plot for P(CHA-BMA) and some mixtures with PS. The similarity of the curves suggests the dominance of P(CHA-BMA) in the relaxation behaviour in the mixtures as was assumed in the concentration fluctuation model.

![Figure 7.10: A co-operativity plot depicting the temperature dependence of the relaxation time in pure P(CHA-BMA) and in the mixtures. The glass temperature was taken to be that at which the relaxation rate was 100 Hz instead of the calorimetric values.](image)

7.3 The $\beta$-Relaxation

The $\beta$-Relaxation in polycarbonates based on bisphenol A has been extensively studied and several molecular assignment to the motions have been made [Kru59, Ish65, Ill61, Leg69]. NMR studies on selectively deuterated polymers enabled Spiess [Spi83] to conclude that the C-CH bonds are fixed while the phenylene units undergo flips in addition to small angle fluctuations. Dynamic
mechanical measurements on BPA-PC [Yee81] led to the conclusion that the relaxation involves the entire monomer unit. Recent dynamic mechanical studies on block copolymers of BPA-PC and TMBPA-PC [Jho92] suggest that the relaxation in BPA-PC is co-operative with the number of units involved ranging between 6 and 9. This argument is based on the fact that BPA-PC and TMBPA-PC have well resolved separated β-relaxation processes but the copolymer exhibits only one averaged secondary relaxation. The two β-relaxation peaks are restored at their corresponding temperatures when the block length is increased to 9 units. Such numbers are definitely too high for a localised relaxation process and the claim of co-operativity does not so far have enough physical argument. It is known [Kim92] that the miscibility and equilibrium phase behaviour of mixtures of polycarbonates with other polymers can be improved by a variation of the polycarbonate structure. This can primarily be achieved by substitutions either onto the phenyl rings or by changing the connector groups between the two rings. The vast interaction of polycarbonates with other polymers and its own derivatives gives an opportunity to design useful blends. Of central interest are the improved properties in the glassy state which has led to studies looking into the effect of mixing BPA-PC with other solid amorphous polymers on its local molecular motions [Bra71,Poc77]. Suppression of the β-peak in BPA-PC has been observed in polymer-polymer [Land89,But91] and in plasticizer-polymer combinations [Fis85]. In the case of the plasticised polymer the suppression was associated with the suppression of free volume fluctuations due to the presence of the plasticizer which resulted to a more ordered glassy state [Fis85]. It has often been concluded from dynamic mechanical experiments that an antiplastisizing effect leads to the suppression of the β-peak in BPA-PC when blended with TMBPA-PC. Since the β-relaxation in polycarbonates is dielectrically active due to the polar carbonyl groups, dielectric spectroscopy was employed to study the influence of blending two similar polycarbonate based polymers on their sub-Tg β-relaxation. This enabled to further examine the
controversial question whether in the blends the secondary molecular motions of these components are co-operative or totally independent. Dielectric spectroscopy has the advantage that the electric fields used interact directly with the dipoles within the sample in a highly specific way as compared to mechanical forces which excite all available internal motions more collectively. In the following a detailed analysis and discussion of the $\beta$-relaxation in BPA-PC / TMBPA-PC mixtures is presented.

7.3.1 Peak-Temperature Shift

Figure 7.11 shows the temperature of the peak maximum deduced for the mixtures from Figure 6.8. The BPA-PC peak is insensitive to composition at the lower temperature tail as compared to the higher temperature part.

*Figure 7.11: Peak-maximum position of the $\beta$-relaxation of the BPA-PC and TMBPA-PC components in the mixtures.*
The TMBPA-PC β-peak shifts by 17 ± 2 K at a BPA-PC concentration of 80% whereas the BPA-PC β-relaxation peak is shifted by almost 40 K at a TMBPA-PC composition of 90%. These results are in agreement with observations from dynamic mechanical measurements reported by Hörth [Hör86] and recently by Kim [Kim92]. Various explanations have been proposed for the shift of the peak in BPA-PC. Hörth attributed it to the strong suppression of the high temperature tail. It was postulated that the BPA-PC β-relaxation could consist of two parts with different relaxation time distributions with the higher temperature part being easier to suppress. A similar argument was given by Landry and Heinrich [Land89] for the BPA-PC β-peak suppression in BPA-PC / PMMA mixtures. They attributed the peak shift to selective inhibition of the local motion in BPA-PC. It is notable that in both BPA-PC and TMBPA-PC the dipole moments which form the dielectric probe are in the polar carbonate group and not on the phenyl rings. However changing the phenyl ring structure (by attaching methyl groups) in going from bisphenol-A to tetramethylbisphenol-A polycarbonate shifts the β-peak by 150 K higher and the peak height increases (Fig. 6.9). It would be expected that if the β-relaxation was due only to the low-temperature carbonyl group motion the peak should be observed in the same temperature range in both BPA-PC and TMBPA-PC. The difference in the peak positions in the two polymers indicates how strongly the carbonyl group motion is coupled to the motions of the phenylene rings. By combining SAXS an WAXS measurements it was shown by Floudas et. al. [Flou93] that TMBPA-PC has a higher free volume and higher free volume fluctuations at $T \leq T_g$ than BPA-PC. Similar results were theoretically deduced by Kim et al. [Kim92] who used the Bondi´s group contribution method to estimate the specific free volume in blends of BPA-PC and TMBPA-PC. According to free volume theories [Fer80] increasing the free volume usually should lower the peak temperature. The shift to higher temperatures of the β-peak in TMBPA-PC implies that the mobility in the tetramethylbisphenol-A segment is lower than that of bisphenol A segment.
This fact is reflected by the radius of the gyration of TMBPA-PC which is larger than that of the BPA-PC [Hel91]. It is therefore conceivable that the apparent suppression of the higher temperature tail and the shift of BPA-PC peak temperature is a consequence of the coupling of the ring motion in BPA-PC with the limited ring motion in TMBPA-PC. This results in a selective de-coupling of the phenylene ring motion from the carbonyl group, an effect which is felt more by the flexible BPA-PC molecules.

### 7.3.2 Relaxation Strength

The nature of intermolecular interactions between the blend components can be determined by obtaining the scaling behaviour of the relaxation strength $\Delta \varepsilon$ as a function of composition. Figure 7.12 shows the variation of the $\beta$-relaxation strength in BPA-PC and TMBPA-PC with composition.

![Figure 7.12: Relaxation strength $\Delta \varepsilon$ of the $\alpha$- and $\beta$-relaxation processes as a function of TMBPA-PC volume fraction ($\Phi_{TMBPA-PC}$). The relaxation strength of the $\alpha$-relaxation (●) was measured for all mixtures at](image)
$T - T_g = 15$ K and for the $\beta$-relaxation in BPA-PC ($\Delta \varepsilon$) at 194 K and at 380 K for the $\beta$-process in TMBPA-PC ($\Box \Delta \varepsilon$)

The relaxation strength can be approximated using the Onsager equation [Ons36]

$$\Delta \varepsilon = \varepsilon_i - \varepsilon_\infty = \frac{4\pi n \mu^2}{9kT} \quad (7.7)$$

where $n$ is the number density of dipole moments and $\mu$ is the dipole moment. This approximation gives a relaxation strength which at a given temperature is proportional to the number of dipole moments. It is shown in Figure 7.12 that the relaxation strengths evaluated at 194 K for the $\beta$-relaxation in BPA-PC and at 380 K for the $\beta$-relaxation process corresponding TMBPA-PC decrease with increase of the volume fraction of the second component. The variation of the $\beta$-relaxation strength with blend composition shows for both components a peak attenuation that results mainly from dilution effects (dotted lines in Figure 7.12). In fact, for a given concentration (Table 7.2), the relaxation strengths of the $\beta$-processes in the mixtures add up to those of the pure components.

A similar behaviour is shown by the $\alpha$-relaxation when compared for different compositions at the same temperature intervals from $T_m$. The relaxation strength decreases with increase of the volume fraction of TMBPA-PC.

<table>
<thead>
<tr>
<th>Volume fraction ($\Phi_{TMBPA-PC}$)</th>
<th>$\Delta \varepsilon$ ($\alpha$-relaxation) at $T - T_g = 15$ K</th>
<th>$\Delta \varepsilon$ ($\beta_{BPA-PC}$) at 194 K</th>
<th>$\Delta \varepsilon$ ($\beta_{TMBPA-PC}$) at 380 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.36</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>0.11</td>
<td>0.34</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>0.22</td>
<td>0.34</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>0.38</td>
<td>0.31</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>0.53</td>
<td>0.30</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>0.68</td>
<td>0.27</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>0.82</td>
<td>0.26</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>0.91</td>
<td></td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.24</td>
<td>0.18</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.2: Relaxation strengths $\Delta \varepsilon$ of the $\alpha$- and $\beta$-relaxation shown in
7 Analysis of results

Figure 7.12

7.3.3 Distribution of Activation Enthalpy

The dynamics of relaxation processes are described by a distribution of relaxation times the temperature dependence of which shows the type of activation processes present in a system. New orientational energy barriers are expected in mixtures which will influence not only the length of the relaxation time but also the width of the relaxation time distribution. For secondary relaxations this distribution may be linked with a distribution of activation energies or a distribution of pre-exponential factors or both. Despite the limitations of the activation complex theory as an explanation for molecular diffusion phenomena, the Starkweather procedure discussed in chapter (4) can be used to determine the free energy of activation $\Delta G^*$, the enthalpy $\Delta H^*$ and the entropy $\Delta S^*$ for the $\beta$-relaxation. The entropy of activation which can be considered to be a characteristic parameter for an activated process is in turn related to the pre-exponential factor in the Arrhenius analysis (eq. 4.19).

Figure 7.13 shows the distribution of the activation energies obtained using the Erying-Starkweather analysis for the $\beta$-relaxation in BPA-PC and TMBPA-PC and in their mixtures.
Figure 7.13: Distribution of the free enthalpy of activation ($\Delta G^*$) for the $\beta$-transition in BPA-PC both in the pure state and in (65/35) BPA-PC / TMBPA-PC mixture.
Figure 7.14: Distribution of the free enthalpy of activation ($\Delta G^*$) for the $\beta$-transition in TMBPA-PC both in the pure state and in (20/80) BPA-PC / TMBPA-PC mixture.
Figure 7.15: Single curve obtained for the $\beta_{\text{TMBPA-PC}}$-relaxation in BPA-PC / TMBPA-PC mixture (20/80) after shifting the points parallel to the $\Delta G^*$ axis. The shift shows that the relaxation exhibits a positive non-zero activation entropy.

Figures 7.13 and 7.14 show the distribution of activation energies for the $\beta$-relaxation in the homopolymers and in their mixtures. The distribution of BPA-PC shows much scattering of the points at the lower energy (high frequency side) which implies a positive non-zero activation entropy. Similar observations are made for TMBPA-PC where the higher energy end falls on a master curve only when the points are shifted horizontally. Notable is the fact that in BPA-PC the mean activation energy is lower in the mixtures than in the pure component in contrast to TMBPA-PC in which the mean is almost constant.

To obtain the $\Delta H^*$, and $\Delta S^* \log (1/\tau T)$ was plotted against the reciprocal of the temperature as illustrated for the pure components in Figure 7.16.
Figure 7.16: Plot for determining the enthalpy ($\Delta H^*$) and the entropy of activation ($\Delta S^*$)

The plot is a straight line whose slope is $-(\Delta H^*/R)$ and the high temperature intercept gives $\ln \left[ \frac{k}{2\pi h} + \frac{\Delta S^*}{R} \right]$. The values obtained are summarised in table 7.3 in which the activation energies obtained from the Arrhenius analysis are shown for comparison. The values of $\Delta H^*$ compare well with $E_a$ although they are systematically lower. For TMBPA-PC an average value of $\Delta S^* = 44.1 \pm 5$ J/mol/K for the $\beta$-relaxation in the homopolymer and in the mixtures is found. Pure BPA-PC has a $\Delta S^*$ which is almost four times that of the pure TMBPA-PC. Activation entropies of about 50 J/mol K have been reported for PMMA [Muz91] and for polycarbonate [Sta89]. The question is whether these non-zero $\Delta S^*$ reflect co-operativity of motion or a feature of an
activated state. It is remarkable how the activation entropy of the $\beta$-relaxation process in BPA-PC drastically decreases with an increase of TMBPA-PC composition. This observation is compatible with apparent shift of the peak position which is further combined with a decrease in the activation energy (see section 7.3.1). The decrease in entropy is reflected in the change of the pre-exponential factors in the Arrhenius equation and suggests that the process becomes more simple in the Starkweather sense as the TMBPA-PC composition increases.

<table>
<thead>
<tr>
<th>$BPA$-$PC$</th>
<th>$TMBPA$-$PC$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{\text{TMBPA}}$</td>
<td>$E_{\text{arrh}}\pm$2 [kJ/mol]</td>
</tr>
<tr>
<td>0</td>
<td>53.8</td>
</tr>
<tr>
<td>0.22</td>
<td>47.2</td>
</tr>
<tr>
<td>0.38</td>
<td>40.5</td>
</tr>
<tr>
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<td>39.3</td>
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<tr>
<td>0.68</td>
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</tr>
<tr>
<td>0.82</td>
<td>37.8</td>
</tr>
<tr>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.3: $\Delta S^*$, and $\Delta H^*$ calculated from Erying-Starkweather analysis and compared with the activation energy values obtained from Arrhenius analysis.
7.4 Conclusions

The results obtained in the foregoing analysis can be summarised as follows:

Glass transition and $\alpha$-relaxation in polymer mixtures
- Polymer mixtures comprising two components with distinctly different glass transition temperatures ($|T_{gA} - T_{gB}| \geq 20$ K) exhibit a single but broadened calorimetric glass transition and a single broadened $\alpha$-relaxation (dynamic glass transition) as compared to the transitions in the pure components.
- The broadening of the $\alpha$-relaxation as shown in both PS/P(CHA-BMA) and BPA-PC/TMBPA-PC mixtures is a function of the temperature interval $T - T_g$ and increases as the glass transition temperature is approached.
- The broadening of the glass transition region and the $\alpha$-relaxation is attributed to the existence of concentration fluctuations.
- The shape of the dielectric $\alpha$-peak in PS/P(CHA-BMA) depends strongly on temperature such that the time - temperature superposition does not hold for the mixtures.
- The shape of the dielectric $\alpha$-relaxation in the one phase regime of miscible blends can be quantitatively described by a models which assumes a Gaussian approximation for the concentration fluctuations and a Vogel-Fulcher-Tamman free volume scaling for the relaxation time which is dominated by one component of the mixture.
- By fitting the measured loss curves in PS/P(CHA-BMA) mixtures with an analytical function from the concentration fluctuation model, the mean square concentration fluctuations $<(\delta \phi)^2>$ at various temperatures above $T_g$ were obtained.
- The assumption that the distribution of concentration in the sample is Gaussian is confirmed by the experimental results.
Within the glass transition the $\alpha$-relaxation strongly depends on the volume of co-operatively relaxing domains. By introducing a reference volume with a certain amplitude for the concentration fluctuations, the size of the domain of co-operativity can be calculated using the random phase approximation of the structure factor $S(q)$. The radius obtained for a spherical reference volume lies between 6-10 nm for the PS/P(CHA-stat-BMA) mixtures of composition $\phi_{PS}$ between 0.2 and 0.5. A value of $r = 4$ nm was estimated for the pure copolymer at $T_g$.

The radius scales with temperature as $r \propto (T - T_0)^\nu$ with $\nu \approx -2/3$ as predicted from the fluctuation approach according to Donth. $T_0$ is the Vogel temperature.

The half widths $\delta_{\nu/2} \log \omega$ of the dielectric loss curves show a temperature dependence as predicted by the fluctuation model $(\delta_{\nu/2} \log(\tau/\tau_g))^{-1/2} \propto T - T_0$ and $(\delta_{\nu/2} \log \omega)^{-1} \propto T - T_0$ which gives the relation $\left(\delta_{\nu/2} \log(\tau/\tau_g)\right) \propto \left(\delta_{\nu/2} \log \omega\right)^2$.

The width of the frequency distribution diverges at $T - T_g \approx C_2$, the WLF parameter.

**The $\beta$-relaxation in BPA-PC/TMBPA-PC mixtures**

Although only one $\alpha$-relaxation is observed in the BPA-PC/TMBPA-PC mixtures, two $\beta$-relaxation processes are observed at the peak temperatures corresponding to the pure components.

The variation of the $\beta$-relaxation strength with blend composition strongly shows for both components a peak attenuation that results mainly from dilution effects.

The mean activation energy of TMBPA-PC is nearly constant throughout the composition range whereas the activation energy of BPA-PC decreases with increasing TMBPA-PC concentration.
• The peak maximum temperature for TMBPA-PC $\beta$-relaxation in the mixtures are close to that of the homopolymer whereas the BPA-PC $\beta$-peak temperature shifts to lower temperatures with increasing TMBPA-PC composition. This shift is accompanied by a decrease in the entropy of activation $\Delta S^*$ which indicates that the BPA-PC $\beta$-relaxation becomes more localised with the increase of TMBPA-PC composition.
8 Summary and Concluding Remarks

The purpose of this work was to study the molecular dynamics in polymer mixtures both around and above the glass transition temperature and in the glassy state. This was achieved by using dielectric spectroscopy (in the frequency range from 10^{-2} Hz to 10 MHz) and differential scanning calorimetry. Mixtures of a statistical copolymer poly(cyclohexylacrylate-stat-butylmethacrylate) and polystyrene and mixtures of bisphenol A and tetramethylbisphenol A polycarbonate were investigated. In both systems the dielectric \( \alpha \)-relaxation was broader in the mixtures than in pure components. The shape and the broadening effect of the loss curves was quantitatively analysed by using a model based on concentration fluctuations in the mixtures which was developed by Fischer and Zetsche [Fis92]. The results obtained for PS/P(CHA-BMA) show an excellent agreement with the assumptions of this model. Evaluation of the loss curves yielded as a result the variance of the concentration distribution \( \langle (\delta \phi)^2 \rangle \) and its temperature dependence. By using an ansatz developed for density fluctuations, the variance of the concentration distribution was compared with small angle neutron scattering measurements for the structure factor \( S(q) \) and the size of the domains characterised by co-operative dynamics in the vicinity of the glass transition was calculated. The radius of these domains in PS/P(CHA-BMA) estimated for isotropic samples at \( T_g \) were between 6 and 10 nm for the composition range \( \phi_{PS} = 0.2 - 0.5 \).

The BPA-PC/TMBPA-PC mixtures displayed only one \( \alpha \)-relaxation and two \( \beta \)-relaxation processes in the temperature ranges corresponding to the \( \beta \)-relaxation in the pure components. The results show no antiplasticization effect as has been suggested in several dynamic mechanical spectroscopy measurements. The attenuation of both \( \beta \)-peaks is mainly due to dilution effects.
From the analysis of the distribution of the free energy of activation $\Delta G^*$, it was shown that the mean activation energy in TMBPA-PC does not change with composition whereas that of BPA-PC decreases with an increase of TMBPA-PC. The entropy of activation $\Delta S^*$ in BPA-PC decreased drastically with increase of TMBPA-PC composition showing that the $\beta$-relaxation process becomes more localised. This is suggested by a shift of the peak to lower temperatures, a suppression of the higher temperature tail and a total composition independence of the lower temperature counterpart.

It is notable that $\alpha$-relaxation strength in BPA-PC/TMBPA-PC decreased with increase of $\phi_{TMBPA-PC}$ which according to the concentration fluctuation model seems to suggest an increase of the volume of co-operativity. It is therefore recommended that computer modelling should be done for this systems in order to study the dynamics both near and above the glass transition temperature and in the glassy state.

The concentration fluctuation model makes the assumption that only one of the components should dominate the dielectric relaxation behaviour of the mixtures. This assumption definitely holds within a certain concentration range. For a more complete picture however it is worthy looking at the dynamics of the dielectrically passive component. A combination of different methods, for example dielectric spectroscopy which monitors the relaxation behaviour of the polar component and scattering experiments which reveal the dynamics of polystyrene, may give more useful information.
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