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Glass transition of heterogeneous polymeric systems studied by calorimetry

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Abstract This personal review focuses on two aspects. First, glass transition dynamics and hence also calorimetry is connected to dynamic heterogeneity. This results in an interplay of the corresponding dynamic length scales and length scales from structural heterogeneities in polymeric samples. Second, the complexity of the dynamic glass transition itself results in different effects of this interplay for different experimental observables. Hence the comparison of results from calorimetry with other relaxation methods gives important clues to an understanding of the complex glass transition phenomenon.

Keywords Calorimetry · Glass transition · Dynamic heterogeneity

Introduction

The investigation of glass transition phenomena in polymeric systems by calorimetry is a widely applied technique. In most cases, the so-called thermal glass transition is studied in a scanning differential calorimeter (DSC), i.e., the step in specific heat $c_p(T)$ measured by scanning temperature with a certain rate [1]. This step corresponds to the freezing in of structural relaxations during cooling because the slowing down molecular reorganization cannot follow the change in temperature anymore. Because of the width of the step, there is a certain arbitrariness in the definition of a characteristic temperature, the glass temperature T_g. But more importantly this step signals the transition from an equilibrium situation at higher temperatures to a thermodynamic non-equilibrium situation below T_g. This complicates the interpretation because the results in the non-equilibrium situation depend on the thermodynamic history of the sample. Hence also small differences between different scanning calorimeter designs like power compensation or heat flux matter for the thermal glass transition.

With the advent of temperature-modulated calorimetry (TMDSC), it became possible to measure the response on small sinusoidal temperature perturbations in equilibrium above T_g. Calorimetry became a spectroscopic technique like for instance dielectric or shear spectroscopy, especially, since the available frequency range has been widened also in calorimetry by heat capacity spectroscopy (HCS) techniques [2]. There calorimetry measures the isothermal frequency response of a dynamic relaxation quantity, the complex heat capacity $c_p^*(\omega)$. The step $\Delta c_p'$ in the real part of heat capacity and, correspondingly, the peak in the imaginary part $c_p''(\omega)$ signal the structural or α relaxation. From the peak position of $c_p''(\omega)$, a characteristic relaxation time can then be assigned to the α relaxation.

A relation between relaxation time (or the inverse measurement frequency) for the structural or α relaxation and the heating rate for the thermal glass transition can be established by finding a pair of both measurements where the peak in the imaginary part $c_p''(\omega)$ and the step in specific heat capacity $c_p(T)$ lie at the same temperature. Often the rule of thumb is applied that for usual scanning rates of 10 K/min at T_g the α relaxation time is around 100 s. But this can vary by about plus/minus one order of magnitude [3].

There is no generally accepted theory of the glass transition in the deeply undercooled liquid [4, 5]. In this personal review, I will argue in favor of two statements:

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1. The α relaxation process in the supercooled state (hence also the calorimetric measurement) is always connected to dynamic heterogeneity. This means that the mobility of different particles in the same sample under identical conditions (for instance different monomers in the same chain) is different on time scales corresponding to the α relaxation time. The particles form subsystems of different mobility [6]. Of course, in equilibrium the mean mobility of all particles becomes equal at long times because of ergodicity.
   This dynamic heterogeneity is also connected to spatial heterogeneity in mobility because particles of similar mobility tend to cluster. I will discuss this in the next section. The effect is called dynamic facilitation, i.e., neighbors of more mobile particles also become more mobile with higher probability [7]. The old view of dynamic heterogeneity as 'islands of mobility' [8] is corroborated by molecular dynamic simulations at high temperatures [9] which show islands of high mobility surrounded by large regions of low mobility.
2. The α relaxation itself in polymeric systems is a complex phenomenon, including mobility on different length scales. While the dynamics on the length scale of interchain distance is similar to non-polymeric glass formers, on larger scales the additional constraint of chain connectivity results in chain modes. These distinct contributions to the glass transition zone in polymers have been summarized under the notion of 'fine structure' [10] or 'thermorheological complexity' [11]. In rheological measurements, the different contributions even show different temperature dependencies. If there are different contributions, it is natural to ask, additionally, to which contributions calorimetry is sensitive.

Usually, calorimetry is a measurement on macroscopic samples with sizes much larger than possible structural heterogeneities like crystalline lamellae, block copolymer microphases, and so on. Then the heat capacity is simply the sum over the contributions of different, separate phases. This enables the identification and characterization of distinct thermodynamic phases in heterogeneous systems, but the results give no direct information on the spatial structure of these heterogeneities. But if the molecular processes responsible for the α relaxation cover a certain spatial range, their typical size will interfere with the size of possible structural heterogeneities. Hence an influence on heat capacity other than a simple sum rule is expected and the results can only be fully understood if one recognizes the spatial character of the relevant motions. Vice versa, calorimetry can even collect information on the relevant length scales of the relaxations.

Naturally, it is impossible to give here a full account of all the work in this field. Hence, I will discuss these aspects for different selected examples from recent literature or own work. I will discuss different kinds of heterogeneous polymeric systems. The important class of semicrystalline polymers will mostly be omitted from this review because there are other exhaustive reviews [12–14].

Dynamical heterogeneity of the glass transition in a structurally homogeneous sample

Before we discuss structural heterogeneous samples, let us look at the simpler case of a homogeneous amorphous sample.

There exists the old view of physical chemistry that in the dense liquid free volume is so sparse that a couple of particles have to move cooperatively to enable the diffusion of the single particles [15]. Adam and Gibbs called this spatial aspect of the mobility cooperatively rearranging region (CRR) [16], but gave no explicit method to calculate the cooperativity, i.e., the number of cooperatively moving particles, or the corresponding length scale from experiment. Simple statistical estimates of configurational entropy for the CRR (for instance Boltzmann entropy with only a few different sub-states for the CRR) gave unreasonable small numbers for the cooperativity <1 [17]. Other approaches try estimates of configurational entropy from statistical models [18] or an experimental separation of the configurational and vibrational contributions to the measured c_{p}. But this is not settled yet.

The fluctuation approach by Donth [19] provides an explicit formulae to calculate the size of independently fluctuating subsystems which are then identified with the CRR. This approach uses data from calorimetry [20]. It starts from the fluctuation dissipation theorem FDT and relates the measured specific heat contribution of the glass transition with entropy fluctuations. They are connected to corresponding temperature fluctuations in the subsystem. Originally, the width of the measured step in $c_{\mathrm{p}}(T)$ over temperature has been taken directly as the size of temperature fluctuations inside the CRR [20]. This was recently modified by the present author [21]. The temperature fluctuations are seen now as the source of mobility fluctuations inside the subsystem. They modulate the local relaxation times and cause the width of the frequency dispersion of the isothermally measured complex $c_{\mathrm{p}}^*(\omega)$. Because the relaxation time dispersions are always narrower than the corresponding frequency dispersions of $c_{\mathrm{p}}^*(\omega)$, this new view gives smaller values for the temperature fluctuations from experiment. This results in somewhat larger sizes for the subsystems or larger cooperativity. Typical values for cooperativity near to T_{g} are of the order of 100 particles. By 'particle' in case of polymers the repeating unit is meant, in all other cases the whole molecule. The uncertainty of the characteristic length is in the 20% range because of some uncertainties in the estimation of parameters from experimental c_p curves [20].

A similar approach by Berthier et al. [22] also starts from the fluctuation dissipation theorem FDT, but uses enthalpy fluctuations instead of entropy fluctuations. Accordingly, specific heat c_p stands in the denominator not numerator. With the same argument as Donth of using only the representative part of c_p for the glass transition, c_p is then substituted by Δc_p. The difference between both approaches has been tested in some cases [23]. But the estimation of the temperature dependence of Δc_p between liquid and glass above T_g is not clear and in several instances even a constant value for Δc_p has been used. The temperature dependence of Δc_p should help to discriminate between the different models if HCS data over a broader frequency and hence also temperature range will become available.

Furthermore, the relation of the heterogeneity according to Ref. [22] to the traditional CRR has to be clarified because the former model gives a heterogeneous correlation length also for an Arrhenius type process [24], traditionally connected to non-cooperative local processes. The understanding of cooperativity as the number of particles surmounting an energy barrier at the same time [23, 25] would correspond to an one-barrier model and is different from the old view where particles in the CRR are relaxed by a diffusing defect one after the other [26]. Hence the relation between of the notion of cooperativity in different approaches is not clear in the moment and deserves further investigations.

Importantly, all these considerations relate to the equilibrium situation above the thermal glass transition at T_g. Cooperativity decreases with increasing temperature [15, 27]. The mobility constraints for the single particles are loosened by the increase in thermal fluctuations or free volume. Hence there is lesser need for cooperativity. This has to be distinguished from the description of the thermal glass transition where in passing from low temperatures an unfreezing of mobility and correspondingly an increase in particles taking part in the motions is expected [25].

Another thermodynamic model investigates Gaussian excitations for glass-former dynamics and thermodynamics. The corresponding picture is also 'hot islands in a sea of kinetically frozen molecules.' The number of particles N_c in these islands is estimated to be 10–20 [28]. The thermodynamic random first-order transition theory RFOT of Wolynes et al. [29] describes the mobility pattern as caused by entropic droplets. With several assumptions on the temperature dependence of configurational entropy and Δc_p they arrive at a size of about 125 beads per CRR near T_g [29], but the division of the molecule in 'beads' remains rather arbitrary. Also the predicted correlation of fragility, the steepness of the temperature dependence of the relaxation time, of the glass transition and Δc_p in a series of poly(*n* butyl methacrylate)s of different molecular weights seems not to work [30].

Of course, these different approaches are specific models and hence researcher tried to find direct ways to proof experimentally dynamic heterogeneity. Nuclear magnetic resonance NMR with multidimensional schemes verified the existence of dynamically different subsystems in polymers near T_g [31]. With additional information from spin diffusion also a characteristic length scale in the nanometer range was determined [32]. This result gave credit to the estimates from calorimetry [20]. A comparison also for non-polymeric glass formers is given by Qiu and Ediger [33]. But the spatial shape of the CRR remains unknown also from NMR [32]. Theoretical approaches predict the shape of a CRR as compact at low temperatures near T_g [4, 29] and fractal or 'stringy' at higher temperatures [29]. But there is no experimental proof for this yet.

To have direct access to spatial information a scattering technique would be preferential. Early attempts with static neutron scattering failed [34]. But this is understandable. The dynamics near to T_g are very sensitive to density. Hence, even if a density contrast is connected with the dynamic mobility pattern it would be far to small to be seen in the static scattering.

Dynamic neutron scattering, better suited to identify only dynamic contributions of interest, is still confined to correlation times smaller than microseconds. Typically, this is above the crossover region [35, 36] in dynamics where the temperature dependence of the α relaxation time and intensity changes, translational and rotational diffusion start to decouple and primary α and secondary relaxations split off. Above the crossover, the dynamical heterogeneity is expected to be in its mature state and not fully developed [27]. This high temperature region can in some cases be clearly distinguished by calorimetry from the temperature region below the crossover near to the conventional glass transition at T_g. For poly(*n* hexyl methacrylate) a saddle-like peculiarity in $c_p''(\omega)$ was found at the crossover by HCS [37], confirmed by an analysis of DSC data by the Narayanaswamy model [38]. To span the whole temperature range between T_g and the crossover temperature for more polymers dynamic heat capacity data for the α relaxation over a large frequency range would be necessary [27]. But HCS is still limited to frequencies below some 10 kHz [39].

The problem of limitation to short time scales arises for the molecular dynamic simulations too. Compact clusters of 30–60 particles are identified as involved in elementary moves ('democratic particle motions') for metabasin transitions in simple glass formers [40]. But how these high temperature heterogeneities in mobility above the crossover temperature are related to low temperature dynamic heterogeneities near to T_g is an open question.

With increase in computational power and experimental possibilities neutron scattering and simulation will reach the crossover temperature from above and calorimetry from below and eventually get an overlap to confirm the length scale of heterogeneity [41]. Although this is not yet reached the existence of the dynamic heterogeneity is confirmed by many methods and even the corresponding length scale of some nanometers near to T_g is widely accepted. I will give examples on this in the following.

Fine structure of the glass transition and distinction between different experimental observables

The second aspect one has to keep in mind is the existence of the 'fine structure' or 'thermorheological complexity' of the α relaxation in polymers showing up in the frequency or time dependence of physical properties [10, 11]. It is the result of a superposition of different contributions to the dynamic glass transition. The main contribution are those relaxations usually termed 'segmental modes' or 'proper glass transition.' The physical picture is that beginning on short time scales the monomeric segments start to explore their configurational degrees of freedom within their local cage and relax cooperatively with their immediate surrounding. This is similar for small molecule glass formers and for polymers and is measured as a calorimetric signal for the α relaxation. This segmental relaxation removes the constraints of the cage formed by the neighbors (neighboring particles or monomeric units) and enables diffusion or flow on length scales larger than the nearest neighbor distance. But for polymers flow is hindered by chain connectivity and hence for longer times other polymer specific modes appear. They are supposed to be similar to Rouse modes. These chain modes do not necessarily contribute to the calorimetric signal. For instance, it is known that the flow transition of polymers, corresponding to the longest chain mode by reptational movement of the whole chain, gives practically no calorimetric signal [42, 43] while it is very prominent in shear rheology. Hence, one should always keep in mind that the different contributions to the broad dispersion zone of the dynamic glass transition in polymers will in general show up differently for different experimental methods [2]. This is an unavoidable effect caused by the different coupling of the measured physical quantities to the molecular mobility and should be distinguished from the purely experimental difficulty of comparison of results from different samples in different experimental equipment.

Glass transition in confinement

An old idea to test the existence and spatial size of dynamic heterogeneities is to use external confinement of varying size and to look for the influence on the dynamics. If by increasingly tighter confinement both length scales become comparable a strong influence is expected.

Classical work was done on small molecule glass formers in porous host systems [44]. A shift in glass transition temperature T_g compared to bulk values was detected. Later also polymers were incorporated in porous glasses [45, 46]. Calorimetry showed a decline of the glass transition step Δc_p for strong confinement below some nanometers. For instance for poly(methyl phenyl siloxane) PMPS the increment in c_p vanished for a pore size smaller than 3–5 nm [47].

This is compatible with the existence of a predefined length scale for the cooperative movements. If external confinement does not allow such movements, the cooperative character of the relaxation and the corresponding calorimetric signature disappear. Only local non-cooperative relaxations remain. This is known as the concept of the 'hindered glass transition' [48, 49].

But in confinement always the problem of possible specific surface interactions between guest and host persists and a separation of the influence of confinement and surface interaction is necessary [50]. The influence of the surface can be minimized by special treatments, e.g., silanization of porous glasses. A special trick is to use the same material for guest and host in a semicrystalline polymer. Here the confinement for the amorphous phase by the crystalline phase in poly(ethylene terephthalate) PET was studied [51]. A correlation of the characteristic length scale of glass transition heterogeneity from calorimetry of 1 to 1.5 nm and the lamellar thickness of the amorphous phase from scattering of 1 to 2.5 nm for different crystallinities was found.

Similar studies were recently done on poly(L-lactic acid) where a dependence of glass transition temperature on semicrystalline morphology, obtained by different crystallization temperatures, was found [52]. Analogously, by varying the isothermal crystallization time different degrees of crystallinity were realized in another study [53]. There also the length scale of cooperativity for the mobile amorphous phase was calculated. It decreased from 3.1 to 1.5 nm when crystallinity increased from 0 to 42%. The decrease resulted from the broadening of the calorimetric glass transition. Contrary, in a later analysis the broad transition was split into two contributions [54]. They were suspected to belong to two different mobile amorphous phases, inter- and intra-spherulithic. Both have correlation lengths of 2.9 and 2 nm, respectively, independent on crystallinity. Obviously, further calorimetric investigations on this polymer are necessary. Structural information from small angle X-ray scattering SAXS suggests a thickness of 9.2 nm for the mobile amorphous layers. This is much more than the length scale of dynamic heterogeneities. Hence this polymer does not confine its amorphous parts and a direct correspondence between structural and dynamic length scales does not exist.

Also curing of thermoset resins in confinement has been studied [55]. Calorimetry on the final network in the smallest pores of 11.5 nm diameter results in two glass transition steps in the DSC curves. The lower glass transition shows the expected depression of T_g while the appearance of a higher transition has been related to the existence a less mobile surface layer. Assuming this two-layer model one can estimate a surface layer thickness of 1.6 nm for the fully cured network. Generally, one would expect that the thickness of the surface layer with dynamics different from the bulk is about the same as the length scale of dynamic heterogeneities. The latter gives also the minimal range of influence of the interface. All the length scales estimated above are compatible with the size of dynamic heterogeneities for homogeneous samples discussed before.

For confinement in thin films the situation is still unclear. After classical work on T_g shifts from dilatometry for film thickness smaller than about 100 nm in supported [56] and free standing polymeric films there are some recent works that notice influence of experimental conditions on the results [57]. Calorimetric investigations on microtome-sliced networks [58] found a decrease in T_g for 40 nm films while high-speed scanning calorimetry found no thickness dependence for 3 nm polystyrene films [59], polystyrene films in the 4–50 nm range and poly(methyl methacrylate) PMMA films in the 10–400 nm range [60–62]. Also revised dielectric investigations for isotactic PMMA found no thickness dependence of T_g down to 6.6 nm [63].

For a comparison to the characteristic length scale from calorimetry near to T_g one must notice that the thickness of the thin films normally does not reach the typical CRR size in the 3 nm range. Additionally, for the short time scales of the high speed calorimetry mentioned above the CRR size may be even smaller [27]. That this indeed can play a role was confirmed by investigations on the calorimetric glass transition temperature and absolute heat capacity of stacks of polystyrene ultrathin films (17–100 nm thickness) in conventional DSC [64]. Contrary to the high-speed calorimetry results the thin film stacks showed a T_g depression at slow heating compatible with the results of dilatometry on single thin films [56].

The depression of T_g in thin films is usually interpreted as the signature of a more mobile surface layer. It may be sufficient that only this surface layer has a thickness comparable to the CRR size while the rest of the film retains bulk properties. This could explain the discrepancy between typical CRR sizes and film thickness.

In thin film studies also surface sensitive experimental methods are used. This includes for instance the healing of surface undulations or the incorporation of colloidal particles into the surface. One should notice that this needs the movement of larger parts or even of the whole polymeric chain. In light of the fine structure of the α relaxation described above this can result in qualitative differences between different measures of dynamics in thin films. A confinement effect on local segmental motions measured by calorimetry must not necessarily mean a comparable effect on Rouse modes [65] or chain diffusion [66].

Calorimetry on nanocomposites

This is the inverse geometry compared to the confined systems above. Now the polymer under study constitutes the matrix, filled with nanoscale particles as inclusions. A change in physical properties of the polymer is expected at the interface between polymer matrix and particles. The characteristic length scale of the dynamic glass transition was defined in the fluctuation approach by the spatial size of independently relaxing subsystems or CRRs. Because a local region cannot relax independently from a neighboring confining interface the minimal range of influence of the interface will obviously correspond to the radius of the CRR. In nanocomposites, this length scale is comparable with the size of the particles and hence the volume fraction of the polymer interface region can be large in highly filled systems. This enables the experimental study of these interface contributions (M. Beiner, to be published).

At the same time, these filled systems are of high interest for practical applications. Beside the old example of carbon-black filled rubbers many new applications for instance for conducting and transparent polymers, reinforced transparent polymers or sensors appear. Though often mechanical properties are of primary interest calorimetry can help to characterize the interface material. This is quite common. But here I emphasize the inverse possibility. By characterization of the thickness of the boundary region one can conclude on the length scale of dynamic heterogeneity, similar to studies under confinement.

An early example of an investigation of the calorimetric glass transition in filled rubber is Ref. [67]. From the dependence of the step height Δc_p at the glass transition on the volume fraction of the filler a thickness of 1.5 nm of an immobilized layer at the interface with the spherical particles was determined. This compares well with the characteristic length of the bulk glass transition in the rubber matrix of about 2.3 nm. For PMMA filled with silica particles, an immobilized layer of about 2 nm thickness was found [68].

Interface layer thicknesses were determined for particle filled polymer matrices by DSC [69], elastic modulus [70], SAXS [71] or dielectrics [72] and for polymer/clay intercalated nanocomposites by wide angle X-ray scattering WAXS [73]. In all cases, the thickness of a few nanometers was compatible with the length scales for bulk dynamic heterogeneity from calorimetry, partially measured on the same samples and evaluated according to the fluctuation approach above. From dielectric intensity, it was possible to calculate the thickness of this layer at different temperatures. It is about 3 nm near to T_g and decreases with increasing temperature [72]. Such studies can contribute to the important question on the temperature dependence of the characteristic length scale of the α relaxation. Here dielectrics with the wider frequency range compared to calorimetry has an advantage. But of course the problem with specific surface interactions remains.

A formal equivalence between polymer nanocomposites and the much simpler model system of thin polymer films has been postulated [74]. Later work highlighted a strong effect of processing conditions on the observed behavior [75]. Better controlled model polymer nanocomposites were build from a polymer sandwiched between two parallel planar silica surfaces [76]. T_g was measured by a fluorescence method with label molecules inside the polymer film. These model composites showed for the strongly with silica interacting polymers PMMA and poly(2-vinyl pyridine) P2VP a large increase in glass temperature. In case of P2VP T_g starts to increase already for relatively large film thicknesses of some 100 nm. Currently, there is no explanation for this long range effect. Possibly, the conformation of the whole chain is disturbed and this influences then more local segmental motions.

Microphase-separated block copolymers or nanophase-separated systems

Block copolymers are somehow similar to nanocomposites. If the different blocks are incompatible they form separate domains. But here both components are connected by the polymer chain. Hence their separation is restricted by the chain length. This results in typical small dimensions of the domains in the nanometer range. Fortunately, the self-organization of the different blocks in domains solves the problem one has with the dispersion of the filler in nanocomposites. To reach smaller domain sizes, the molecular weight of the chain has to decrease. But this also decreases the thermodynamic driving force for demixing of the different blocks. Hence they have to be highly incompatible to preserve the phase separated structure.

An extreme case are nanophase separated systems where the incompatible parts are the polar main chain and the non-polar alkyl side chains of high polymers [77, 78]. It is thought that the alkyl side chains of several monomeric units of the same or different main chains aggregate. The size of the alkyl nanodomains increases with side chain length as confirmed by SAXS [79]. A cooperative dynamic glass transition, called α_{PE}, can take place inside these separate alkyl domains if their size reaches a certain threshold. This relaxation is distinct from the α relaxation of the main chains. Hence one can find in calorimetry two separate glass transition signals for these homopolymers. As an example for poly(decyl methacrylate) the estimated size of the length scale of cooperativity inside the alkyl domains from calorimetry is 0.6–0.7 nm, while the geometric size of these domains from SAXS for a simple one-dimensional model is about 1.1 nm [78, 79]. Although no detailed information on the spatial shape of the nanodomains is available, yet this simple estimate gives a reasonable agreement.

The glass transition temperature of the separate process in the alkyl nanodomains is independent of the chemical nature of the main chain and scales with the length of the side chains, i.e., the size of the domains [80]. This confirms the separation of main and side chains. The shift in T_g to lower values for smaller domains is a confinement effect, expected for a hindered glass transition [80]. The advantage of calorimetry compared to for instance dielectrics in this case is that it can confirm the cooperative nature of this process [77], distinct from a local secondary relaxation.

Miscible polymer blends

As a final example of heterogeneous polymeric systems, I want to discuss miscible polymer blends [81]. One could naively expect that miscible polymer blends are homogeneous systems because the chains of both components are intimately mixed. But the notion of homogeneity or inhomogeneity depends on the property under consideration or the corresponding length scale [82]. This becomes immediately clear for the so-called self-concentration model of Lodge and McLeish for polymer blends [83]. Because of chain connectivity the immediate neighborhood of one monomer contains with a higher probability monomers from the same chain than from the other blend component. Local probes like for instance NMR will find a more heterogeneously distributed situation while other measurement methods with a larger probe volume as for instance calorimetry will measure values corresponding more to the mean composition of the whole sample and hence will notice a more homogeneous situation.

The surprise for miscible polymer blends was that the α relaxation time of both blend components can be orders of magnitude different. This was found by NMR spectroscopy or dielectrics. Hence both components show dynamic heterogeneity regarding the dynamic glass transition [82]. Contrary, calorimetry usually shows only one step in heat capacity at the glass transition but strongly broadened. This single step is even used as a criterion for miscibility. But is has been shown that the reverse conclusion is misleading. Even for a miscible poly(ethylene oxide) PEO/PMMA blend two separate calorimetric glass transitions can be identified [84, 85].

From the influence of self-concentration on the dynamic glass temperature one can conclude on the relevant volume. With a corresponding model of blend dynamics and the combination with Adam Gibbs, Ref. [86] found from dielectric measurements in combination with calorimetric data in polyisoprene/poly(vinylethylene) blends that no more the Kuhn segment length is relevant. A cooperativity length scale was anticipated. This was later consequent realized in Ref. [87]. But another recent paper questions the way of inclusion of concentration fluctuations in models for the blend dynamics [88]. A relevant length scale of only 0.5–1 nm was calculated, much smaller than even the Kuhn segment length [89]. But the arguments in Ref. [88] correspond to dielectrics not calorimetry. In the criticism of the self-concentration model a temperature independent length scale was assumed which is surely not the case. Hence the discussion of these length scales in miscible blends is not settled.

An interesting experiment was done by Zheng and Simon [90]. In a blend of poly(alpha methyl styrene) with its own, chemically identical, oligomer thermal concentration fluctuations are avoided but the strong dynamical asymmetry in the α relaxation between the components is retained. Calorimetry finds a strongly broadened glass transition. It was separated in the contributions from both components and the corresponding length scale calculated from the self-concentration model. A rather large value for the relevant length scale of 2.7 nm resulted from the small value of 0.056 for the self-concentration. From the same calorimetric data, the characteristic length scale according to the fluctuation approach was calculated. In dependence on polymer concentration values from 1.5 to 2.5 nm were found. Hence they are in tendency higher than the Kuhn segment length of 1.7 nm. If one includes the correction according to Ref. [21], the length scales come even nearer to 2.7 nm and give a consistent picture for the relevant volume of the α relaxation from self-concentration model and fluctuation approach.

Another aspect in dynamically strong asymmetric polymer blends is a mutual confinement effect. Below T_g of the high T_g component (for instance poly(vinyl acetate) PVAc) its less mobile chains act similar as a static confinement for the more mobile chains of the lower T_g component (for instance PEO) [91]. This corresponds to the case of the hindered glass transition (see above) and speeds up the more mobile component. Hence the more mobile component in a blend with a lesser mobile component can become even more mobile than in the bulk at the same temperature.

Conclusions

The estimation of characteristic length scales or cooperativities for the α relaxation by the fluctuation approach from calorimetric data is an important tool in studying molecular mobility. Especially important in the future are more data on the temperature dependence of the cooperativity. This demands experimental progress for a broader frequency range in calorimetry or HCS and systematic studies for a wider class of materials.

Especially in nanostructured samples the interface region between different phases represents a large part of the whole system and correspondingly plays an important role for the properties. By studying the glass transition in such samples by calorimetry one can identify this interface material and vice versa get information about the length scales responsible for the dynamic glass transition. Hence calorimetry not only characterizes significant material properties but additionally contributes to an important unsolved problem in condensed matter research.

The selective sensitivity on cooperative motions makes calorimetry an essential tool compared to other relaxational methods. The comparison to other results for instance from dielectrics enables to distinguish between non-cooperative local processes and the cooperative α relaxation. This gives additional credit to the assignment of unknown relaxation processes to molecular models.

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