

*Supercooled Liquid Dynamics: Advances and Challenges*

R. Richert, in "Structural Glasses and Supercooled Liquids: Theory, Experiment, and Applications", P. Wolynes, V. Lubchenko (Eds.), Wiley, (in press)

The outline of the phenomenology and current understanding of supercooled liquid dynamics demonstrates that all aspects such as primary and secondary relaxations, fragility, heterogeneity, and physical aging are highly entangled. It has been emphasized that the JG type secondary relaxation affects much of the behavior characteristic of viscous liquids. In cases where no separate secondary process is detected, e.g. in dielectric spectroscopy, it might indicate that these modes do not couple to the experimental observable rather than being absent altogether. Discriminating secondary relaxations that are statistically highly independent of the primary modes has been a crucial step towards a better understanding the role of the JG relaxation. How the slow secondary relaxation is involved in the crossover temperature scenario at  $T_x$ , in heterogeneous dynamics, in the strong-fragile pattern, in the translation-rotation decoupling, and how it relates to the so-called excess wing are all issues for which no satisfactory answers are available. As long as we treat the  $\alpha$ - and  $\beta$ -processes of structural relaxation independently and while models of the temperature dependences above and below  $T_x$  remain separated, our understanding of the supercooled state is bound to stay incomplete.

192. *Heat Capacity in the Glass Transition Range Modeled on the Basis of Heterogeneous Dynamics*

R. Richert, J. Chem. Phys. 134 (2011) 144501.1 - 144501.7

A heterogeneous version of the Tool-Narayanaswamy-Moynihan (TNM) model is proposed, in which enthalpy relaxation is heterogeneous in the sense that the overall non-exponential relaxation originates from the superposition of independently and exponentially relaxing domains with individual time constants. Analogous to rate exchange at a constant temperature, there is only a single fictive temperature that controls the rate at which all time constants can change considerably during a temperature scan. The model is shown to be consistent with differential scanning calorimetry (DSC) data taken across the glass transition of polystyrene, propylene carbonate, and glycerol. In contrast to the standard homogeneous TNM model, the heterogeneous counterpart fits DSC up-scans for  $As_2Se_3$  for cooling rates of 0.31, 2.5, and 20 K/min with a common set of parameters.

191. *Dielectric Properties of Epoxy Based Nano-composites for High Voltage Outdoor Insulation*

G. Iyer, R. S. Gorur, R. Richert, A. Krivda, P. Mahonen, IEEE Trans. Dielectr. Electr. Insul. (in press)

Epoxy samples with micro, nano and micro + nano particles have been evaluated for their electrical performance in high voltage insulation applications. The dielectric strength of these samples was measured in accordance with the ASTM D-149 test. Dielectric spectroscopy was used to understand the role of space charge and interfaces in these materials. The dielectric losses and dielectric strength of the nano and the micro + nano samples are better than their micro-filled counterparts. The results of dielectric spectroscopy suggest significant improvements in the electrical performance by using materials containing nano-fillers when compared to materials containing micro-fillers. However, the dielectric strength measurement shows only marginal improvement. Hence, alternative techniques may be required to characterize the electrical performance.

190. *Experimental Approaches to Heterogeneous Dynamics*

R. Richert, N. Israeloff, C. Alba-Simionesco, F. Ladieu, D. L'Hôte, in "Dynamical Heterogeneities in Glasses, Colloids, and Granular Media", L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, W. van Saarloos (Eds.), Oxford University Press, Oxford, 2011, p.152 - 202

Dynamic heterogeneity refers to the independence of fast and slow modes in a system displaying dispersive relaxation and is not an alternative model to the dynamics in complex materials, but rather a required approach for rationalizing an increasing number of experimental results on supercooled liquids. The last twenty years has seen the advent of numerous experimental techniques aimed at studying the heterogeneous nature of viscous liquids. The methods either demonstrate heterogeneity *per se*, or provide information on the time and length

scale involved in this concept. This chapter reviews the experimental techniques that focus on molecular and polymeric glass-formers, the challenges involved, and the results obtained in this relatively new field. Most approaches have particular strengths and weaknesses, so that only the synergistic efforts of combining numerous approaches will advance our understanding of the heterogeneous nature of dynamics significantly.

189. *Appearance of a Debye Process at the Conductivity Relaxation Frequency of a Viscous Liquid*

R. Richert, A. Agapov, A. P. Sokolov, J. Chem. Phys. 134 (2011) 104508.1 - 104508.7

The existence of a Debye type ultra-slow process in dielectric spectra of bulk polyalcohols and similar materials has been reported repeatedly in the recent literature. Its loss peak is observed at frequencies that are decades below those of the primary structural relaxation, in a range where the loss signal is usually dominated by dc-conductivity or even electrode polarization. We show that this peak originates from an incomplete filling of the capacitor volume, e.g., as a result of gas bubbles, a situation that gives rise to a Debye process at the conductivity relaxation frequency of the material, where the values of storage and loss components of permittivity are identical. The result implies that these peaks are not endemic to the liquid and can lead to various misinterpretations of the dielectric relaxation spectra. Techniques avoiding the occurrence of such artefacts are discussed.

188. *On the Level of Mechanical Loss in Metallic Glasses*

D. Bedorf, R. Richert, K. Samwer, Eur. Phys. J. B 80 (2011) 325 - 329

Metallic glass samples with compositions  $Zr_{65}Al_{17.5}Cu_{27.5}$  and  $Pd_{77}Cu_6Si_{17}$ , for which loss factors of up to  $10^{-2}$  have been reported, are reinvestigated with an electrostatic vibrating cantilever technique that detects dissipation factors  $\tan\delta$  as low as  $10^{-4}$ . It is found that  $\tan\delta \approx 4 \times 10^{-4}$  is a typical value for these alloys well below  $T_g$ , suggesting that previous results were limited by instrumental resolution. While aging the glasses increases their elastic moduli considerably, the measured loss factor is affected only marginally by thermal history.

187. *Dynamics of Nanoconfined Supercooled Liquids*

R. Richert, Annu. Rev. Phys. Chem. 62 (2011) 65 - 84

Near their glass transition temperature  $T_g$ , supercooled liquids display dramatic changes regarding the dynamics if subject to geometrical restrictions on the scale of 2 to 200 nm. Confinement induced shifts of  $T_g$  of 25 K have been reported, equivalent to relaxation times that differ by several orders of magnitude compared with the bulk liquid at the same temperature. Both acceleration and frustration of structural relaxations have been observed, and the effects can depend strongly on the physical and chemical properties of the interface, on soft versus hard confinement, and on the size and dimensionality of the confining topology. An attempt is made to extract a unifying picture from the past 20 years of very diverse observations that involve experiments, simulations, and model considerations.

186. *Dynamic Coupling of a Small Rigid Probe to Viscous Ortho-terphenyl*

W. Huang, R. Richert, J. Chem. Phys. 133 (2010) 214501.1 - 214501.4

We have measured the dielectric relaxation of 2,2,6,6 tetramethyl-piperidine-1-oxyl (TEMPO) as a rotational probe in supercooled *ortho*-terphenyl (OTP). Due to the significant dipole moment of TEMPO compared with OTP, its contribution to the loss spectra can be identified already at moderate concentrations. For time scales ranging from 10  $\mu$ s to 1 s, it is found that the tumbling mode of TEMPO is a true replica of the structural relaxation of OTP regarding average time constant, relaxation time dispersion, and the temperature dependence. While the present dielectric results are consistent with a decoupling of a spinning mode (about the nitroxyl dipole axis) of TEMPO from viscosity, they do not agree with the strong decoupling of the tumbling mode derived from ESR experiments.

185. *Reverse Calorimetry of a Supercooled Liquid: Propylene Carbonate*

R. Richert, Thermochim. Acta (in press)

Using propylene carbonate as an example for a glass-forming liquid with generic behaviour, a technique based on dielectric relaxation experiments at high electric fields is reviewed and explained in unprecedented detail. Analogous to microwave heating, the sample absorbs energy from the field, and the resulting configurational changes are measured and linked to the configurational modes of the heat capacity. Evidence is provided for the

heterogeneous nature of the slow degrees of freedom that are responsible for the heat capacity step near  $T_g$ . Moreover, the thermal and dielectric relaxation times are not only subject to the same overall dispersion, but are locally correlated and the dielectric and thermal time constants are identical within a 15 % margin. Only for the fastest few percent of the thermal relaxation times can deviations from these correlations be found.

184. *On the Features of the Secondary Relaxations: The Case of Cyclohexane Derivatives*  
A. Mandanici, M. Cutroni, R. Richert, J. Non-Cryst. Solids 357 (2011) 264 - 266

Recent results on the dynamics of ethylcyclohexane obtained using high resolution dielectric spectroscopy and mechanical spectroscopy at ultrasonic frequencies have been analyzed in comparison with experimental data on relaxations occurring in different materials having in common the presence of the cyclohexyl ring in their molecular structure. On the basis of experimental evidence concerning several cyclohexane-derived materials, some features of the secondary relaxations have been outlined that could be applicable to a wider class of materials.

183. *Dynamics of Glass-Forming Liquids. XIV. A Search for Ultra-Slow Dielectric Relaxation in Glycerol*

R. Richert, J. Chem. Phys. 133 (2010) 074502.1 - 074502.5  
and: Virtual Journal of Biological Physics Research 20 (2010) Issue 5

A recent dielectric study of various polyalcohols reported on the general occurrence of an ultra-slow process with Debye type character in hydrogen bonded liquids [R. Bergman, H. Jansson, and J. Swenson, J. Chem. Phys. **132**, 044504 (2010)], whereas previous work suggested that such behavior is specific to monoalcohols only. Clarifying this issue is highly relevant for assessing models aimed at rationalizing these modes that are slower than the primary structural relaxation and associated with a single time constant. To this end, the dielectric relaxation of glycerol is measured at different electrode distances with high accuracy. In this manner, electrode polarization can be separated from the dielectric signals intrinsic in the supercooled liquid. In the frequency range below the loss peak frequency  $\omega_{\max}$  of the  $\alpha$ -process, only dc-conductivity is required to understand the dielectric properties of supercooled glycerol within a margin of  $\varepsilon'' \approx \pm 0.1$  and thus no indication of an ultra-slow peak is found. More quantitatively, any dielectric Debye like mode located around  $10^{-5}\omega_{\max}$  would need to have an amplitude smaller than 0.4 % of that of the primary dielectric process to be consistent with the present findings, in contrast to previous claims of  $> 50$  %.

182. *Dielectric Spectroscopy and Dynamics in Confinement*

R. Richert, Eur. Phys. J. Special Topics 189 (2010) 37 - 46

There are numerous reasons, such as frequency range and sensitivity, to employ dielectric spectroscopy for investigating how confinement alters the dynamics of liquids, supercooled liquids, or polymers. However, care has to be taken to account for the fact that the sample is a heterogeneous dielectric, i.e. a mixture of the confining matrix material and the liquid filler whose dynamics are of interest. Since dielectric permittivity is not an additive quantity, extracting the dynamics of the filler can be complicated or even impossible, and the Maxwell-Wagner relations will not always solve the problem. Some guidelines on how to interpret dielectric data on confined systems will be presented.

181. *Confinement Effects in Bulk Supercooled Liquids*

R. Richert, Eur. Phys. J. Special Topics 189 (2010) 223 - 229

Supercooled liquids are known to display heterogeneous dynamics, with slow and fast relaxation modes being independent and even spatially separated in dynamically distinct domains. In such a situation, it is imaginable that the very fast modes are surrounded by material that is practically frozen on the relaxation time scale of that fast mode. Here, we show experimental evidence of such a confinement effect. For the fastest few percent of all modes, equilibration appears to be linked to a common process (e.g. macroscopic softening), while the remaining majority equilibrate on the time scale of their individual time constant, as expected for heterogeneous dynamics.

180. *Reply to Comment on "Measuring the Configurational Heat Capacity of Liquids"*

L.-M. Wang, R. Richert, Phys. Rev. Lett. 104 (2010) 239603.1 - 239603.1

In a recent Comment, Pick questions the validity of how the configurational heat capacity,  $\Delta c_p$ , is derived from high field dielectric relaxation measurements. This technique exploits that slow degrees of freedom absorb energy from a time dependent field (as in microwave heating), and that dielectric relaxation times track increased configurational temperatures  $T_{\text{cfg}}$  via the changes in  $\tan\delta$ . The Comment is concerned with two points: i) the relation,  $T_{\text{cfg}} = \tau_T p / c_p$ , is missing a time dependent term, and ii) unity is assumed for the ratio,  $h = \tau_D / \tau_T$ , of dielectric ( $\tau_D$ ) to thermal ( $\tau_T$ ) relaxation times.

179. *Comment on "Hidden Slow Dynamics in Water"*

R. Richert, Phys. Rev. Lett. 104 (2010) 249801.1 - 249801.1

In a recent Letter, Jansson *et al.* reported on a slow dielectric process in aqueous materials which the authors assumed hidden below the dc-conductivity contribution,  $\epsilon''(\omega) = \sigma_{\text{dc}} \epsilon_0^{-1} \omega^{-1}$ , that dominates the loss  $\epsilon''$  for  $\omega \rightarrow 0$ . The technique used to seek an obscured process at low frequencies involves inserting an insulating layer (Teflon) in order to suppress dc-conductivity. In apparent support of this 'blocking electrode' idea, the impedance with added Teflon reveals a peak where the measurement without Teflon displays mainly dc-conductivity.

178. *Calorimetry Based on Energy Absorbed From Time-Dependent Fields*

R. Richert, J. Non-Cryst. Solids 357 (2011) 726 - 730

The energy that a supercooled liquid absorbs from a time dependent field is used to determine the time scales involved in the dynamic heat capacities of the slow degrees of freedom. The time resolved changes in fictive temperatures are obtained from dielectric relaxation data derived from the same field that provides the energy input. For a generic molecular glass-former, it is found that dielectric and thermal time scales are locally correlated and agree within 15 %. For a monohydroxy alcohol and an ionic liquid, however, such an identity between dielectric and calorimetric time scales is not observed. It is demonstrated that only the field induced change of the fundamental susceptibility,  $\chi(\omega)$ , can be exploited for this dynamic calorimetry, whereas  $\chi_2(\omega)$  is not sensitive to these effects.

177. *Glass Transition and Fragility in the Simple Molecular Glassformer CS<sub>2</sub> from CS<sub>2</sub>-S<sub>2</sub>Cl<sub>2</sub> Solution Studies*

Z. Zhao, W. Huang, R. Richert, C. A. Angell, J. Chem. Phys. 132 (2010) 154505.1 - 154505.6

With an interest in finding the fragility for a simple, single component, molecular glassformer, we have determined the dielectric relaxation and glass transition behavior for a series of glasses in the CS<sub>2</sub>-S<sub>2</sub>Cl<sub>2</sub> and CS<sub>2</sub>-toluene systems. Crystallization of CS<sub>2</sub> can be completely avoided down to the composition 20 mol% second component, and the fragility proves almost independent of CS<sub>2</sub> content in each system. Since the glass temperature  $T_g$  obtained from both thermal studies and from dielectric relaxation (using  $T_{g,\text{diel}} = T_{\tau=100s}$ ) is quite linear over the whole composition range in each system, and since relaxation time data for pure CS<sub>2</sub> fall on the same master plot when scaled by the linearly extrapolated  $T_g$  value, we deduce that pure CS<sub>2</sub> has the same high fragility as the binary solutions. The value is  $m = 86$ , as for *ortho*-terphenyl (OTP). Based on observations of independent studies for the vibrational density of states (VDoS) (of inherent structures for OTP and instantaneous, at-temperature structures for CS<sub>2</sub>), we attribute the high fragility to an excess vibrational heat capacity originating in the behavior of the low frequency modes of the VDoS (the boson peak modes). Both low frequency DoS and anharmonicity increase with increasing temperature, augmenting the configurational entropy drive to the top of the system energy landscape. The surprising implication is that fragility is determined in the vibrational, not configurational, manifold of microstates.

176. *Capacitive Measurement of Mercury Column Heights in Capillaries*

S. Frey, R. Richert, Rev. Sci. Instrum. 81 (2010) 034702.1 - 034702.3

The detection of changes of volume, e.g. in expansivity or aging measurements, are often translated into mercury column height within a glass capillary. We propose a capacitive technique for measuring the meniscus position using a cylindrical capacitor with mercury as the inner electrode, the capillary material as the dielectric, and a metal coat covering the outside surface of the capillary as the second electrode. The measured capacitance changes linearly with meniscus height, as long as the top mercury level remains within the range of the outer electrode. With the demonstrated noise level of 48 nm for our preliminary setup, meniscus height changes beyond 100 nm can be observed via the capacitance.

175. *Structural Relaxation Dynamics in Binary Glass-forming Molecular Liquids with Ideal and Complex Mixing Behavior*

L.-M. Wang, R. P. Liu, Y. J. Tian, R. Richert, J. Phys. Chem. B 114 (2010) 3618 - 3622

The glass transition and structural relaxation dynamics of various binary glass-forming liquids are investigated with dielectric relaxation measurements across the entire composition range. Three categories of solutions with weak, intermediate, and strong mixing effects, namely methyl-*m*-toluate in methyl *o*-toluate, methyl *m*-toluate in di-*n*-butyl phthalate, and 1,2-propandiol in 2-hexylamine, are selected to address the mixing behaviors from near-ideal to non-ideal cases. The glass transition temperatures, fragility indices, and stretching exponents of the solutions are determined and their composition dependence is the focus of this study. The experimental measurements show that mixing generally generates a negative deviation of fragility *m* relative to the composition average of the results of two neat components (ideal mixing law). This excess negative fragility proves to be a universal feature of binary systems, and the increase of the non-ideal mixing degree results in a more pronounced negative deviation. In contrast, the composition dependence of the stretching exponent is more complex, and a transition from the negative to positive deviation is observed for substantial non-ideal character. The study assists understanding the dynamics of multi-component glass formers.

174. *Physical Aging and Heterogeneous Dynamics*

R. Richert, Phys. Rev. Lett. 104 (2010) 085702.1 - 085702.4

Many experimental results of physical aging are consistent with homogeneous aging models that are based upon a single 'inner clock'  $\zeta$  or fictive temperature  $T_f$ , but incompatible with the established heterogeneous nature of relaxation in glass-forming materials and the concomitant distribution of  $\zeta$  and  $T_f$  values. This work demonstrates that physical aging follows the conceptually simpler model of heterogeneous dynamics that differs significantly from the homogeneous counterpart in the rate at which equilibrium is approached. However, the very fast modes within the relaxation time dispersion age according to a common 'inner clock', because their fictive temperatures are slaved to macroscopic softening. Evidence is provided for such a transition from heterogeneous to homogeneous aging as the frequency is increased into the excess wing regime. The results explain why aging in dispersive systems appears homogeneous and consistent with time aging-time superposition in cases where observations are based on the high frequency behavior.

173. *Dynamical and Quasi-static Structural Relaxation Paths in Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> Glass*

A. Kahl, T. Koeppel, D. Bedorf, R. Richert, M. L. Lind, M. D. Demetriou, W. L. Johnson, W. Arnold, K. Samwer, Appl. Phys. Lett. 95 (2009) 201903.1 - 201903.3

By sequential heat treatment of a Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> metallic glass at temperatures and durations for which  $\alpha$ -relaxation is not possible, dynamic and quasi-static relaxation paths below the glass transition are identified via ex-situ ultrasonic measurements following each heat treatment. The dynamic relaxation paths are associated with hopping between non-equilibrium potential energy states of the glass, while the quasi-static relaxation path is associated with reversible  $\beta$ -relaxation events towards quasi-equilibrium states. These quasi-equilibrium states are identified with secondary potential energy minima that exist within the inherent energy minimum of the glass, thereby supporting the concept of the sub-basin/meta-basin organization of the potential- energy landscape proposed by Stillinger and co-workers.

172. *Reverse Dynamic Calorimetry of a Viscous Ionic Liquid*

W. Huang, R. Richert, J. Chem. Phys. 131 (2009) 184501.1 - 184501.7

We compare the time scale of thermal relaxation with that of the electric modulus in the deeply supercooled regime of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Thermal relaxation refers to the process of configurational temperatures of the slow degrees of freedom equilibrating towards the vibrational temperature, which is a reliable indicator for the time scale of structural relaxation. Energy is supplied to the sample by absorption from a sinusoidal electric field with amplitude as high as 387 kV/cm and frequencies in the 0.2 Hz to 56 kHz range, analogous to microwave heating. The time resolved response of configurational temperature as well as the low field dielectric properties are measured in a single high field impedance setup. Near  $T_g$ , we find that the macroscopic field (or modulus *M*) relaxes considerably faster than the structure (in terms of thermal relaxation, solvation dynamics, and probe rotation), although the liquid is entirely composed of mobile ions.

171. *Time-resolved Non-linear Dielectric Responses in Molecular Systems*

R. Richert, W. Huang, J. Non-Cryst. Solids 356 (2010) 787 - 793

Impedance measurements in the 0.1 Hz to 50 kHz range are performed beyond the linear response regime, using a technique where peak fields as high as 450 kV/cm are possible. The main focus is on the effects of the energy that is transferred irreversibly from the external field to a molecular glass-forming liquid. Because the slow degrees of freedom absorb this energy, their heterogeneous configurational temperatures are increased before the heat is transferred to the phonons on the time scale of structural relaxation. We also discuss a time resolved variant of high field impedance spectroscopy, where the harmonic field is applied for a number of cycles at a low field, followed by the same signal at a much higher field. Fourier analysis of the resulting voltage and current traces provides a period by period time resolved picture for the response of the configurational temperature with a 5 mK resolution, resulting from a sensitivity on the  $5 \times 10^{-5}$  level for  $\tan \delta$ . It turns out that this energy absorption is responsible for an extremely pronounced non-linearity in the electric field, where the dielectric relaxation can be accelerated by a factor of 2 prior to changing the temperature.

170. *Viscous Nonpolar Liquids in Confinement Studied by Mechanical Solvation*

W. Wen, R. Richert, J. Chem. Phys. 131 (2009) 084710.1 - 084710.7

Using surface selective triplet state solvation techniques, we study the relaxation behavior of non-polar liquids near their glass transition in confinement to porous glass with 4 nm pore diameter. As specific liquid-surface interactions are not expected for alkanes, we ask whether a substantial frustration of the dynamics is a general phenomenon for such liquids, and how the effects change with surface silanization. We find that interfacial dynamics display relaxation times that are increased by orders of magnitude for several non-polar molecular liquids. Silanization removes this frustration effect almost entirely. Regarding the comparison of native versus silanized pore surfaces, it is concluded that the strong adhesive forces involved in alkanes wetting silica can explain the sluggish interfacial dynamics. The findings are not consistent with finite size effects.

169. *Diffusion-Controlled and 'Diffusionless' Crystal Growth near the Glass Transition: Relation between Liquid Dynamics and Growth Kinetics of Seven ROY Polymorphs*

Y. Sun, H. Xi, M. D. Ediger, R. Richert, L. Yu, J. Chem. Phys. 131 (2009) 074506.1 - 074506.9

The liquid dynamics of 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile, named ROY for its red, orange, and yellow crystal polymorphs, was characterized by dielectric spectroscopy and differential scanning calorimetry. Four of these polymorphs show fast "diffusionless" crystal growth at low temperatures while three others do not. ROY was found to be a typical fragile organic liquid. Its  $\alpha$  relaxation process has time-temperature superposition symmetry across the viscous range ( $\tau_\alpha = 100$  s - 100 ns) with the width of the relaxation peak characterized by a constant  $\beta_{\text{KWW}}$  of 0.73. No secondary relaxation peak was observed, even with glasses made by fast quenching. For the polymorphs not showing fast growth in the glassy state, the growth rate has a power-law relation with  $\tau_\alpha$ ,  $u \propto \tau_\alpha^{-\xi}$ , where  $\xi \approx 0.7$ . For the polymorphs showing fast crystal growth in the glassy state, the growth is so fast near and below the glass transition temperature  $T_g$  that thousands of molecular layers can be added to the crystalline phase during one structural relaxation time of the liquid. In the glassy state, this mode of growth slows slightly over time. This slowdown is not readily explained by the effect of physical aging on the thermodynamic driving force of crystallization, the glass vapor pressure, or the rate of structural relaxation. This study demonstrates that from the same liquid or glass, the growth of some polymorphs is accurately described as being limited by the rate of structural relaxation or bulk diffusion, whereas the growth of other polymorphs is too fast to be under such control.

168. *Dynamics of Glass-Forming Liquids. XIII. Microwave Heating in Slow Motion*

W. Huang, R. Richert, J. Chem. Phys. 130 (2009) 194509.1 - 194509.14

Using time-resolved non-linear dielectric relaxation measurements at fields as high as 450 kV/cm, the non-thermal effects of energy absorption are studied for simple and associating polar liquids in their supercooled state. The experiment is a low frequency analogue of microwave heating and facilitates tracking the flow of energy in time, as it accumulates in slow degrees of freedom and transfers eventually to the vibrational heat bath of the liquid. Most findings agree with a phenomenological model of heterogeneous relaxation regarding structure and configurational temperature. The relevant thermal behavior of monohydroxy alcohols differs considerably from the cases of simple non-associating liquids, due to their distinct origins of the prominent dielectric absorption mode for the two classes of liquids. Non-thermal effects are observed as dynamics that are

accelerated without increasing sample temperature, but for the present low frequencies the changes remain too small to explain the high efficiencies reported for microwave chemistry. Limitations as to how rapidly the faster relaxation time constants are able to adjust to temperature separate the modes of the dispersive  $\alpha$ -relaxation into a 'relaxation' and an 'aging' regime, thereby explaining the incompatibility of heterogeneous dynamics with physical aging.

167. *Insulated Electrodes for Eliminating Conductivity in Dielectric Relaxation Experiments*

R. Richert, Eur. Phys. J. B 68 (2009) 197 - 200

In a variety of samples, conductivity is a limiting factor regarding the resolution of dielectric loss peaks of interest. One approach to eliminating the signal that originates from conductivity is the use of insulating layers on one or both electrodes. For the typical case, it is shown that insulation layers add errors rather than improving the situation.

166. *On the Harmonic Analysis of Non-linear Dielectric Effects*

W. Huang, R. Richert, Eur. Phys. J. B 66 (2008) 217 - 221

We investigate the nonlinear dielectric effects in a polar viscous liquid, propylene carbonate, by analyzing the voltage and current traces obtained for a sinusoidal electric field at a frequency of 1 kHz and field amplitudes as high as 162 kV/cm. The main source of non-linear behavior results from the energy absorbed from the field and is understood quantitatively. However, there is a qualitative difference in the behavior of the field induced change,  $\Delta\epsilon''(E)$ , and the third harmonic amplitude of the current,  $I_{3\omega}$ . Although both  $\Delta\epsilon''(E)$  and  $I_{3\omega}$  are considered reliable measures of non-linear behavior, we show here that the third harmonic signal reflects only those non-linear responses that are instantaneous on the time scale of the test frequency.

165. *Prevalence of Approximate  $\sqrt{t}$  Relaxation for the Dielectric  $\alpha$  Process in Viscous Organic Liquids*

A. I. Nielsen, T. Christensen, B. Jakobsen, K. Niss, N. B. Olsen, R. Richert, J. C. Dyre, J. Chem. Phys. 130 (2009) 154508.1 - 154508.15

This paper presents dielectric relaxation data for organic glass-forming liquids compiled from different groups and supplemented by new measurements. The main quantity of interest is the "minimum slope" of the  $\alpha$  dielectric loss plotted as a function of frequency in a log-log plot (i.e., the numerically largest slope above the loss peak frequency). The data consisting of 347 spectra for 53 liquids show prevalence of minimum slopes close to  $-1/2$ , corresponding to approximate square-root-time dependence of the dielectric relaxation function at short times. The paper further studies possible correlations between minimum slopes and: 1) Temperature quantified via the loss-peak frequency; 2) How well an inverse power law fits data above the loss peak; 3) Degree of time-temperature superposition; 4) Loss-peak half width; 5) Deviation from non-Arrhenius behavior; 6) Loss strength. For the first three points we find correlations that indicate a special status of liquids with minimum slopes close to  $-1/2$ . For the last three points only fairly insignificant correlations are found with the exception of large-loss liquids, which have minimum slopes that are numerically significantly larger than  $1/2$  and loss peak widths that are significantly smaller than those of most other liquids. We conclude that – excluding large-loss liquids – approximate  $\sqrt{t}$  relaxation appears to be a generic property of the  $\alpha$  relaxation of organic glass formers.

164. *On the Features of the Dielectric Response of Supercooled Ethylcyclohexane*

A. Mandanici, W. Huang, M. Cutroni, R. Richert, Philos. Mag. 88 (2008) 3961 - 3971

The main relaxation observed in supercooled ethylcyclohexane in the 50 Hz – 20 kHz frequency range using high resolution dielectric spectroscopy displays an unusual relaxation pattern. The slope of the dielectric loss profile above the peak frequency progressively tends to zero with increasing temperatures. The observed features could be compatible with the existence of different underlying processes. This work exploits a simple approach based on scaling and provides relevant information on the properties of the primary and secondary relaxation in ethylcyclohexane. We show that the apparently anomalous behaviour is due to the superposition of a secondary process to the dielectric  $\alpha$ -process and support the thesis that the  $\beta$ -relaxation observed in the glassy phase could have an intramolecular origin.

163. *Heat Capacity and Entropy at the Glass Transition*

R. Richert, in "The XV<sup>th</sup> International Congress on Rheology, The Society of Rheology 80<sup>th</sup> Annual Meeting", A. Co, L. G. Leal, R. H. Colby, A. J. Giacomin (Eds.), AIP Conf. Proc. 1027 (2008) 1297 - 1299

Frequency resolved non-linear dielectric relaxation experiments at high electric fields are used to show that viscous liquids are not only dynamically but also thermodynamically heterogeneous. The understanding of the nanoscopic heat-flow is quantitative and allows us to extract the configurational contribution to heat capacity and entropy. It is found that the excess heat capacity is largely configurational only for liquids that are not fragile in terms of the strong-fragile pattern.

162. *The Physics of Heating by Time-Dependent Fields: Microwaves and Water Revisited*

W. Huang, R. Richert, J. Phys. Chem. B 112 (2008) 9909 - 9913

Heating samples by microwave radiation is a particular example of the more general phenomenon where materials absorb energy from an external time dependent field of an electric, magnetic, or mechanical nature. How this compares with conventional heating is a question of continued interest. Here, we show that the origin of the absorptivity determines whether energy accumulates in the slower configurational degrees of freedom or transfers rapidly to the phonon bath, where only the latter situation is equivalent to conventional heating. Based upon time resolved measurements of the configurational temperatures, evidence is provided for simple liquids displaying non-thermal behaviour if heated by external fields, with molecules being more mobile than expected on the basis of the actual temperature. However, water and related materials are the exception regarding absorptive heating, because energy is transferred to the phonons more rapidly than it is absorbed from the field and non-thermal effects thus remain absent.

161. *Merging of the  $\alpha$  and  $\beta$  Relaxations and Aging via the Johari-Goldstein Modes in Rapidly Quenched Metallic Glasses*

J. Hachenberg, D. Bedorf, K. Samwer, R. Richert, A. Kahl, M. D. Demetriou, W. L. Johnson, Appl. Phys. Lett. 92 (2008) 131911.1 - 131911.3

This paper provides evidence that physical aging of deeply and rapidly quenched metallic glasses is promoted by the Johari-Goldstein slow  $\beta$ -relaxation, resulting in a significant irreversible increase of the mechanical modulus on initial heating. Dynamic mechanical analysis has been used to characterize relaxation phenomena of a strong and a fragile metallic glass. In addition we can extrapolate the temperature dependence of  $\beta$ - and  $\alpha$ - relaxation peaks to higher temperatures and calculate the merging temperature for both types of glasses.

160. *Why Retardation Takes More Time Than Relaxation in a Linear System*

J. Jäckle, R. Richert, Phys. Rev. E 77 (2008) 031201.1 - 031201.6

For a linear dielectric medium, it is shown that the ratio of average relaxation to retardation time is given by the ratio of the high over low frequency limit of the dielectric constants,  $\tau_e/\tau_M = \epsilon_s/\epsilon_\infty$ . This statement holds for dispersive dynamics, i.e. it is not limited to the special case of exponential responses. A difference equation for the charge build-up is established which provides a rationale for why retardation requires more time than its relaxation counterpart. The relevance to experimental situations is also discussed.

159. *Calorimetric versus Kinetic Glass Transitions in Viscous Monohydroxy Alcohols*

L.-M. Wang, Y. Tian, R. Liu, R. Richert, J. Chem. Phys. 128 (2008) 084503.1 - 084503.8

An extensive comparison of calorimetric and dielectric measurements is carried out for generic molecular liquids and monohydroxy alcohols with focus on the identification of the dielectric modes which are associated with the glass transition. For generic liquids, the calorimetric glass transition temperatures ( $T_{g\text{-cal}}$ ) are always greater than their kinetic counterparts ( $T_{g\text{-kin}}$ ), but limited to  $T_{g\text{-cal}} - T_{g\text{-kin}} \leq 3$  K. Also, the non-exponentiality parameters of the Tool-Narayananwamy-Moynihan-Hodge model applied to the calorimetric data and the stretching exponents of the dielectric measurements show remarkable agreement. The same behavior is found for glass-forming monohydroxy alcohols, provided that the faster and smaller non-Debye relaxation rather than the large dielectric Debye process is assigned to the structural relaxation. The study emphasizes that the dielectric signature of the glass transition in monohydroxy alcohols is a dispersive loss peak that is faster and significantly smaller than the prominent Debye feature.

158. *Dynamics of Glass-Forming Liquids. XII. Dielectric Study of Primary and Secondary Relaxations in Ethylcyclohexane*

A. Mandanici, W. Huang, M. Cutroni, R. Richert, J. Chem. Phys. 128 (2008) 124505.1 - 124505.7

The dynamics of ethylcyclohexane are investigated by high resolution dielectric spectroscopy aiming to characterize the relevant relaxational features of this simple system in its fluid, supercooled liquid, and glassy state. The dielectric signature of structural relaxation is a primary loss peak with amplitude  $\Delta\epsilon = 0.01$ , and a secondary loss process is found in the glassy state. This  $\beta$ -relaxation is compared with a 'slow' process revealed by ultrasonics and with previously found  $\gamma$ - and  $\chi$ -processes in similar materials containing the cyclohexyl group. The results suggest that this secondary process is an intramolecular mode rather than a Johari-Goldstein process, consistent with its persistence in the liquid state at 'slow' relaxation times which exceed those of the  $\alpha$ -process. The dielectric activity of such a slow process requires that the dipole magnitude changes with the intramolecular transition, whereas a change in dipole direction only would be masked by the faster structural relaxation.

157. *Measuring the Configurational Heat Capacity of Liquids*

L.-M. Wang, R. Richert, Phys. Rev. Lett. 99 (2007) 185701.1 - 185701.4

A high electric field impedance experiment on supercooled molecular liquids is employed to transfer energy to the slow degrees of freedom by absorption from the external field and subsequently detect the increase of their 'configurational temperature' via the change of the dielectric relaxation times. The link between the added energy and effective temperature is the configurational heat capacity, which can be determined quantitatively. It turns out that the configurational contribution to the heat capacity accounts for most of the excess (liquid over crystal) heat capacity for stronger liquids, but for only half of the heat capacity step in the case of more fragile systems. It is also observed that the 'configurational temperature' gradually approaches the phonon temperature on the structural relaxation time scale.

156. *Primary and Secondary Relaxation Time Dispersions in Fragile Supercooled Liquids*

L.-M. Wang, R. Richert, Phys. Rev. B 76 (2007) 064201.1 - 064201.8

The relaxation time dispersions of the primary ( $\alpha$ ) and secondary ( $\beta$ ) dielectric relaxations are studied for molecular glass-forming liquids regarding their dependence on structural relaxation time (or lack thereof observed as time-temperature superposition, TTS), their changes with fragility, and a possible correlation of the values for the  $\alpha$ - and  $\beta$ -processes. Towards more fragile liquids, the width  $w_\alpha$  of the  $\alpha$ -peak at the glass transition temperature  $T_g$  is known to increase significantly. Additionally, we observe that TTS extends over a broader range of peak relaxation times in the case of higher fragility, with the approach to exponential (Debye) relaxation being delayed to faster dynamics. The width  $w_\beta$  of the  $\beta$ -relaxation at  $T_g$  is somewhat lower for more fragile liquids and appears correlated with that of the primary relaxation. The extrapolated coincidence of the dispersions of the  $\alpha$  and  $\beta$  process occurs at the fragility 'limit' of  $m = 170$ , implying that  $w_\alpha \leq w_\beta$  for all molecular supercooled liquids. Materials of high fragility are also those with no clear low-frequency cutoff in the relaxation time distribution, i.e. their susceptibilities require Havriliak-Negami instead of Cole-Davidson fits. For sorbitol, the value of  $w_\beta$  is seen to change steadily through the  $\alpha$ - $\beta$ -merging region, whereas  $w_\alpha$  displays a kink at the crossover temperature.

155. *Wide Frequency Range Capacitive Detection of Loss in a Metallic Cantilever using Resonance and Relaxation Modes*

R. Richert, Rev. Sci. Instrum. 78 (2007) 053901.1 - 053901.5

The impedance of a capacitor which embraces a charged cantilever is used to measure the mechanical properties of the cantilever material. The technique has been tested with an amorphous metallic specimen, but is applicable for many other solids. The material damping can be measured at the resonance frequency of the cantilever via the width of the resonance curve or by recording the ring-down behavior. Additionally, several decades in frequency are accessible below the resonance frequency, where values as low as  $\nu = 0.03$  Hz are achieved easily. The data is analyzed with a single equation that captures the damping at all frequencies in terms of the material specific Young's modulus  $E$  and its loss angle  $\tan\delta = E''/E'$ .

154. *Glass Transition Dynamics and Boiling Temperatures of Molecular Liquids and Their Isomers*

L.-M. Wang, R. Richert, J. Phys. Chem. B 111 (2007) 3201 - 3207

The relation between a dynamic and a thermodynamic temperature, glass transition  $T_g$  and boiling point  $T_b$ , is investigated for various glass forming liquids, with emphasis on monohydroxy alcohols. As is well known,  $T_b$  and  $T_g$  are positively correlated across a large variety of liquids. However, we found that the same quantities show a negative correlation within an isomeric series, i.e.  $T_b$  decreases with increasing  $T_g$  for different isomers of the same chemical formula. For the alcohol series,  $C_nH_{2n+1}OH$  with  $3 \leq n \leq 10$ , a master curve of the negative  $T_g - T_b$  correlation is obtained if the temperatures are normalized to the respective values of the  $n$ -alkanols. This  $T_g - T_b$  dependence of isomeric liquids is linked to entropic effects and responsible for much of the scatter of the correlation observed for a large number of molecular organic glass-formers with  $45 \text{ K} < T_g < 250 \text{ K}$ . Dielectric relaxation is measured for three groups of isomers: (a) 3-methoxy-1-butanol and 2-*iso*-propoxyethanol; (b) 1,4-, 1,2-, and 2,4-pentanediol, and (c) di-*n*- and di-*iso*-butyl phthalate. Two key parameters of the dynamics, fragility  $m$  and stretching exponent  $\beta$ , are found to be indistinguishable within isomers of moderately different  $T_g$ 's. Larger fragility differences are readily expected with pronounced structural change, but no systematic trend is observed within an isomer series. The results provide a useful tool for assessing  $T_g$ ,  $m$ , and  $\beta$  for marginal glass-formers on the basis of their isomers.

153. *Comparing Calorimetric and Dielectric Polarization Modes in Viscous 2-ethyl-1-hexanol*

H. Huth, L.-M. Wang, C. Schick, R. Richert, J. Chem. Phys. 126 (2007) 104503.1 - 104503.4

Dielectric relaxation and dynamic heat capacity measurements are compared for 2-ethyl-1-hexanol near its glass transition temperature  $T_g$  in order to further clarify the origin of the prominent Debye type loss peak observed in many monohydroxy alcohols and other hydrogen bonding liquids. While the dielectric spectrum  $\epsilon''$  displays two distinct polarization processes that are separated a factor of 2000 in terms of the peak frequency, the heat capacity  $c_p$  shows only a single peak. The dielectric process with lower amplitude and higher peak frequency coincides with the calorimetric signal, whereas the large dielectric Debye signal is not associated with calorimetric modes. We conclude that the Debye process corresponds to a transition among states which differ in energy only in the case of an external electric field.

152. *Enhanced Diffusivity in Supercooled Liquids*

R. Richert, K. Samwer, New J. Phys. 9 (2007) 36.1 - 36.11

The enhancement of self and probe diffusivity over the Stokes-Einstein values by orders of magnitude is observed in the viscous regime of polymers, molecular glass-formers, and supercooled metallic systems. We investigate an alternative to identifying enhanced diffusivity with the fast components of the primary structural relaxation process: High translational mobility is being associated with cooperative dynamics in string-like topologies, which is responsible for fast diffusive particle motion and the slow secondary  $\beta$ -relaxation observed below the dynamic crossover temperature in fragile glass-formers. This approach provides a unifying view of diffusivity across the different classes of glass-forming materials.

151. *Nonlinear Features in the Dielectric Behavior of Propylene Glycol*

S. Weinstein, R. Richert, Phys. Rev. B 75 (2007) 064302.1 - 064302.5

We investigate the nonlinear dielectric effects in a glass-forming polar liquid, propylene glycol, by high voltage frequency-domain impedance experiments. The peak amplitudes of the sinusoidal electric fields are varied between 14 and 283 kV/cm. Two competing nonlinear effects are observed: a decrease of the dielectric constant reminiscent of the Langevin effect and an increase of the dielectric loss which originates from the irreversible transfer of energy from the electric field to the slow degrees of freedom of the viscous liquid. By virtue of the frequency dependence of the two features, the positive and negative changes are easily separable. Both effects can be rationalized quantitatively without adjustable parameters.

150. *Probing Heterogeneous Thermal Relaxation by Nonlinear Dielectric Spectroscopy*

S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128.1 - 205128.7

The application of time-dependent electric fields to a sample that exhibits dielectric loss results in the irreversible transfer of energy from the external field to the slow degrees of freedom in the material. These slow modes are coupled only weakly to the phonon bath and elevated fictive temperatures are thus associated with

considerable persistence times. Assuming locally correlated heterogeneities regarding dielectric and thermal relaxation times, extremely pronounced nonlinear dielectric effects are predicted. For two glass-forming systems, glycerol and propylene glycol, the predicted effects are observed experimentally by high field impedance spectroscopy. For example, the dielectric loss of glycerol measured at 283 kV/cm increases by more than 6 % over its low field value. This non-linearity displays a characteristic frequency dependence, with the loss at frequencies below the peak value being field invariant, while the high frequency wing experiences a near uniform relative increase of the loss. If the dielectric and thermal time constants are assumed to be independently distributed, the model fails to explain the findings.

149. *Glass Transitions in Viscous Monohydroxy Alcohols: Calorimetry versus Dielectric Relaxation*

L.-M. Wang, R. Richert, *Int. J. Thermophys.* 29 (2008) 2055 - 2061

We present an extensive comparison of the calorimetric and dielectric measurements of the glass transitions in both monohydroxy alcohols and other molecular liquids, with only these alcohols displaying an additional pronounced dielectric Debye peaks. It is found that the calorimetric  $T_g$ 's of the non-Debye liquids with moderate cooling and heating rates ( $\pm 20$  K/min, for example) are slightly greater than the kinetic ones which are determined as the temperatures at which the relaxation time is 100 s. Because the difference does not exceed 3 K, this relation of calorimetric and kinetic  $T_g$ 's is used as 'standard'. We identify two kinetic glass transitions from the dielectric relaxation of Debye type monohydroxy alcohols and find that the Debye process is not the signature of the glass-transition.

148. *Solvation Dynamics and Electric Field Relaxation in an Imidazolium- $PF_6$  Ionic Liquid: From Room Temperature to the Glass Transition*

N. Ito, R. Richert, *J. Phys. Chem. B* 111 (2007) 5016 - 5022

Time-resolved phosphorescence spectra and anisotropy of quinoxaline were measured in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-HFP), in its supercooled state near the glass transition temperature. The solvation dynamics results are compared with the rotational motion of the probe and with the dielectric behavior of the neat ionic liquid. The dynamics in the viscous state are highly dispersive and show a super-Arrhenius temperature dependence, as typical for glass-forming materials. Combined with room temperature results, solvation dynamics is observed to follow the structural relaxation times in terms of  $\eta/T$  for more than ten decades, from sub-nanoseconds at room temperature to seconds near the glass transition temperature  $T_g$ . The dielectric modulus relaxation follows this trend only for temperatures  $T > 1.2 T_g$  and departs significantly from  $\eta/T$  in the  $1.1 T_g > T > T_g$  range. This deviation is reminiscent of the enhanced translational diffusion or fractional Stokes-Einstein behavior observed in many fragile supercooled liquids. Because the electric field relaxation in BMIM-HFP includes dc-conductivity, this correlation function involves translational motion and thus displays the effect of enhanced diffusivity. A microscopic model is required to rationalize the decoupling of solvation dynamics from the longitudinal time scales and the limitation of this effect to the viscous regime with  $T < 1.2 T_g$ .

147. *Nonlinear Dielectric Response and Thermodynamic Heterogeneity in Liquids*

R. Richert, S. Weinstein, *Phys. Rev. Lett.* 97 (2006) 095703.1 - 095703.4

If large amplitude time-dependent fields (e.g. dielectric, magnetic, mechanical) are applied to a sample that displays relaxational modes, some energy of the external field is absorbed by the slow degrees of freedom. The weak coupling of these modes to the phonon bath leads to long persistence times of the resulting higher fictive temperature. Assuming heterogeneities regarding dielectric and thermal relaxation times, extremely strong nonlinear dielectric effects are predicted and experimentally verified. For glycerol at  $T = 213$  K, the dielectric loss measured at 280 kV/cm increases by more than 6 % over its low field value. This non-linearity shows a characteristic frequency dependence and implies that dielectric and thermal time constants are locally correlated in viscous liquids.

146. *Solvation Dynamics in Viscous Polymer Solutions: Propylene Carbonate Confined by Poly(methylmethacrylate)*

F. He, R. Richert, *Phys. Rev. B* 74 (2006) 014201.1 - 014201.7

Solvation dynamics of a triplet state probe is used to explore the dynamics of supercooled propylene carbonate (PC) when modified by the presence of poly(methyl methacrylate) (PMMA) in viscous polymer solution. In the

PMMA weight fraction range 0 to 0.32, the relaxation time for dipolar solvation increases by a factor of approximately 1500, if evaluated at a constant temperature. This is equivalent to a shift of the PC glass-transition temperature  $T_g$  by + 6.4 K as a result of geometrical restriction by the presence of 32 wt% PMMA. In terms of the estimated average PC-PMMA distance, the relaxation time approaches the bulk value much more rapidly compared with size effects of confinement in porous glasses or microemulsion droplets. The interpretation of this feature is that a reduced PMMA concentration not only increases the average PC-PMMA distance, but also changes from a solid to a more open topology of the confining material. Accordingly, the slowest dynamics in these mixtures are not found near a single polymer chain, but only in the more concentrated polymer environments where a larger fraction of the cooperative volume is immobilized by macromolecules.

145. *Dielectric Study of Probe Rotation in Viscous Liquids* (INVITED PAPER)  
W. Huang, R. Richert, *Philos. Mag.* 87 (2007) 371 - 382

Dielectric molecular probes are employed to assess the averaging required for a transition from heterogeneous to more hydrodynamic rotational behavior in supercooled liquids. The degree of averaging is controlled by the size of the probe molecule relative to the liquid constituents. Larger solutes exhibit longer time constants and more exponential dynamics as a result of effective time averaging over fluctuating environments. With this approach the time scale of rate exchange is measured across a range of 8 decades, in which the characteristic relaxation time varies from 5 s to 50 ns. The sharp transition from dispersive to exponential probe rotation suggests that rate exchange occurs on the time scale of the slowest time constant of structural relaxation. No change in the environmental fluctuation to structural relaxation time ratio is observed across this wide range of frequencies.

144. *Confined Viscous Liquids: Interfacial versus Finite Size Effects* (INVITED PAPER)  
F. He, L.-M. Wang, R. Richert, *Eur. Phys. J. Special Topics* 141 (2007) 3 - 9

Confining a supercooled liquid to spaces of several nanometer in diameter can lead to dramatic changes in the relaxation dynamics of the material. In many cases, the effect is reported as a confinement induced shift of the glass transition temperature  $T_g$ . Both positive and negative values for  $\Delta T_g$  have been observed and the length scale of the confining geometry is considered the main variable. We review the dynamics of glass-forming liquids in both hard and soft confinement of < 10 nm spaces, with focus on results from solvation dynamics experiments. It is shown that the interface is instrumental in determining the dynamics, giving rise to relaxation time gradients across the cooperativity length scale of the liquid. Depending on the interfacial conditions, dynamics can become faster or slower for the same liquid, same size of confinement, and identical experimental technique used. No indications of true finite size effects are observed, and the pore or droplet size is relevant only indirectly through the relative number of molecules near the surface.

143. *Solvent Response and Dielectric Relaxation in Supercooled Butyronitrile*  
N. Ito, K. Duvvuri, D. V. Matyushov, R. Richert, *J. Chem. Phys.* 125 (2006) 024504.1 - 024504.8

We have measured the dynamics of solvation of a triplet state probe, quinoxaline, in the glass-forming dipolar liquid butyronitrile near its glass transition temperature  $T_g = 95$  K. The Stokes-shift correlation function displays a relaxation time dispersion of considerable magnitude and the optical linewidth changes along the solvation coordinate in a non-monotonic fashion. These features are characteristic of solvation in viscous solvents and clearly indicate heterogeneous dynamics, i.e., spatially distinct solvent response times. Using the dielectric relaxation data of viscous butyronitrile as input, a microscopic model of dipolar solvation captures the relaxation time, the relaxation dispersion, and the amplitude of the dynamical Stokes shift remarkably well.

142. *Fragility and Thermodynamics in Non-Polymeric Glass-Forming Liquids*  
L.-M. Wang, C. A. Angell, R. Richert, *J. Chem. Phys.* 125 (2006) 074505.1 - 074505.8

For non-polymeric supercooled liquids, the empirical correlation  $m = 56T_g\Delta C_p(T_g)/\Delta H_m$  provides a reliable means of correlating dynamic and thermodynamic variables. The dynamics are characterized by the fragility or steepness index  $m$  and the glass transition temperature  $T_g$ , while thermodynamics enter in terms of the heat capacity step  $\Delta C_p$  at  $T_g$  and the melting enthalpy  $\Delta H_m$ . The combination of the above correlation with the 2/3 rule for the  $T_g/T_m$  ratio yields an expression,  $m = 40\Delta C_p(T_g)/\Delta S_m$ , which was rationalized as the correlation of the thermodynamic and kinetic fragilities. Defining a thermodynamic fragility via  $\Delta C_p(T_g)/\Delta S_m$  also reveals that the slopes in Kauzmann's original  $\Delta S(T)/\Delta S_m$  vs.  $T/T_m$  plot reflect the fragility concept [*Chem. Rev.* **43**, 219 (1948)],

so long as  $T_m/T_g = 1.5$ . For the many liquids whose excess heat capacity is a hyperbolic function of temperature, we deduce that the fragility cannot exceed  $m = 170$ , unless the  $T_g/T_m = 2/3$  rule breaks down.

141. *Response to "Comment on 'On the dielectric susceptibility spectra of supercooled o-terphenyl'" [J. Chem. Phys. 123, 154502 (2005)]*

R. Richert, J. Chem. Phys. 124 (2006) 187102.1 - 187102.2

The recent claim of time-temperature superposition (TTS) for *o*-terphenyl (OTP) in its viscous regime is revisited in order to clarify whether peak versus area normalization of the dielectric loss profiles impacts the results derived from the master plot. In the case of OTP, noise is the main source of differences between the two options. Using synthetic noisy data, it is shown that an area normalized master plot is more sensitive to deviations from TTS than the peak normalized counterpart. As a result, OTP is characterized by a stretching exponent  $\beta = 0.50 \pm 0.03$  in the 248 - 284 K temperature range.

140. *Dynamics of Glass-Forming Liquids. XI. Fluctuating Environments by Dielectric Spectroscopy*

W. Huang, R. Richert, J. Chem. Phys. 124 (2006) 164510.1 - 164510.7

The dielectric relaxation of a 1 wt% mixture of di-*n*-butylether in 3-methylpentane has been measured across a range of 8 decades, in which the characteristic relaxation time varies from 5 s to 50 ns. Each loss spectrum is a superposition of the dispersive solvent peak and a Debye peak which is one decade slower and readily assigned to the larger and more dipolar solute molecules. Fluctuating environments or rate exchange is made responsible for the Debye nature of probe rotation, implying that the environmental relaxation times fluctuate on time scales which are faster than the rotational correlation decay of the probe molecule. Within the experimental range from 2.2 s to 42 ns regarding the mean  $\alpha$ -relaxation time, the results are consistent with the exchange time matching the upper limit of structural relaxation times or 2-3 times their average value. As  $T_g$  is approached, no indication for a variation in exchange behavior or for slower environmental fluctuations is found.

139. *Dynamics of a Supercooled Ionic Liquid Studied by Optical and Dielectric Spectroscopy*

N. Ito, W. Huang, R. Richert, J. Phys. Chem. B 110 (2006) 4371 - 4377

We have measured the dynamics of solvation of a triplet state probe, quinoxaline, in the glass-forming ionic liquid dibutylammonium formate near its glass transition temperature  $T_g = 153$  K. The Stokes-shift correlation function displays a relaxation time dispersion of considerable magnitude and the optical linewidth changes systematically along the solvation coordinate. The solvent dynamics in the viscous regime is compared with the rotational behavior of the solute and with the dielectric relaxation of the ionic liquid. Among the different quantities derived from the dielectric experiments, the relaxation of the macroscopic electric field, i.e., the modulus  $M(t)$ , matches best the solvent response  $C(t)$  regarding time scale and stretching exponent. Many other properties are reminiscent of the behavior of polar molecular liquids which lack the ionic character.

138. *Relaxational Features of Supercooled and Glassy m-Toluidine*

A. Mandanici, R. Richert, M. Cutroni, X. Shi, S. A. Hutcheson, G. B. McKenna, J. Non-Cryst. Solids 352 (2006) 4729 - 4734

Recent investigations performed by dielectric and mechanical spectroscopy have provided detailed information about the dynamical response of *m*-toluidine in the supercooled and glassy states. In the present work we analyze the properties of the  $\alpha$  relaxation process on the basis of dielectric and shear mechanical data, discussing the unusual behaviour of this fragile glass-former. The nature of the secondary relaxation is elucidated by high resolution dielectric measurements and discussed in terms of the Coupling Model and previous neutron scattering and simulation results.

137. *From Heterogeneous Probe Rotation to the Hydrodynamic Limit* (INVITED PAPER)

W. Huang, R. Richert, J. Non-Cryst. Solids 352 (2006) 4704 - 4709

The recognition of heterogeneous dynamics in single component supercooled liquids has greatly advanced our understanding of the dynamics in glass-forming materials. However, details such as persistence times and length scales associated with dynamically distinct domains remain to be resolved. The rotational correlation function of probe molecules in viscous liquids is used as a tool for exploring the rate exchange or the time a domain memorizes its initial relaxation rate. With high precision dielectric experiments, the dynamics of probe

molecules is observed to slow down with increasing size of the guest relative to the host molecules. For the case of di-*n*-butylether in 3-methylpentane, the situation of purely exponential probe dynamics within dispersive host relaxation is achieved as a result of time averaging. The results suggest that rate exchange occurs on a time scale which is equal to the longest structural relaxation time of the system.

136. *Enhanced Translational Diffusion of Rubrene in Sucrose Benzoate*

J. R. Rajian, W. Huang, R. Richert, E. L. Quitevis, J. Chem. Phys. 124 (2006) 014510.1 - 014510.8

The translational diffusion of rubrene in the fragile molecular glass-former, sucrose benzoate (SB), (fragility index  $m \approx 94$ ), has been studied from  $T_g + 6$  K to  $T_g + 71$  K ( $T_g = 337$  K) by using the technique of holographic fluorescence recovery after photobleaching. In the temperature range of the measurements, the translational relaxation functions were observed to decay exponentially, indicating that Fick's law of diffusion governs the translational motion of rubrene in sucrose benzoate. The value of the translational diffusion coefficient  $D_T$  obtained from the 1/e time of the translational relaxation function varied from  $5.3 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$  at 343 K to  $5.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at 408 K. The temperature dependence of  $D_T$  for diffusion of rubrene in SB is compared to that of the viscosity and the dielectric relaxation time  $\tau_D$  of SB. The temperature dependence of  $D_T$  is weaker than that of  $T/\eta$  for  $T < 1.2 T_g$  but tracks the reciprocal of the dielectric relaxation time  $1/\tau_D$  for  $1.05 T_g < T < 1.21 T_g$ . The translational diffusion coefficient at  $T_g$  is enhanced by a factor of  $\approx 2.5 \times 10^2$  over the value predicted by the Stokes-Einstein equation at  $1.2 T_g$ . The decoupling of probe diffusion from the viscosity is characterized by a scaling law,  $D_T \sim \eta^{-\xi}$ , with  $\xi = 0.729$ .

135. *Heterogeneous Thermal Excitation and Relaxation in Supercooled Liquids*

S. Weinstein, R. Richert, J. Chem. Phys. 123 (2005) 224506.1 - 224506.9

We investigate a phenomenological model which rationalizes the effects of dielectric hole burning on the basis of heterogeneous dielectric and specific heat relaxation in supercooled liquids. The quantitative agreement between model predictions and dielectric hole-burning observations is lost if the assumption of correlated dielectric and thermal relaxation times is removed from the model. This suggests that dynamically distinct domains in real liquids are associated with a time constant which characterizes both the structural and thermal relaxation behavior. The calculations demonstrate that the observed burn-induced modifications reflect the spectral selectivity and persistence time of the fictive temperatures within these domains, and that 100 or more cycles of the sinusoidal burn field can be required to saturate the heat accumulated in the slow degrees of freedom. It is also shown that the recovery of dielectric holes is entirely accounted for by the model, and that the persistence times do not provide direct insight into rate exchange processes. Additionally, the model predicts that the heating effects considered here are a significant source of non-linear dielectric behavior, even in the absence of deliberate frequency selective hole-burning.

134. *Diluent Effects on the Debye-Type Dielectric Relaxation in Viscous Monohydroxy Alcohols*

L.-M. Wang, S. Shahriari, R. Richert, J. Phys. Chem. B 109 (2005) 23255 - 23262

With the recognition that the Debye type dielectric relaxation of liquid monohydroxy alcohols does not reflect the structural relaxation dynamics associated with the viscous flow and the glass transition, its behavior upon dilution is expected to differ from that of real  $\alpha$ -processes. We have investigated the Debye-type dielectric relaxation of binary alcohol/alkane mixtures across the entire concentration range in the supercooled regimes. The focus is on 2-ethyl-1-hexanol in two non-polar liquids, 3-methylpentane and squalane, which are more fluid and more viscous than the alcohol, respectively. The Debye relaxation is found to occur only for alcohol mole fractions  $x > 0.2$  and is always accompanied by a non-Debye relaxation originating from the alcohol component. Prior to its complete disappearance, the Debye relaxation is subject to broadening. We observe that the Debye dynamics of 2-ethyl-1-hexanol is accelerated in the more fluid 3-methylpentane, while the more viscous squalane leads to longer Debye relaxation times. The present experiments also provide evidence that the breakdown of the Debye relaxation amplitude does not imply the absence of hydrogen bonded structures.

133. *Dynamics of Glass-Forming Liquids. X. Dielectric Relaxation of 3-Bromopentane as Molecular Probes in 3-Methylpentane*

W. Huang, S. Shahriari, R. Richert, J. Chem. Phys. 123 (2005) 164504.1 - 164504.7

The glass-forming liquids 3-bromopentane (3BP) and 3-methylpentane (3MP) are readily miscible across the entire composition range, although their polarities differ considerably. As noted by Berberian [J. Non-Cryst.

Solids **131-133**, 48 (1991)], the nearly matching molar volumes makes this binary system appear ideal for probe sensitized measurements. We have performed a dielectric study of these mixtures in the range of 3BP mole fractions  $x$  from  $2 \times 10^{-4}$  to 0.75. In the limit of low concentrations,  $x < 0.5$  %, the dielectric loss peak of 3BP is slower by a factor of 2.5 relative to that of 3MP. Additionally, the relaxation behavior of the guest is more exponential than that of the host liquid. We interpret the distinct dynamics of the guest as a result of temporal averaging over the heterogeneous host dynamics, with the exchange time being near the longest structural time constant of the system.

132. *On the Dielectric Susceptibility Spectra of Supercooled *o*-Terphenyl*

R. Richert, J. Chem. Phys. 123 (2005) 154502.1 - 154502.3

Supercooled *o*-terphenyl has been the subject of many investigations, including dielectric relaxation spectroscopy. Due to the low dielectric strength and the tendency to crystallize at elevated temperatures, a detailed shape analysis of the loss profile from the glass transition temperature  $T_g$  to  $\sim 1.2 \times T_g$  is not available for the neat glass-former. Assessing the origin of the different temperature dependences of translational and rotational motion in supercooled liquids and its possible connection to heterogeneity requires this knowledge regarding the possible changes in the relaxation time distribution across the 100 s to 100 ns relaxation time range. This note provides this information for *o*-terphenyl on the basis of a master curve representation: time-temperature superposition applies with a constant stretching exponent of  $\beta = 0.5$  in the range of interest.

131. *Effect of Dispersion on the Relaxation-Retardation Time Scale Ratio*

N. Ito, R. Richert, J. Chem. Phys. 123 (2005) 106101.1 - 106101.2

A simple relation between relaxation (modulus) and retardation (permittivity, compliance) times is determined for cases of dispersive instead of purely exponential response functions. An analytical solution for the Cole-Cole case and numerical treatments of the Cole-Davidson function reveal that the ratio of the relaxation to retardation time constant is given by the ratio of the high to low frequency dielectric constant raised to the power of  $1/x$ , where  $x$  is the exponent that gauges the deviation from exponentiality.

130. *Identification of Dielectric and Structural Relaxations in Glass-forming Secondary Amides*

L.-M. Wang, R. Richert, J. Chem. Phys. 123 (2005) 054516.1 - 054516.9

Dielectric relaxation dynamics of secondary amides is explored in their supercooled state near the glass transition temperature  $T_g$  by investigating *N*-ethylacetamide and its mixtures with *N*-methylformamide. All the samples are found to exhibit giant dielectric permittivities, reaching over 500 in *N*-methylformamide-rich mixtures around  $T_g$ . For both the neat and binary systems, the predominant relaxation peak is of the Debye-type throughout the viscous regime, which is an unexpected feature for a glass-former with intermediate fragility. Present results combined with earlier reported high-temperature data reveal that the dielectric strength  $\Delta\epsilon_D$  of the Debye relaxation extrapolates to zero at frequencies  $10^{10}$  -  $10^{11}$  Hz, which is about two orders of magnitude lower than the phonon frequency limit typical of the structural relaxation. This Debye process is remarkably similar to the dielectric behavior of many monohydroxy alcohols, which implies a common nature of purely exponential relaxation dynamics in these liquids. Based on the dielectric properties, we conclude that the Debye relaxation in the secondary amides is not a direct signature of the primary or  $\alpha$ -relaxation, the latter being obscured at low temperatures due to the relatively low permittivity and close spectral proximity to the Debye peak. As in the case of monohydroxy alcohols, dielectric polarization and structure fluctuate on different time scales in secondary amides. The Kirkwood-Fröhlich correlation factors for Debye type liquids are also discussed.

129. *Triplet Excitation Transfer in Glassy Systems: Spatial and Spectral Diffusion*

N. Ito, R. Richert, J. Chem. Phys. 122 (2005) 234508.1 - 234508.7

Triplet excitation transfer among benzophenone molecules dissolved in glassy 2-methyltetrahydrofuran is studied by recording the emission and the optical depolarization as a function of wavelength and time. The transport mechanism is based upon exchange interaction and subject to the random character of both jump distances and site energies. Optical anisotropy data is used to gauge the probability of an excitation to remain on its original site. The anisotropy is observed to decrease by a factor of 2 from high to low energies within the inhomogeneously broadened emission band, clearly indicating hopping mediated thermalization within the density of states. Within their excited state lifetime the excitons do not reach the steady state energies, but solvation allows the observation of that energy level. Unexpectedly, we find that the transfers at very short times

do not contribute as much to spectral diffusion as the subsequent transport. Because the short time hops target sites as close as  $\approx 1$  nm, this observation suggests spatially correlated site energies for these short distances.

128. *Ideal Mixing Behavior of the Debye Process in Supercooled Monohydroxy Alcohols*

L.-M. Wang, R. Richert, J. Phys. Chem. B 109 (2005) 8767 - 8773

Glass-forming monohydroxy alcohols exhibit two dielectric relaxation signals with super-Arrhenius temperature dependence: a Debye peak and an asymmetrically broadened  $\alpha$ -process. We explore the behavior of these distinct relaxation features in mixtures of such liquids by dielectric measurements. The study focuses on the viscous regime of two binary systems: 2-methyl-1-butanol with 2-ethyl-1-hexanol and 1-propanol with 3,7-dimethyl-1-octanol. We find that the logarithmic relaxation time,  $\log(\tau)$ , of the Debye peak follows an ideal mixing law (linear change with mole fraction), even in the case of mixing structurally dissimilar components. By contrast, the  $\log(\tau)$  versus mole fraction curve for the  $\alpha$ -process is non-linear, indicative of slower structural relaxation relative to the expectation based upon ideal mixing behavior. The latter observation is analogous to the effect of composition on viscosity, heat of mixing, and glass transition temperature, whereas the ideal mixing of  $\log(\tau)$  seen for the Debye peak is the exception. We conclude that the unusual ideal-mixing behavior of dielectric relaxation in monohydroxy alcohols is not a result of structural similarity, but rather yet another evidence of the Debye process being decoupled from other dynamic and thermodynamic properties.

127. *Debye Type Dielectric Relaxation and the Glass Transition of Alcohols*  
(LETTER)

L.-M. Wang, R. Richert, J. Phys. Chem. B 109 (2005) 11091 - 11094

Many hydrogen-bonded liquids, especially glass-forming cases, display a dielectric relaxation behavior which differs qualitatively from that of other simple liquids. The majority of models aimed at explaining this unusual dielectric behavior associate the prominent Debye process with structural relaxation, viscous flow, and the glass transition. We perform dielectric and calorimetric studies of glass-forming mixtures of 2-ethyl-hexylamine and 2-ethyl-1-hexanol across the entire composition range. The kinetic glass transition temperature derived from the large dielectric Debye peak decreases, while that of the much smaller and asymmetrically broadened peak increases upon adding amine. Only the latter feature coincides with the calorimetric glass transition results, implying that molecular structure and dielectric polarization fluctuate on time scales which can differ by orders of magnitude in many hydrogen-bonding liquids.

126. *Dynamics of Supercooled Liquids in the Vicinity of Soft and Hard Interfaces*

F. He, L.-M. Wang, R. Richert, Phys. Rev. B 71 (2005) 144205.1 - 144205.10

Using solvation techniques we explore the dynamics of nanoconfined and interfacial supercooled liquids near their glass transition temperatures. Confinement is accomplished by the use of porous glasses with pore diameters between 4 and 7.5 nm, and by microemulsions with droplet sizes between 2.6 and 5 nm. Via the attachment of the probe molecules to the inner surface of porous glasses filled with 3-methylpentane, the interfacial layer is measured selectively for different surface curvatures and shows an increase of the relaxation time by more than three orders of magnitude over that of the bulk liquid. This frustration is most pronounced at the pore boundary and decreases gradually across the first few nanometers distance away from the interface. Nanoconfinement realized by glass-forming microemulsions with the confining material being more fluid than the intramicellar droplets reverse the situation from frustrated dynamics in 'hard' confinement to accelerated relaxation behavior in the case of 'soft' boundaries. Without changing the size of the geometrical restriction of propylene glycol, 'hard' versus 'soft' boundary conditions changes the glass transition shift  $\Delta T_g$  from + 6 K to - 7 K. The findings can be rationalized on the basis of certain interfacial dynamics which differ from bulk behavior, with the penetration of this effect into the liquid being governed by the length scale of cooperativity. This picture explains both the more dispersed relaxation times in confinement and the dependence of the average relaxation time on pore size.

125. *Dynamics of Glassy and Liquid m-Toluidine Investigated by High-Resolution Dielectric Spectroscopy*

A. Mandanici, M. Cutroni, R. Richert, J. Chem. Phys. 122 (2005) 084508.1 - 084508.4

The glass-former *m*-toluidine displays the characteristic properties of a fragile supercooled liquid, which suggest the existence of a slow secondary relaxation process. In view of the recently realized importance of such a secondary relaxation feature, we have conducted a dielectric search for the secondary process in viscous and

glassy *m*-toluidine. Based on high resolution experiments on the distilled liquid, a secondary process can be identified which has the properties typical of a Johari-Goldstein  $\beta$ -relaxation. As a result, the previous hypothesis that the methyl group might be responsible for suppressing the secondary dynamics in glassy *m*-toluidine no longer holds.

124. *Dielectric Responses in Disordered Systems: From Molecules to Materials*  
(INVITED PAPER)

R. Richert, J. Non-Cryst. Solids 351 (2005) 2716 - 2722

With many current technologies, non-crystalline materials are required to perform on increasingly limited spatial scales approaching several 10 nm. The dynamics of molecules is one of the important aspects of disordered materials as it defines the glass transition. Dielectric relaxation techniques are capable of observing the dynamics in glass-forming systems across 18 orders of magnitude, but the typical experimental approaches address macroscopic effects in bulk samples. Here, we explore the various possibilities of applying dielectric and related techniques in order to gain insight into the dynamics on a nanoscopic or even molecular level.

123. *Dynamics of Glass-Forming Liquids. IX. Structural versus Dielectric Relaxation in Monohydroxy Alcohols*

L.-M. Wang, R. Richert, J. Chem. Phys. 121 (2004) 11170 - 11176  
and: Virtual Journal of Biological Physics Research 8 (2004) Issue 11

The prominent Debye-type but non-Arrhenius dielectric relaxation is a feature common to many monohydroxy alcohols in their liquid state. Although this exponential process is often considered to reflect the primary structural relaxation, only a faster, smaller, and non-exponential relaxation peak correlates with viscous flow and mechanical relaxation. We provide dielectric relaxation data for 2-methyl-1-butanol, 2-ethyl-1-hexanol, and 3,7-dimethyl-1-octanol across 10 decades in time. Based on these and previous results, we show that there exists a variety of dielectric to mechanical relaxation time ratios in the viscous regime, but a universal value of 100 for that ratio appears to evolve in the high temperature limit. The temperature dependence for both the relaxation time and strength of the Debye peak differs from the typical behavior of structural dynamics in terms of the  $\alpha$ -process. The implications of these findings for rationalizing the Debye type dielectric process of hydrogen-bonded liquids are discussed.

122. *Dynamics of Glass-Forming Liquids. VIII. Dielectric Signature of Probe Rotation and Bulk Dynamics in Branched Alkanes*

S. Shahriari, A. Mandanici, L.-M. Wang, R. Richert, J. Chem. Phys. 121 (2004) 8960 - 8967  
and: Virtual Journal of Biological Physics Research 8 (2004) Issue 9

We have measured the dielectric relaxation of several glass forming branched alkanes with very low dielectric loss in the frequency range 50 Hz to 20 kHz. The molecular liquids of this study are 3-methylpentane, 3-methylheptane, 4-methylheptane, 2,3-dimethylpentane, and 2,4,6-trimethylheptane. All liquids display asymmetric loss peaks typical of supercooled liquids and slow  $\beta$ -relaxations of similar amplitudes. As an unusual feature, deliberate doping with 2-ethyl-1-hexanol, 5-methyl-2-hexanol, 2-methyl-1-butanol, 1-propanol, or 2-methyl-THF at the 1 wt% level generates additional relaxation peaks at frequencies below those of the  $\alpha$ -relaxation. The relaxation times of these sub- $\alpha$ -peaks increase systematically with the size of the dopant molecules. Because these feature are spectrally separate from the bulk dynamics, the rotational behavior and effective dipole moments of the probes can be studied in detail. For the alcohol guest molecules, the large relative rotational time scales and small effective dipole moments are indicative of hydrogen bonded clusters instead of individual molecules.

121. *Dielectric Relaxation in Aqueous Solutions of Hydrazine and Hydrogen Peroxide: Water Structure Implications*

A. Minoguchi, R. Richert, C. A. Angell, J. Phys. Chem. B 108 (2004) 19825 - 19830

We report dielectric relaxation studies of aqueous solutions of two water-like molecules, hydrazine and hydrogen peroxide, in the neighborhood of their glass transition temperatures  $T_g$ . These solutions behave in a rather simple manner, reminiscent of the diols and diamines of which they are the limiting cases. Their relaxations near  $T_g$  are more nearly exponential than in most other cases and they show essentially no secondary relaxations. Supercooled hydrazine solutions are the more stable. At the composition 20 mol %  $N_2H_4$ , the liquid exhibits precise time-temperature-superposition (TTS) behavior. At higher  $N_2H_4$  contents a weak deviation from

TTS appears. The temperature dependence of the relaxation time follows the Vogel-Fulcher-Tammann (VFT) equation, and the strength parameters  $D$  is similar to that of glycerol, a liquid of intermediate fragility. The VFT divergence temperature  $T_0$  lies close to the Kauzmann temperature  $T_K$  determined earlier from calorimetric studies implying that the thermodynamic and kinetic measures of fragility are very similar.  $T_g$  values assessed from  $T(\tau = 100 \text{ s})$  agree well with observed calorimetric  $T_g$ 's. Extrapolation of the relaxation time behavior to pure water would imply a  $T_g$  for water of 135 - 140 K, however the dielectric behavior of amorphous solid water in the temperature range 130 - 160 K is completely different from that of the solutions showing no sign of the loss peak exhibited by all the solutions. Based on the solution behavior, water controversially must either remain glassy up until the temperature of crystallization, or be an almost ideally strong liquid above 136 K. Having shown elsewhere how this implies glassy character up to LDA crystallization, and a  $T_g$  above 160 K, we now examine the implications for water structure reorganization on dissolution of solutes, certain glycols excepted. It appears that the water in these solutions behaves like ice III rather than ice I.

120. *Dielectric Studies Deny Existence of Ultraviscous Fragile Water*

A. Minoguchi, R. Richert, C. A. Angell, Phys. Rev. Lett. 93 (2004) 215703.1 - 215703.4

The glass transition, a relaxation phenomenon, sets the low temperature limit to the liquid state. Glassy water that forms only under extreme quenching conditions is unstable against crystallization. Opinions differ on whether the glass transition can be observed at all. Here we measure the dielectric  $\tan\delta$  for easily glassforming, waterlike aqueous solutions,  $\text{H}_2\text{O}-\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}-\text{N}_2\text{H}_4$ , to characterize the behavior of such systems during passage through their glass transitions. All show unambiguous  $T_g$  values of 136 - 140 K, the value generally assigned to pure water. However the behavior of  $\epsilon''/\epsilon'$  is quite different from that in amorphous water in the same temperature range. Our findings eliminate "ultraviscous fragile liquid" as a possible description of water between 136K and crystallization, but leave "ultraviscous strong liquid" a possibility to be considered.

119. *Exponential Probe Rotation in Glass-Forming Liquids*

L.-M. Wang, R. Richert, J. Chem. Phys. 120 (2004) 11082 - 11089  
and: Virtual Journal of Ultrafast Science 3 (2004) Issue 6

Using time resolved optical depolarization, we have studied the rotational behavior of molecular probes in supercooled liquids near the glass transition temperature  $T_g$ . Simultaneously, the dynamics of the liquid immediately surrounding these rigid probes is measured by triplet state solvation experiments. This direct comparison of solute and solvent dynamics is particularly suited for assessing the origin of exponential orientational correlation functions of probe molecules embedded in liquids which exhibit highly non-exponential structural relaxation. Polarization angle dependent Stokes shift correlation functions demonstrate that probe rotation time and solvent response time are locally correlated quantities in the case of smaller probe molecules. Varying the size of both guest and host molecules shows that the size ratio determines the rotational behavior of the probes. The results are indicative of time averaging being at the origin of exponential rotation of probes whose rotational time constant is slower than solvent relaxation by a factor of 20 or more.

118. *Binary Glass-Forming Materials: Mixtures of Sorbitol and Glycerol*

K. Duvvuri, R. Richert, J. Phys. Chem. B 108 (2004) 10451 - 10456

The dynamics of sorbitol/glycerol mixture across the entire composition range has been characterized by dielectric relaxation measurements for frequencies between 10 mHz and 10 MHz. We explore the gradual change in the glass transition temperature ( $T_g$ ), fragility ( $m$ ), non-exponentiality ( $\beta_{\text{KWW}}$ ), and occurrence of a secondary Johari-Goldstein-type relaxation as a function of the mole fraction. Regarding the crystallization tendency at room temperature and the freezing of molecular motion below  $T_g$ , these mixtures differ qualitatively from aqueous solutions of sugars or other polyols.

117. *Slow Dynamics and the Glass Transition in Confining Systems*

(INVITED PAPER)

L.-M. Wang, F. He, R. Richert, Mater. Res. Soc. Symp. Proc. 790 (2004) P8.6.1 - P8.6.12

The slow dynamics associated with the structural relaxation of glass forming materials near the glass transition is very sensitive to the effects of small confining geometries. Based upon the experimental results of triplet state solvation dynamics, we explore the extent to which confinement effects can be rationalized solely in terms of interfacial dynamics which are modified relative to the bulk situation. The importance of the interfacial conditions is emphasized by observing the changes due to the surface chemistry, by comparing relaxation times

at and further away from the surface, and by studying the effects of 'soft' versus 'hard' confining materials. While 'hard' confinement by porous solids is observed to result in slower dynamics and an increased glass transition temperature  $T_g$  for propylene glycol, our 4.6 nm nanodroplets suspended in a more fluid environment display faster structural relaxation, equivalent to a reduction of  $T_g$  as observed in free standing polymer films.

116. *Intramicellar Glass Transition and Liquid Dynamics in Soft Confinement*

L.-M. Wang, F. He, R. Richert, Phys. Rev. Lett. 92 (2004) 095701.1 - 095701.4

and: Virtual Journal of Nanoscale Science & Technology 9 (2004) Issue 10

We explore the dynamics of viscous propylene glycol (PG) near its glass transition for the case of soft spatial confinement. The supercooled liquid is geometrically restricted by the reverse micelles of a glass-forming PG/AOT/decalin microemulsion, with the intramicellar dynamics being probed by triplet state solvation dynamics. While hard confinement by porous solids is known to result in slower dynamics and an increased glass transition temperature  $T_g$  of PG, the nano-droplets suspended in a more fluid environment display faster structural relaxation, equivalent to a reduction of  $T_g$  as observed in free standing polymer films.

115. *Dielectric Hole Burning: Signature of Dielectric and Thermal Relaxation Time Heterogeneity*

K.R. Jeffrey, R. Richert, K. Duvvuri, J. Chem. Phys. 119 (2003) 6150 - 6156

We have calculated the effects of dielectric hole burning on the basis of the frequency dependent dielectric relaxation  $\epsilon(\omega)$  and specific heat  $c_p(\omega)$  of glycerol and assuming heterogeneous dynamics where the dielectric and thermal relaxation times are correlated quantities. The heat generated in the sample is determined from the time dependent electric field and polarization, i.e., without involving steady-state approximations. The calculations mimic the protocol of recent hole-burning experiments on glycerol [K. Duvvuri and R. Richert, J. Chem. Phys. **118**, 1356 (2003)], including the high-field burn-process, the phase-cycle employed to eliminate the linear response to the high field, the detection in terms of the electric modulus  $M(t)$ , and the signal normalization. Without using any fit parameters, this model is capable of quantitatively reproducing the amplitudes, shapes, and peak positions of observed dielectric holes, together with their dependence on the burn frequency and the waiting time between the pump and probe processes. Therefore, frequency selective local heating of the modes of motion associated with the structural relaxation resulting from the dielectric loss fully accounts for the dielectric hole burning effects.

114. *Solvation Dynamics in the Plastic Crystal and Supercooled Liquid State of Ethanol*

R. Richert, J. Phys.: Condens. Matter 15 (2003) 5429 - 5438

The dynamics of ethanol in its plastic crystalline and supercooled liquid state has been measured using triplet state solvation dynamics techniques. This study focuses on temperatures near the respective glass transitions  $T_g$  of the two distinct phases, where the structural relaxation times are between 1 ms and 10 s. In the plastic crystal, the correlation times of the Stokes shift dynamics match the longitudinal time constants of the system as derived from dielectric relaxation data. Additionally, a maximum of the time resolved optical linewidths is indicative of heterogeneous dynamics in the plastic crystal. The supercooled liquid state is obtained after quenching the liquid from room temperature to below  $T_g$  and displays relaxation times that are a factor of 100 faster compared with the plastic crystal at the same temperature. The results do not reveal different translational contributions to solvation for the two phases.

113. *Solvation Dynamics of Molecular Glass-Forming Liquids in Confinement*

(INVITED PAPER)

R. Richert, M. Yang, J. Phys.: Condens. Matter 15 (2003) S1041 - S1050

Triplet state solvation dynamics experiments on geometrically confined glass-forming liquids are performed in order to study the effects of confinement on length scales of several nanometers. Variations of the surface chemistry of porous glasses and the spatially selective observation of the interfacial liquid layer indicate that the surface interactions determine the difference between the dynamics of the bulk and confined situation. For 3-methylpentane in pores of 7.5 nm diameter, the time scale of interfacial dynamics is slowed down by three orders of magnitude, while structural relaxation remains bulk like already a few nanometers away from the silica surface. The time-resolved optical linewidths indicate dynamical heterogeneity in confined liquids, but the signature differs from the bulk case.

112. *Dielectric Hole Burning in the High Frequency Wing of Supercooled Glycerol*  
K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356 -1363

We have performed dielectric hole burning experiments on supercooled glycerol at frequencies up to 5 decades above the peak frequency of the dielectric loss. While most observations of heterogeneous dynamics refer to the slower than average relaxation times, this study confirms the existence of independent relaxation time scales across the high frequency wing of the relaxation time distribution. In this short time regime, the persistence time of the spectrally selective modifications is solely a matter of the burn frequency and no longer determined by the structural relaxation time. For a fixed value of the burn field, the amplitudes of the relaxation pattern changes measured along the  $\log t$  scale (horizontal holes) are independent of the burn frequency  $\omega_b$  and dielectric loss  $\epsilon''(\omega_b)$ . This latter feature is observed in a range of burn frequencies which exceed the loss peak frequency by a factor of 10 to  $3 \times 10^5$ , where  $\epsilon''(\omega_b)$  varies between 16 and 0.17.

111. *Dynamics of Glass-Forming Liquids. VII. Dielectric Relaxation of Supercooled Tris-naphthylbenzene, Squalane, and Decahydroisoquinoline*  
R. Richert, K. Duvvuri, L.-T. Duong, J. Chem. Phys. 118 (2003) 1828 - 1836

We have measured the dielectric relaxation of several molecular organic supercooled liquids,  $\alpha\beta$ -tris-naphthylbenzene ( $C_{36}H_{24}$  and  $C_{36}H_{10}D_{14}$ ), squalane, and decahydroisoquinoline. The dynamics is studied in the frequency range  $10^{-2}$  Hz to  $10^7$  Hz, equivalent to temperatures between  $T_g$  and approximately  $1.2 \times T_g$ . For the very low dielectric loss materials, a resolution of  $\tan \delta \approx 3 \times 10^{-5}$  is required in order to observe the details of the relaxation behavior. Characteristic quantities like fragility, relaxation time dispersion, time-temperature superposition, and the slow Johari-Goldstein type  $\beta$ -relaxation are among the properties discussed.

110. *Dielectric Hole Burning in an Electrical Circuit Analog of a Dynamically Heterogeneous System*  
R. Richert, Physica A 322 (2003) 143 - 154

The dielectric properties of a dynamically heterogeneous material are represented by an  $R$ - $C$  network in order to study the effects of spectrally selective Joule heating for the situation encountered in (non-resonant) dielectric hole burning (DHB). The energy irreversibly transferred to the system is calculated for a finite number of high electric field sine waves, corresponding to the 'burn' cycle preceding the polarization measurement in a DHB experiment. As a result of the residual polarization, heating continues after the externally applied voltage is set to zero. Modelling temperature dependent relaxation times by a common negative temperature coefficient for the resistive elements is the only non-linearity of the electrical circuit analog required to obtain the typical features observed in DHB experiments.

109. *Spatially Resolved Dynamics of Supercooled Liquids Confined in Porous Glasses: Importance of the Liquid-Glass Interface*  
(INVITED PAPER)

R. Richert, M. Yang, in "Dynamics and Friction in Submicrometer Confining Systems", Y. Braiman, J. M. Drake, F. Family, J. Klafter (Eds.), ACS Symposium Series Vol. 882, ACS Books, Washington DC, 2004, p.181 - 192

The dynamics of liquids is notorious to be affected by geometrical confinement, provided that sufficiently small length scales of order several nanometers are involved. Regarding the viscous regime of glass-forming materials, the dynamics in confinement are often characterized by a glass transition shift relative to the bulk material. We discuss several problems associated with this approach and show evidence for the important role of interfacial dynamics. In particular, we assess the spatial dependence of relaxation times within a pore of 7.5 nm diameter as measured by site selective triplet state solvation dynamics experiments.

108. *Surface Induced Glass Transition in a Confined Molecular Liquid*  
(LETTER)

R. Richert, M. Yang, J. Phys. Chem. B 107 (2003) 895 - 898

The structural relaxation of a glass-forming simple liquid, 3-methylpentane, is studied by triplet state solvation dynamics as a function of the distance from the surface in porous silica. By bonding the optical probes to the pore surface, we observe interfacial dynamics which are three orders of magnitude slower compared with the

bulk, equivalent to a surface induced glass transition. Consistent with length scales of cooperativity, these effects disappear for distances from the surface exceeding a few nanometers.

107. *Dynamics of Glass-Forming Liquids. VI. Dielectric Relaxation Study of Neat Decahydro-Naphthalene*

K. Duuvvuri, R. Richert, J. Chem. Phys. 117 (2002) 4414 - 4418

We have measured the dielectric relaxation of neat *cis/trans*-decahydro-naphthalene (decalin) in its supercooled regime as a function of temperature. The fragility of this non-aromatic molecular glass-former is extremely high,  $m = 147$ , and the distribution of relaxation times in terms of the stretching exponent is accordingly wide,  $\beta \approx 0.33$ . Regarding molecular organic liquids, such high fragilities have been observed before only for aromatic systems, e.g., toluene and triphenyl-phosphite. It turns out that the structural relaxation of neat decalin differs significantly from that of the 17.2 mol % chlorobenzene doped counterpart reported earlier.

106. *Heterogeneous Dynamics in Liquids: Fluctuations in Space and Time (INVITED TOPICAL REVIEW)*

R. Richert, J. Phys.: Condens. Matter 14 (2002) R703 - R738

The disordered nature of glass forming melts gives rise to non-Arrhenius and non-exponential behaviour of their dynamics. With respect to the microscopic details involved in the structural relaxation, these materials have remained an unsolved puzzle for over a century. The observation of spatial heterogeneity regarding the dynamics provides an important step towards understanding the relation between the macroscopic properties of soft condensed matter and the molecular mechanisms involved. On the other hand, dynamic heterogeneity is the source of several new questions: What is the length scale and persistence time associated with such clusters of relaxation time? What is the signature of heterogeneity at high temperatures and in the glassy state? How do these features depend on the particular material and on the correlation function used for probing these heterogeneities? This work attempts to review the various approaches to heterogeneous dynamics, the generally accepted results, as well as some controversial issues. Undoubtedly, heterogeneity has provoked a number of novel experimental techniques targeted at studying glass-forming liquids at the molecular level. It shall be emphasized that the picture of heterogeneity is a requirement for rationalizing an increasing number of experimental observations rather than just an alternative model for the dynamics of molecules.

105. *Solvation Dynamics and Probe Rotation in Glass-Forming Liquids (INVITED PAPER)*

M. Yang, R. Richert, Chem. Phys. 284 (2002) 103 - 114

We have measured optical depolarization and solvation dynamics using triplet state molecular probes in various glass-forming organic liquids of low molecular weight. Optical depolarization yields the single particle rotational correlation function  $r(t)$  of the guest molecules, while mechanical solvation dynamics reflect the time resolved shear modulus  $G(t)$  specifically of those host molecules which surround the probe. Using the ratio  $m_{\text{guest}}/m_{\text{host}}$  of molecular weights as an indicator for the relative sizes, it is observed that large  $m_{\text{guest}}/m_{\text{host}}$  values lead to much slower and more exponential probe rotation compared with the structural relaxation of the environment. As  $m_{\text{guest}}$  approaches  $m_{\text{host}}$ , the time dependencies of  $r(t)$  and  $G(t)$  become very similar. It appears that a larger and relatively immobile guest molecule has little effect on the otherwise cooperative dynamics of the surrounding solvent.

104. *Heterogeneous Solvent Dynamics and Time-Resolved Optical Linewidths (INVITED PAPER)*

R. Richert, J. Non-Cryst. Solids 307-310 (2002) 50 - 56

The time resolved inhomogeneous optical linewidth observed in solvation dynamics experiments is sensitive to the nature of the solvent dynamics, homogeneous or heterogeneous. Linewidth data are assessed with regard to intrinsic non-exponentiality, the length scale of heterogeneity, and the time scale of rate exchange. For the glass-forming solvent under study, heterogeneity is found for average relaxation times in the range 54 s ... 3 ms and in the regime of nanosecond dynamics.

103. *The Modulus of Dielectric and Conductive Materials and its Modification by High Electric Fields*

(INVITED PAPER)

R. Richert, J. Non-Cryst. Solids 305 (2002) 29 - 39

An alternative to measuring dielectric polarization or conductivity in the time domain under the usual constant field conditions is to record the voltage at constant charge. In this case the voltage is proportional to the dielectric modulus  $M(t)$ , defined in the frequency domain via  $M^*(\omega) = 1/\varepsilon^*(\omega)$ . The method allows to measure dynamics at extremely long times, while electrode polarization (EP) effects remain small in  $M(t)$  signals. Dielectric hole burning on vitreous ionic conductors and the elimination of EP can be achieved by combining the modulus technique with a preceding high sinusoidal electric field.

102. *Observation of Heterogeneity in the Nanosecond Dynamics of a Liquid*

M. Yang, R. Richert, J. Chem. Phys. 115 (2001) 2676 - 2680

We have measured the time-integrated fluorescence of coumarin 153 in a glass-forming solvent in order to assess the inhomogeneous linewidth as a function of temperature. A maximum of this width is observed at a temperature where the structural relaxation time of the solvent matches the excited state lifetime of the dye of a few nanoseconds. This feature can be explained only on the basis of a relaxation time dispersion which originates from a spatial distribution of solvent response times. Therefore, liquid dynamics in the regime of nanosecond time scales are heterogeneous with respect to the structural relaxation time.

101. *Spectral Diffusion in Liquids with Fluctuating Solvent Responses: Dynamical Heterogeneity and Rate Exchange*

R. Richert, J. Chem. Phys. 115 (2001) 1429 - 1434

A recent theory for the time dependence of inhomogeneous line shapes is extended to account for fluctuations of the solvent response times  $\tau$  in both space (heterogeneity) and time (rate exchange). Different simulation techniques are outlined for solving the Ornstein-Uhlenbeck type spectral diffusion in the situation expected for supercooled liquids. For intrinsically exponential solvent dynamics, slow rate exchange (or static heterogeneity) has to be assumed in order to reproduce measurements of the Stokes shift correlation function  $C(t)$  and inhomogeneous linewidth  $\alpha(t)$  simultaneously.

100. *Theory of Time Dependent Optical Linewidths in Supercooled Liquids*

R. Richert, J. Chem. Phys. 114 (2001) 7471 - 7476

The time resolved inhomogeneous broadened lineshape is derived from analytical theory for a liquid which exhibits spatial heterogeneity regarding the solvent response times. The results demonstrate that it is the heterogeneous nature of supercooled liquids which gives rise to asymmetric lines and to a maximum in the linewidth as a function of time while the average emission energy experiences a red-shift. The time dependence of the calculated and of the observed linewidths agree quantitatively, but differ significantly from the behavior expected for systems with homogeneous dynamics.

99. *Comment on "Hole-Burning Experiments within Glassy Models with Infinite Range Interactions"*

R.V. Chamberlin, R. Richert, Phys. Rev. Lett. 87 (2001) 129601.1 - 129601.1

In a recent Letter, Cugliandolo and Iguain (CI) have investigated an infinite-range model in the context of nonresonant spectral hole burning (NSHB). CI claim that they can reproduce the results of NSHB experiments by a model with *no spatial structure*. CI have failed to prove spectral selectivity, such that it remains unclear whether their  $\Delta\Phi$  results are true spectral holes. Until spectral selectivity has been established in the model, we do not consider the result of hole-burning experiments to be reproduced. In any case, the infinite-range model of CI exhibits behavior that is inconsistent with several features in the NSHB from real materials.

98. *Spectral Selectivity in the Slow  $\beta$ -Relaxation of a Molecular Glass*

R. Richert, Europhys. Lett. 54 (2001) 767 - 773

The time resolved electric field relaxation in glassy D-sorbitol is measured by dielectric hole-burning, *i.e.* with and without a preceding high electric sinusoidal burn field. The question is whether the burn induced

modifications of the response are frequency selective (dielectric 'holes') and thus indicative of heterogeneous dynamics, where slow and fast responses coexist in the material. For burn fields between 250 and 440 kV/cm such holes in the responses are observed, whose positions shift linearly with the inverse burn frequency. Recovery time measurements indicate that these modifications of the Johari-Goldstein process in glassy D-sorbitol are long lived.

97. *Scaling versus Vogel-Fulcher Type Structural Relaxation in Deeply Supercooled Materials*

R. Richert, *Physica A* 287 (2000) 26 - 36

A recent scaling law analysis using  $\tau \propto (T-T_c)^{-\gamma}$  with  $T_c < T_g$  has concluded that the resulting fits are superior over the Vogel-Fulcher-Tammann temperature dependence as regards the structural relaxation time of supercooled liquids [R.H. Colby, *Phys. Rev. E* 61 (2000) 1783]. This issue is investigated based upon dielectric retardation data of poly(vinylacetate) which cover 16 decades in time, from 3 ns to over 1 year. In contrast to Colby's conclusions, the observed temperature dependence rules out a temperature invariant exponent  $\gamma$  as well as a clear cut critical temperature  $T_c$ .

96. *Triplet State Solvation Dynamics: Basics and Applications*

(*FOCUS ARTICLE*)

R. Richert, *J. Chem. Phys.* 113 (2000) 8404 - 8429

Applying solvation dynamics experiments to viscous liquids or glassy materials near their glass transition involves long lived triplet probes, whose time dependent phosphorescence signals depend upon the local dipolar orientational dynamics, mechanical responses, and polarities. The current understanding of experimental results regarding steady state and time dependent optical lineshapes and positions is reviewed with emphasis on the relation to the macroscopic dielectric properties. Several applications are discussed in detail, where advantage is taken of the spatially local instead of ensemble averaging character of this technique. These examples include studies of dynamical heterogeneity, rotational solute/solvent coupling, secondary relaxations in the glassy state, as well as confinement and interfacial effects.

95. *Local Dielectric Relaxation by Solvation Dynamics*

R. Richert, in "Broadband Dielectric Spectroscopy", F. Kremer, A. Schönhalz (Eds.), Springer, Berlin, 2002, p. 571 - 595

This chapter is concerned with a method of measuring dielectric relaxation phenomena locally, in order to compliment the information regarding the dynamics of molecules inferred from the various macroscopic dielectric techniques outlined in previous chapters. In a simplified picture, these solvation dynamics experiments measure the dielectric relaxation of a liquid as a response to a step in the dielectric displacement of a molecule rather than the macroscopic effects following a field step applied to a capacitor. The time dependent dielectric polarization in the immediate vicinity of a probe molecule gives rise to a Stokes-shift of the luminescence. This tendency of the emission wavenumbers  $\nu$  to shift towards the red is monitored by recording the emission spectra  $I(\nu)$  as a function of time using straightforward techniques of optical spectroscopy. The key quantity for assessing the dynamics of the liquid is the time dependent average emission energy  $\langle \nu(t) \rangle$ .

94. *Relaxations in Confinement as Probed by Solvation Dynamics*

(*INVITED PAPER*)

H. Wendt, R. Richert, *J. Phys. IV France* 10 (2000) Pr7-67 - Pr7-72

Solvation dynamics data of the probe quinoxaline in the glass-forming liquid 2-methyltetrahydrofuran (MTHF) is employed to study the orientational dynamics of a liquid which is geometrically confined by porous glasses. In order to discriminate pure confinement from interfacial effects, we compare in detail the relaxation results obtained in pores with native and silanized glass surfaces with those for the bulk liquid. For the present case of highly viscous MTHF near  $T_g$ , the molecular orientation in silanized pores is almost identical to that observed in the bulk liquid. This indicates that confinement effects remain small and that the interfacial interaction between liquid molecules and the pore wall can dominate and are strongly affected by the surface chemistry. We also demonstrate how solvation dynamics techniques can be used to measure the dynamics selectively at the interface.

93. *Heterogeneous Relaxation Patterns in Supercooled Liquids Studied by Solvation Dynamics*  
H. Wendt, R. Richert, Phys. Rev. E 61 (2000) 1722 - 1728

We have measured the solvation dynamics of a dipolar supercooled liquid near its glass transition in a temperature range in which the average structural relaxation time varies more than four orders of magnitude. The analysis of the time dependent average emission energy and the inhomogeneous linewidth of the  $S_0 \leftarrow T_1$  (0-0) transition reveals that the orientation correlation decay pattern intrinsic in each relaxing unit is associated with a stretching exponent  $\beta_{\text{intr}} = 1.00 \pm 0.08$  in the entire range  $T_g \leq T \leq T_g + 6$  K. Our analysis also allows to detect fluctuations in terms of the resulting apparent homogeneity within the long time tail of the decay. Even at times significantly exceeding the average structural relaxation time, no sign of a transition towards purely exponential or otherwise homogeneous behavior could be observed. This implies that even at  $t \approx 50 \times \langle \tau \rangle_{\text{KWW}}$  the individual time constants remain correlated to their initial values at  $t = 0$ .

92. *Dynamic Thermal Expansivity near the Glass Transition*  
(LETTER)

C. Bauer, R. Richert, R. Böhmer, T. Christensen, J. Non-Cryst. Solids 262 (2000) 276 - 281

Dielectric techniques were used to investigate the thermal expansivity of polystyrene films. Capacitive scanning dilatometry employs temperature ramping in order to monitor the non-linear structural relaxation in the glass transformation range and to quantify liquid fragility. In the linear response regime, the complex thermal expansivity is obtained as a function of the temperature cycling frequency and is observed to reflect the structural relaxation.

91. *Heterogeneous and Homogeneous Diffusivity in an Ion-Conducting Glass*

R. Richert, R. Böhmer, Phys. Rev. Lett. 83 (1999) 4337 - 4340

The nature of ion diffusivity in the vitreous conductor  $2 \text{Ca}(\text{NO}_3)_2 \cdot 3 \text{KNO}_3$  (CKN) was studied by nonresonant dielectric hole burning. Spectral holes in the electric field relaxation are probed subsequent to a high electric sinusoidal burn field. For sufficiently high pump frequencies we are able to induce spectrally selective modifications in the relaxation of the electric modulus, indicating that ionic diffusivity is a spatially varying quantity in glassy CKN. Homogeneous behavior occurs in the regime of low pump frequencies, in which the resistivity approaches its steady state value. Thus, longer ranged ionic motions lead to a spatial averaging over the heterogeneity of local ion diffusivities.

90. *Dielectric Beta-Relaxations in the Glassy State of Salol?*

H. Wagner, R. Richert, J. Chem. Phys. 110 (1999) 11660 - 11663

The recently observed possibility to suppress the  $\beta$ -relaxation intensity of *o*-terphenyl by annealing at temperatures below the glass transition guided us to ask, whether the absence of a dielectric  $\beta$ -process in many glass-forming materials, e.g. salol, is a matter of the slow cooling rates usually employed to enter the glassy state. In order to assess this issue, we have quenched liquid salol to well below  $T_g$  at a rate of  $dT/dt = -490$  K/min. Opposed to the case of cooling rates around  $-5$  K/min or slower, this highly quenched sample displays a symmetric dielectric relaxation peak near  $f = 10^3$  Hz with an appreciable relaxation strength,  $\Delta\epsilon = 6 \times 10^{-3}$ . This novel feature of salol disappears irreversibly after a temperature excursion towards the glass transition at  $T_g = 220$  K.

89. *Orientation and Dynamics of Chainlike Dipole Arrays: Donor-Acceptor-Substituted Oligophenylenevinylenes in a Polymer Matrix*

C. Former, H. Wagner, R. Richert, D. Neher, K. Müllen, Macromol. 32 (1999) 8551 - 8559

We have investigated the orientational behaviour of a series of novel oligophenylenevinylenes which carry a sequence of hyperpolarizable and dipolar donor-acceptor (DA) pairs, designed to allow for a free rotation of the DA orientation in a plane perpendicular to the long molecular axis. The studies include both the measurement of effective dipole moments which are relevant for the degree of polar ordering required for second-harmonic generation, as well as the assessment of the time scales involved in the orientational motion of the effective dipole moment. The comparison between calculated dipole moments and those measured for different oligomers in toluene solution and in a polystyrene matrix confirm that a DA-pair separation of  $\approx 10$  Å along the oligomer leads to a high chromophore concentration in the sample, yet without the unfavourable effect of aggregation or antiparallel alignment of neighbouring dipole pairs. Both, the bulkiness of the oligomer molecules and the

electrostatic coupling of adjacent dipoles, give rise to an improved stability of the field-induced chromophore alignment. In contrast to the monomeric stilbene-like model compounds, the time scale of oligomer reorientation parallels the structural relaxation time of the polymeric host material.

88. *Capacitive Scanning Dilatometry and Frequency-Dependent Thermal Expansion of Polymer Films*

C. Bauer, R. Böhmer, S. Moreno-Flores, R. Richert, H. Sillescu, D. Neher, Phys. Rev. E 61 (2000) 1755 - 1764

The dilatometric properties of polymer films near and above their glass-transition temperatures were explored using capacitive high-frequency detection in temperature ramping as well as in harmonic temperature cycling experiments. The broad applicability of capacitive scanning dilatometry (CSD) is demonstrated by the investigation of macromolecular systems of vastly different polarity such as polystyrene, polybutadiene and polyvinylacetate. From temperature cycling experiments the real and imaginary parts of the frequency dependent thermal expansion coefficient are determined in the sub-Hz regime.

87. *Dielectric and Mechanical Relaxation of Glass-Forming Liquids in Nanopores (INVITED PAPER)*

H. Wendt, R. Richert, Mater. Res. Soc. Symp. Proc. 543 (1999) 15 - 26

We have measured the time resolved phosphorescence of different probe molecules in glass-forming solvents under the condition of geometrical confinement in porous glasses. This solvation dynamics technique probes the local dielectric relaxation in the case of a dipolar chromophore in polar liquids. In the absence of dipolar interactions, the observed Stokes shifts reflect the local density or mechanical responses. Therefore, both orientational and translational modes of molecular motions can be measured for liquids imbibed in porous silica glasses. The effect of confinement on the relaxations of supercooled liquids is strongly dependent on the surface chemistry and can be rationalized on the basis of the cooperativity concept. As in the bulk case, we find that the relaxations in nano-confined liquids display heterogeneous dynamics. The density relaxation turns out to be more sensitive to the thermal history relative to the orientational features of molecular motion. By selectively positioning the chromophores at the liquid / solid interface, we observe also that the structural relaxation of the liquid in the immediate vicinity of the glass surface is slowed down but not entirely blocked.

86. *Cooperativity and Heterogeneity of the Dynamics in Nano-Confined Liquids (INVITED PAPER)*

H. Wendt, R. Richert, J. Phys.: Condens. Matter 11 (1999) A199 - A206

We have measured the time resolved Stokes-shift of the probe molecule quinoxaline in glass-forming solvents of different polarities under the condition of geometrical confinement, for which this solvation dynamics technique is particularly suitable. While solvation probes the local dielectric relaxation in polar liquids, it is associated with the local mechanical responses in non-polar systems. The effect of porous glasses on the relaxations of supercooled liquids is strongly dependent on the surface chemistry and can be rationalized on the basis of the cooperativity concept. We also present evidence for the heterogeneous nature of relaxation dynamics in nano-confined liquids. In a further experiment, in which the chromophores are selectively positioned at the liquid/solid interface, we observe that the relaxation in the immediate vicinity of the glass surface can be qualitatively similar to the bulk behaviour.

85. *Equilibrium and Non-Equilibrium Type  $\beta$ -Relaxations: D-sorbitol versus o-terphenyl*

H. Wagner, R. Richert, J. Phys. Chem. B 103 (1999) 4071 - 4077

A previous observation, which indicated that the  $\beta$ -relaxation intensity of *o*-terphenyl is sensitive to the thermal history, is substantiated by dielectric relaxation experiments. Unlike the  $\beta$ -processes of other materials, only the quenched glassy state of *o*-terphenyl displays this secondary relaxation feature. The  $\beta$ -intensity is observed to decay gradually upon annealing and disappears altogether in the equilibrium liquid state at  $T > T_g$ . We compare the case of *o*-terphenyl with the concomitant signatures of D-sorbitol, which represents the more typical case of a glass-former which exhibits the slow  $\beta$ -process also in the liquid state including the  $\alpha$ - $\beta$ -merging scenario. We also present data of this  $\alpha$ - $\beta$ -merging for D-sorbitol confined to pores of 5 nm diameters, indicating that no longer ranged correlations are involved in the secondary process.

84. *Measurement and Analysis of Time-Domain Electric Field Relaxation: The Vitreous Ionic Conductor 0.4 Ca(NO<sub>3</sub>)<sub>2</sub> - 0.6 KNO<sub>3</sub>*

H. Wagner, R. Richert, J. Appl. Phys. 85 (1999) 1750 - 1755

We have measured the electric modulus  $M(t)$  of the ionic conductor 0.4 Ca(NO<sub>3</sub>)<sub>2</sub> - 0.6 KNO<sub>3</sub> (CKN) by recording the electric field relaxation  $E(t)$  under the constraints of a constant displacement  $D_0$ . The vitreous material CKN is studied in its glassy state for temperatures  $240 \text{ K} \leq T \leq 330 \text{ K}$  and for times  $7 \times 10^{-3} \text{ s} \leq t \leq 3 \times 10^5 \text{ s}$ . In this range the dc-conductivity varies from  $3 \times 10^{-11}$  to  $5 \times 10^{-17} \text{ S/cm}$  according to an Arrhenius behaviour. We show that the time dependent resistivity  $\rho(t)$ , instead of the conductivity  $\sigma(t)$ , is an appropriate quantity for assessing the time dependent and steady state effects of ionic diffusivity on the basis of experimental modulus data  $M(t)$  recorded in the time domain. Even substantial electrode polarization remains uncritical as regards this data analysis.

83. *Spatial Uniformity of the  $\beta$ -relaxation in D-sorbitol*

H. Wagner, R. Richert, J. Non-Cryst. Solids 242 (1998) 19 - 24

We compare the signatures of the slow  $\beta$ -relaxation of D-sorbitol as observed by two different techniques, macroscopic dielectric relaxation and solvation dynamics, over a wide range of temperatures. The latter technique senses the local dielectric relaxation in the immediate vicinity of a chromophore, which is present only at very low concentrations. The conformity of locally sensitized and macroscopically averaged results for the glassy state indicates that the secondary relaxation is a spatially uniform feature. If the  $\beta$ -process were confined to certain spatial domains, it should not be detectable by solvation probes.

82. *Purely Mechanical Solvation Dynamics in Supercooled Liquids: The  $S_0 \leftarrow T_1$  (0-0) Transition of Naphthalene*

H. Wendt, R. Richert, J. Phys. Chem. A 102 (1998) 5775 - 5781

We have measured the Stokes shift and its dynamics for the probe molecules naphthalene ( $\Delta\mu \approx 0$ ) and quinoxaline ( $\Delta\mu \approx 1.3 \text{ D}$ ) in *n*-propanol and other glass-forming solvents. The Stokes shift for naphthalene ( $\approx 63 \text{ cm}^{-1}$ ) turns out to be independent of the solvent polarity over a wide range of the static dielectric constants. Its time dependence is governed by the structural (or  $\alpha$ - or shear stress) relaxation time of *n*-propanol, without any signature of the strong dielectric relaxation. For this solvent, structural and dipolar contributions can be distinguished because the time scale for dipole reorientation is a factor of 25 slower than the  $\alpha$ -relaxation time. We conclude that the solvation of naphthalene reflects excitation-induced changes in the van der Waals interactions, which makes it an ideal probe for assessing shear stress or mechanical relaxations on microscopic spatial scales near  $T_g$ .

81. *Dynamic Heterogeneity, Spatially Distributed Stretched-Exponential Patterns, and Transient Dispersions in Solvation Dynamics*

R. Richert, M. Richert, Phys. Rev. E 58 (1998) 779 - 784

In the context of determining the extent of dynamical heterogeneity of relaxation processes, it has proven useful to represent the ensemble averaged autocorrelation function  $\phi(t)$  in the general form  $\phi(t) = \int g(\tau) \chi(t/\tau) d\tau$ , instead of focusing on the usual special case in which the basis functions  $\chi(t/\tau)$  are exponentials. In practice,  $\phi(t)$  is often fit by a stretched exponential,  $\phi(t) = \exp[-(t/\tau)^\beta]$ . Here, we analyse the properties of the probability density  $g(\tau)$  for the case in which  $\phi(t)$  is a superposition of stretched exponentials and is itself a stretched exponential, with stretching exponent greater than or equal to those of the basis functions,  $\chi(t/\tau)$ . Various degrees of non-exponentiality intrinsic in each basis function translate into different values for the time dependent variance,  $\sigma^2(t)$ , of the stochastic quantity  $\chi(t/\tau)$ , in which  $\tau$  is considered to be a spatially varying characteristic time scale. We state a simple but exact solution for  $\sigma^2(t)$  and assess its relation to experimental data on the inhomogeneous optical linewidth,  $\sigma_{\text{inh}}(t)$ , measured in the course of solvation processes in a supercooled liquid.

80. *Nature of the Non-exponential Primary Relaxation in Structural Glass-Formers Probed by Dynamically Selective Experiments*  
R. Böhmer, R.V. Chamberlin, G. Diezemann, B. Geil, A. Heuer, G. Hinze, S.C. Kuebler, R. Richert, B. Schiener, H. Sillescu, H.W. Spiess, U. Tracht, M. Wilhelm, J. Non-Cryst. Solids 235-237 (1998) 1 - 9

Several experimental methods feature the potential to distinguish between slow and fast contributions to the non-exponential, ensemble averaged primary response in glass-forming materials. Some of these techniques are based on the selection of subensembles using multi-dimensional nuclear magnetic resonance, optical deep bleaching, and nonresonant spectral hole burning. Others, like the time-dependent solvation spectroscopy, measure microscopic responses induced by local perturbations. Using several of these methods it could be demonstrated for various glass-forming materials that the non-exponential relaxation results from a superposition of dynamically distinguishable entities. The experimental observation that subensembles can be selected very efficiently indicates a large degree of heterogeneity. This observation implies that their intrinsic response is compatible with single exponential relaxation.

79. *Dynamics of Glass-Forming Liquids. V. On the Link between Molecular Dynamics and Configurational Entropy*  
R. Richert, C.A. Angell, J. Chem. Phys. 108 (1998) 9016 - 9026

We compare dielectric relaxation  $\tau(T)$  data of several low molecular weight glassforming liquids with the predictions of the Adam-Gibbs theory using experimental data for the configurational entropy  $S_c(T)$ . Combination of Adam-Gibbs and Vogel-Fulcher equations yields an expression for  $S_c(T)$  which can be compared with experimental data. Good agreement is found for a range of temperature near  $T_g < T < T_B$  which depends on the fragility of the liquid and on the presence of a  $\beta$ -relaxation. For fragile liquids,  $T_B$  coincides with a qualitative change in the temperature dependence of the relaxation time scale or viscosity, with the temperature  $T_B$ , where Johari-Goldstein type  $\beta$ -processes tend to merge into the  $\alpha$ -process, and with other crossover temperatures. For non-fragile liquids,  $T_B / T_g$  increases, and the deviations from the Adam-Gibbs equation weaken or disappear altogether. The significance of  $T_B$ , and of the  $S_c(T)$  temperature dependence implied by the VFT fitting, are discussed in terms of the landscape paradigm.

78. *Molecular Dynamics Analysed in terms of Continuous Measures of Dynamic Heterogeneity (INVITED PAPER)*  
R. Richert, J. Non-Cryst. Solids 235-237 (1998) 41 - 47

We analyse the relaxation data of a supercooled liquid in terms of  $\phi(t) = \int g(\ln \tau) \varphi(t/\tau) d\ln \tau$  using a Kohlrausch, Williams, and Waats (KWW) type integral kernel  $\varphi(t/\tau)$  with exponent  $\beta_{\text{hom}}$ , which serves for varying the degree of homogeneity inherent in the response of each relaxor, while the concomitant  $g(\ln \tau)$  outlines the extent of dynamic heterogeneity. The simulated time dependence of solvation free energies as a function of  $\beta_{\text{hom}}$  is compared with experimental solvation dynamics data,  $\nu(t)$  and  $\sigma_{\text{inh}}(t)$  derived from time resolved inhomogeneously broadened optical lineshapes. The experimental findings indicate  $0.8 \leq \beta_{\text{hom}} \leq 1$ , which states that the dynamical nature of the relaxation process is dominated by the spatial variation of relaxation times, while the possible extent of homogeneous dispersion remains small.

77. *Dynamics of Glass-Forming Liquids. IV. True Activated Behavior above 2GHz in the Dielectric  $\alpha$ -Relaxation of Organic Liquids*  
C. Hansen, F. Stickel, R. Richert, E.W. Fischer, J. Chem. Phys. 108 (1998) 6408 - 6415

We have measured the dielectric relaxation of butylbenzene and of the glass-former propylbenzene in the frequency range  $10^{-2}$  Hz to  $2 \times 10^{10}$  Hz in order to characterize the variation of relaxation times with temperature for these low loss liquids. Additionally, salol has been remeasured above 1 GHz with improved resolution. Using the sensitive data representation  $[-d\log_{10}(f_{\text{max}}/\text{Hz})/d(1/T)]^{-1/2}$  versus  $1/T$  we find demarcation temperatures  $T_A$ , at which the temperature dependence changes from a Vogel-Fulcher type law within the limits  $T_B \leq T \leq T_A$  to Arrhenius behaviour for  $T > T_A$ , corresponding to a position of the loss peak  $f_{\text{max}} > 2$  GHz. The activation energies derived from dielectric relaxation data for  $T > T_A$  are associated with the energy of vaporization,  $E^{\ddagger} \propto \Delta E_{\text{vap}}$ . A comparison of dielectric relaxation times  $\tau_D$  to viscosity data in this wide range of temperatures suggests the relation  $\tau_D \propto \eta/T$  rather than  $\tau_D \propto \eta$ .

76. *Dielectric Relaxation under Constant Charge Conditions*  
R. Richert, H. Wagner, in "Recent Research Developments in Macromolecules Research",  
S.G. Pandalai (Ed.), Research Signpost, Trivandrum, 1997  
Recent Res. Devel. in Macromol. Res. 2 (1997) 1 - 10

The common technique of dielectric  $\epsilon^*(\omega)$  or  $\alpha(t)$  measurements involves the application of a polarization invariant electric field to a capacitor filled with the material under study and the detection of the temporal evolution of the resulting current or charge flow. The counterpart condition of applying a given dielectric displacement and monitoring the electric field relates to the dielectric modulus  $M(t)$  with  $M^*(\omega) = 1/\epsilon^*(\omega)$ . Isothermal and thermally stimulated experimental techniques for directly accessing the relaxation  $M(t)$  are outlined and discussed as regards their relation to the dielectric retardation  $\alpha(t)$  and to dc-conductivity  $\sigma_{dc}$ . We also address several microscopic processes which are inherently linked to the dielectric modulus through their common feature of displaying a redistribution of charge.

75. *The Dielectric Modulus: Relaxation versus Retardation*  
R. Richert, H. Wagner, Solid State Ionics 105 (1998) 167 - 173

Experiments which access the quantity  $\epsilon^*(\omega)$  are usually termed dielectric relaxation methods, although  $\epsilon^*(\omega)$  and  $\alpha(t)$  actually refer to dielectric retardation. The true dielectric relaxation, the modulus  $M(t)$ , corresponds to the decay of the electric field under the conditions of a constant dielectric displacement. We have measured the polarization in terms of a real dielectric *relaxation* technique by studying the decay of the electric field  $E(t) \propto M(t)$  for times  $10^{-3} \text{ s} \leq t \leq 10^6 \text{ s}$  under constant charge conditions. This conceptually straightforward method bears the advantage of the ability to measure extremely large retardation times. Using also the equivalent thermally stimulated technique we investigate the equilibrium and non-equilibrium dynamic response of amorphous condensed matter well below its caloric glass-transition.

74. *Dipolar Dynamics of Low Molecular Weight Organic Materials in the Glassy State*  
C. Hansen, R. Richert, J. Phys.: Condens. Matter 9 (1997) 9661 - 9671

We have measured the dielectric relaxation of several low molecular weight glass-forming materials for temperatures ranging from 25 K to  $T \approx T_g$  and for values of the loss-tangent down to  $\tan\delta \approx 10^{-7}$ . For the materials under study (salol, glycerol, *N*-methyl- $\epsilon$ -caprolactam, 2-methyltetrahydrofuran, 3-methylpentane, and *o*-terphenyl) a  $\beta$ -relaxation appearing in quenched samples can be suppressed effectively by annealing at  $T < T_g$ , thereby facilitating the study of the dipole dynamics in the absence of the secondary process. As a general behaviour of the remaining dielectric losses at  $f = 1 \text{ kHz}$  we find a variation of  $\log_{10}(\epsilon'') = a + b T$  ( $b \approx 0.015 \text{ K}^{-1}$ ) signaling the increasing constraint in angular degree of freedom as the temperature is lowered and a further increase or peak of  $\epsilon''$  in the range  $25 \text{ K} < T < 50 \text{ K}$ . According to a comparison with the crystalline counterparts, the latter effects are characteristic features of the disordered solid state.

73. *Interfacial Effects on the Dynamics of Cooperatively Rearranging Regions*  
C. Streck, X. Yan, R. Richert, Ber. Bunsenges. Phys. Chem. 101 (1997) 1735 - 1737

The glass-forming liquid 2-methyltetrahydrofuran is particularly well described by the theory of Adam and Gibbs as regards the coupling between molecular dynamics and configurational entropy near the glass transition temperature at  $T_g = 91 \text{ K}$ . Therefore, the underlying physical picture of cooperatively rearranging regions captures the temperature dependence of orientational dynamics for the bulk liquid on the basis of the configurational entropy. We demonstrate that geometrical confinement of such a liquid to nanopores gives rise to a dynamical coupling of the liquid to the rigid pore wall resulting in a non-ergodic regime for long times, whereas the short time dynamics remain unaffected.

72. *Dielectric Anomalies in the  $\beta$ -Relaxation of Glassy 1,4-Polybutadiene*  
C. Hansen, R. Richert, Acta Polymer. 48 (1997) 484 - 489

We have measured the dielectric relaxation of the polymeric glass-former 1,4-polybutadiene in the glassy and supercooled liquid state. The loss spectra  $\epsilon''(\omega)$  of the  $\beta$ -relaxation are measured between the lower detection limit at  $T = 125 \text{ K}$  and  $T = 225 \text{ K} > T_\beta$ , with  $T_\beta \approx 210 \text{ K}$  being the  $\alpha$ - $\beta$ -merging temperature. The related storage data  $\epsilon'(\omega)$  indicates that the  $\beta$ -process is a signature of suppressing the higher frequency polarization with increasing temperature, rather than giving rise to additional polarizability at frequencies below the average

relaxation frequency of the  $\beta$ -process. This observation, as confirmed by data obtained for *o*-terphenyl and salol, contrasts the previous understandings of the mechanism underlying the Johari-Goldstein type  $\beta$ -process in glasses. A tentative link between the  $\beta$ -process and high frequency vibrational modes is established.

71. *Dynamic Heterogeneity by Higher Moments of a Relaxing Quantity*  
R. Richert, Mater. Res. Soc. Proc. 455 (1997) 127 - 132

A relaxation experiment usually acquires a measure for the mean energetic distance of the system from the thermodynamic equilibrium and its temporal evolution. For sufficiently small perturbations necessary to assure linear responses such data is bound to remain undecisive as regards the spatial nature of the relaxation process, heterogeneous or homogeneous. The technique of solvation dynamics near the glass transition can probe the entire distribution of site specific energies and its approach towards equilibrium, so that apart from the mean solvation energy  $\nu(t)$  also higher moments in terms of the inhomogeneous optical linewidth  $\sigma_{\text{inh}}(t)$  become accessible. While  $\nu(t)$  maps the dielectric relaxation behaviour of the liquid,  $\sigma_{\text{inh}}(t)$  is found to be sensitive to the spatial nature of the underlying process. Contrasting experiment and simulation leads to the conclusion, that the relaxation time is a site specific quantity, i.e. the heterogeneous nature is found to dominate.

70. *Evidence for Dynamic Heterogeneity near  $T_g$  from the Time Resolved Inhomogeneous Broadening of Optical Line Shapes*  
(LETTER)  
R. Richert, J. Phys. Chem. B 101 (1997) 6323 - 6326

The temporal evolution of inhomogeneous spectra emitted by dye molecules in the course of their solvation within a supercooled liquid is analysed, where the average emission energy  $\nu(t)$  probes the dielectric relaxation. The observed increase in the optical linewidth,  $\sigma_{\text{inh}}(t)$ , near the glass transition is compared to corresponding simulations under the conditions of spatially heterogeneous and homogeneous solvation dynamics. From this data on higher moments of the relaxing quantity we conclude on the spatial variation of relaxation times.

69. *Dynamics of Glass-Forming Liquids. III. Comparing the Dielectric  $\alpha$ - and  $\beta$ -Relaxation of 1-propanol and *o*-terphenyl*  
C. Hansen, F. Stickel, T. Berger, R. Richert, E.W. Fischer, J. Chem. Phys. 107 (1997) 1086 - 1093

We have measured the dielectric relaxation of the glass-former 1-propanol for temperatures between 65 K and 350 K in the frequency range  $10^2$  Hz to  $2 \times 10^{10}$  Hz and the photon correlation spectroscopy decays near  $T_g$ . Attributing the strong Debye-type process of 1-propanol to distinct -OH group effects leaves two faster processes related to the structural relaxation which can be identified as  $\alpha$ -relaxation and Johari-Goldstein type  $\beta$ -relaxation characteristic of non-hydrogen-bonding supercooled liquids. From the temperature dependent relaxation times  $\tau(T)$  regarding the three distinct loss-peaks we can specify an  $\alpha$ - $\beta$ -bifurcation temperature  $T_\beta$  which coincides with characteristic qualitative changes in the  $\tau(T)$  behaviour, as also observed for *ortho*-terphenyl and other glass-forming liquids. This assignment is confirmed by the correlation times derived from incoherent quasielastic light-scattering data obtained from the simultaneously measured photon-correlation spectroscopy.

68. *Dielectric Relaxation under Constant-Charge Conditions*  
(INVITED PAPER)

R. Richert, H. Wagner, in "Dielectric and Related Phenomena: Materials Physico-Chemistry, Spectrometric Investigations, and Applications", A. Wlochowicz (Ed.), Proceedings of SPIE Vol. 3181, International Society for Optical Engineering, Bellingham, 1997, p.49 - 58

The common technique of dielectric  $\varepsilon^*(\omega)$  or  $\varepsilon(t)$  measurements involves the application of a polarization invariant electric field to a capacitor filled with the material under study and the detection of the temporal evolution of the resulting current or charge flow. The counterpart condition of applying a given dielectric displacement and monitoring the electric field relates to the dielectric modulus  $M(t)$  with  $M^*(\omega) = 1/\varepsilon^*(\omega)$ . Isothermal and thermally stimulated experimental techniques for directly accessing the relaxation  $M(t)$  are outlined and discussed as regards their relation to the dielectric retardation  $\varepsilon(t)$  and to dc-conductivity  $\sigma_{\text{dc}}$ . We

also address several microscopic processes which are inherently linked to the dielectric modulus through their common feature of displaying a redistribution of charge.

67. *Dielectric Loss Spectra of Organic Glass Formers and Chamberlin Cluster Model*  
C. Hansen, R. Richert, E.W. Fischer, J. Non-Cryst. Solids 215 (1997) 293 - 300

Dielectric loss spectra  $\epsilon''(\omega)$  of 11 different glass-forming materials measured in the frequency range  $10^{-3}$  Hz to  $10^6$  Hz and at various temperatures are analysed within the framework of a gaussian distribution of independently relaxing domains put forward by Chamberlin. The relaxation time distribution  $G(\ln \tau)$  derived from this model is shown to be paralleled by the results of an unbiased numerical transform of  $\epsilon''(\omega)$  into the most appropriate  $G(\ln \tau)$ . The deviations of loss spectra from a power law of the form  $\log(\epsilon'') \propto \log(\omega)$  are well accounted for by the cluster-model and appear to an inherent feature of the  $\alpha$ -process. However, the values obtained for the scaled cluster sizes  $x_0 = \xi/\sigma$  are too small to be compatible with the anticipated gaussian probability density of cluster sizes, so that the applicability of the proposed dielectric function does not necessarily justify all assumptions of the model.

66. *Glass-Forming Liquids in Mesopores Probed by Solvation Dynamic and Dielectric Techniques*  
(INVITED PAPER)

X. Yan, C. Streck, R. Richert, Mater. Res. Soc. Proc. 464 (1997) 33 - 44

The orientational dynamics of organic supercooled liquids of low molecular weight confined to the geometry of porous glasses are studied by two highly related techniques, the optical method of probing the dynamics of solvation regarding a chromophoric host molecule and dielectric relaxation spectroscopy. The dielectric results display marked effects of the confinement to mesopores in terms of altered structural dynamics which appear to separate into a faster and slower responses relative to the bulk liquid. We also demonstrate that there is no trivial relation between the  $\epsilon^*(\omega)$  data and the liquid dynamics in these heterogeneous samples. These effects are partially paralleled by the solvation dynamics results, but with the spatial range inherent in the optical technique being inconsistent with associating the fast and slow dynamical components to spatially distinct regimes. We conclude on the slow component being a signature of non-ergodicity which arises from the competition between the length scale of cooperativity and the pore size.

65. *Geometrical Confinement and Cooperativity in Supercooled Liquids Studied by Solvation Dynamics*

R. Richert, Phys. Rev. B 54 (1996) 15762 - 15766

The molecular dynamics of supercooled liquids confined to the mesopores of sol-gel glasses are interpreted in terms of the spatial competition between the average length scale of cooperativity assumed to increase with time and the geometrical confinement on scales between 2.5 nm and 7.5 nm. Opposed to relating the fast and slow relaxation components to spatially distinct regimes, the picture of a mesoscopically uniform but cooperative relaxation as stimulated by the theoretical work of Jäckle is proposed. It will be demonstrated that rationalizing the data along these lines leads to a consistency with the theory while relaxing some of the conceptual problems encountered in previous interpretations. The data supports the idea that the relaxation in restricting geometries proceeds like in the bulk liquid until the length scale  $\xi(t) \propto \log(t)$  of cooperativity reaches the pore size leading to non-ergodic behaviour within the experimental time scale. For a characteristic cooperativity length  $\xi_c$  the data analysis yields  $\xi_c(T) \propto T$  and  $\xi_c(T_g) \approx 3$  nm. The solvation dynamics results under study are compared to analogous dielectric relaxation data.

64. *Rate-Memory and Dynamic Heterogeneity of First-Order Reactions in a Polymer Matrix*  
R. Richert, A. Heuer, Macromol. 30 (1997) 4038 - 4041

The kinetics of the photochromic first-order reaction merocyanine  $\rightarrow$  spiropyran in PPMA [*Macromol.* 21 (1988) 923] is reanalysed. We apply a method which is conceptually analogous to a technique for discriminating between homogeneous or heterogeneous dynamics on the basis of generalized time correlation functions. The requirement for such an analysis is to selectively prepare a fast or slow sub-ensemble of relaxation sites and to monitor their dynamics relative to those of the entire ensemble, which has been realized experimentally for an isomerization reaction probing the potential barriers imposed by the polymer matrix. For the case of heterogeneous dynamics expected here, a prediction can be made for the decay related to a sub-ensemble of the

fast relaxors which does not involve assumptions about the extent of the rate-memory or, equivalently, of the temporal fluctuations of activation barriers.

63. *Thermally Stimulated Modulus Relaxation in Polymers: Method and Interpretation*

H. Wagner, R. Richert, *Polymer* 38 (1997) 5801 - 5806

We have measured the thermally stimulated decay of the dielectric modulus  $M(T,t)$  for poly(vinylacetate) by monitoring the electric field  $E(t)$  under the condition of a constant dielectric displacement for  $t > 0$ . This thermally stimulated polarization experiment is realized by cooling the sample at zero field to well below its glass transition temperature, applying a certain amount of charge, and then recording the voltage of the sample capacitor  $U(T,t)$  while ramping the temperature. The result of a temperature invariant distribution of relaxation times observed previously in isothermal experiments allows a direct translation of  $M(T,t)$  data into the variation of a characteristic relaxation time  $\tau(T)$  or of a fictive temperature  $T_f(T)$  as a function of the actual temperature.

62. *Structural Relaxation of Glass-Formers Confined to Sol-Gel-Type Porous Glasses*

X. Yan, C. Streck, R. Richert, *Ber. Bunsenges. Phys. Chem.* 100 (1996) 1392 - 1395

We combine the results of dielectric relaxation spectroscopy and solvation dynamics measurements for the glass-forming liquid 2-methyltetrahydrofuran spatially confined to the pores of sol-gel glasses with pore diameters  $\phi = 2.5, 5.0, \text{ and } 7.5 \text{ nm}$ . Although both techniques probe the orientational polarization of the polar liquid, a dielectric experiment is bound to sense macroscopic effects, whereas the solvation method probes the molecular dynamics on microscopic scales. When the temperature approaches the glass-transition at  $T_g$  upon cooling, an interfacial liquid layer with strongly frustrated dynamics grows in thickness and is thus able to block the connectivity among the pores. As a result the structural  $\alpha$ -process is subject to an enhanced spatial restriction near  $T_g$  and a transition from constant pressure to constant volume conditions might occur as the pore connectivity becomes obstructed by immobile liquid.

61. *Donor/Acceptor-Substituted Phenylenevinylenes*

G. Klärner, C. Former, X. Yan, R. Richert, K. Müllen, *Adv. Mater.* 8 (1996) 932 - 935

The 4,4-donor/acceptor-substituted stilbenes are widely used in nonlinear optics (NLO), for which the dipole moment and the hyperpolarizability are the factors of prime importance. In comparison with 4,4-substituted stilbenes, the donor/acceptor-substituted vinylene unit in stilbene is suitable for homologization to distyryl benzenes, higher oligomers, and to the analogous poly(*p*-phenylenevinylene)s. The existence of pronounced dipole moments in each repeat unit raises a question concerning the interaction of the dipole centers within the  $\pi$ -conjugated chains. An understanding of this interaction is important for dielectric spectroscopy, but also for the polarization stability of NLO building blocks.

60. *Dielectric Relaxation of the Electric Field in Poly(vinylacetate): A Time Domain Study in the Range  $10^{-3} \text{ s}$  to  $10^6 \text{ s}$*

H. Wagner, R. Richert, *Polymer* 38 (1997) 255 - 261

We have measured the polarization of poly(vinylacetate) in terms of a real dielectric *relaxation* technique by studying the decay of the electric field  $E(t)$  for times  $10^{-3} \text{ s} \leq t \leq 10^6 \text{ s}$  under the condition of a constant dielectric displacement for  $t > 0$ . This represents a direct measurement of the dielectric modulus  $M(t)$ , opposed to the conventional method of measuring the dielectric *retardation*  $\varepsilon(t)$ , or its frequency domain analogue  $\varepsilon^*(\omega)$ . The advantages of accessing  $M(t)$  are a simple experimental setup and for polar materials experimental times which are shorter by at least a factor of  $\varepsilon_s/\varepsilon_\infty$  relative to  $\varepsilon(t)$  decays. The latter effect bases on the well known relation  $\tau_L = \varepsilon_s/\varepsilon_\infty \tau_D$  between transversal and longitudinal dielectric time constants. For the polymer under study, we find that no significant change of the relaxation time distribution occurs within the experimental time window, i.e. from well above the glass transition at  $T_g$  (if defined via  $\tau_g = \tau(T_g) = 100 \text{ s}$ ) to temperatures below  $T_g$  where the average retardation times  $\langle \tau \rangle$  attain values of up to  $10^7 \text{ s}$ .

59. *Dynamics of Solvation in Supercooled Liquids Confined to the Pores of Sol-Gel Glasses*

C. Streck, Yu.B. Mel'nichenko, R. Richert, *Phys. Rev. B* 53 (1996) 5341 - 5347

We have measured the solvation dynamics of the probe molecule quinoxaline in a glass-forming solvent, 2-methyltetrahydrofuran, geometrically confined to the pores of sol-gel glasses having nominal pore diameters  $\phi = 2.5, 5.0, \text{ and } 7.5 \text{ nm}$ . Within the time range  $1 \text{ ms} \leq t \leq 1 \text{ s}$  the  $\alpha$ -process and a second extremely slow process are

observed. On the basis of emission spectra, the latter relaxation is assigned to a surface layer with strongly frustrated dynamics, opposed to the picture of a certain fraction of pores entirely filled with liquid of reduced molecular mobility. According to the Stokes-shift results for porous samples, the thickness of this surface layer increases significantly with  $T_g \leftarrow T$  for the system under study. The results are compared with solvation dynamic experiments for the bulk solvent and with dielectric relaxation measurements.

58. *Solvation Energy of Ions and Dipoles in a Finite Number of Solvent Shells*

R. Richert, J. Phys.: Condens. Matter 8 (1996) 6185 - 6190

The contributions of a polar solvent in thermodynamic equilibrium to the solvation free energy of a dipole and of an ion are estimated analytically as a function of distance within the framework of the Mean Spherical Approximation theory and compared to the analogous results derived from simple electrostatic arguments. For equal sized solute and solvent molecules, accumulating 90 % of the total energy in media of moderate polarity involves a number of  $\sim 1$  and  $\sim 7$  solvent shells for dipole and ion solvation, respectively. For solvents characterized by high values of  $\epsilon$  only upper bounds for the energy relevant solvent range can be stated. Relative to the continuum picture, the MSA calculation predicts an increase of the coupling range by  $\sim 50$  %, without a significant dependence on the dielectric constant  $\epsilon$ .

57. *Non-exponential  $^2\text{H}$  Spin-Lattice Relaxation and Slow Translational Exchange in Disordered Systems*

I. Roggatz, E. Rössler, M. Taupitz, R. Richert, J. Phys. Chem. 100 (1996) 12193 - 12198

We present an analysis of  $^2\text{H}$  spin-lattice relaxation of deuterated benzene in the glass former tricresyl phosphate. Whereas pronounced non-exponential relaxation is observed well below the glass transition temperature  $T_g$  (180K) a crossover to exponential relaxation is found at  $T \approx T_g$ . By assuming a distribution of barriers for the rotational jump process of benzene in the glassy matrix we are able to describe all relaxation curves in the temperature range  $20\text{K} < T < 160\text{K}$ . The crossover from non-exponential to exponential relaxation is described by additionally assuming translational exchange processes of benzene molecules between sites with different barriers for rotational jumps. Within a simple model we are able to determine exchange rates over more than two decades. Comparing the results with diffusion data we conclude that the obtained rates correspond to diffusion coefficients in the range  $10^{-18} < D/\text{m}^2\text{s}^{-1} < 10^{-16}$  and that translational rotational coupling does not hold near  $T_g$ . The further potential of the method in order to determine very slow exchange processes is discussed.

56. *A Simple Current-to-Voltage Interface for Dielectric Relaxation Measurements in the Range  $10^{-3}$  Hz to  $10^7$  Hz*

R. Richert, Rev. Sci. Instrum. 67 (1996) 3217 - 3221

A new circuit is presented for detecting low level harmonic currents as needed in dielectric relaxation spectroscopy in the low to medium frequency range. For a standard operational amplifier based current to voltage converter, a special feedback network is designed such that the output voltage is fairly insensitive to frequency over many decades if a sine generator is coupled to the input via a capacitor with a lossy dielectric. In combination with a gain-phase analyser or lock-in amplifier this system measures  $\epsilon^*(\omega)$  in the frequency range  $10^{-3}$  Hz to  $10^7$  Hz with high resolution needed for conclusive dielectric relaxation spectroscopy.

55. *Memory Effects above  $T_g$  in Poled Guest/Host Polymers*

S. Schüssler, U. Albrecht, R. Richert, H. Bässler, Macromol. 29 (1996) 1266 - 1268

We present systematic experiments of electric-field-poling and relaxation of 4-(dimethylamino)-4'-nitrostilbene doped at 1 wt % in poly-(isobutylmethacrylate) in a sandwich configuration of ITO-electrodes using the second harmonic generation technique. A novel ultraslow relaxation mode at temperatures far above the glass transition temperature  $T_g$  has been identified qualitatively with a special repoling technique. Isothermal alignment and relaxation of the chromophore orientations show significant differences in their mean rates and in their sensitivity to variations of the field strength and presence of small amounts of plasticizer molecules. A tentative qualitative model is proposed in which the necessity for considering non-linear responses is postulated.

54. *Analysis of the Energy Landscape for Charge Transport in Polar Glassy Materials*

R. Richert, R.F. Loring, J. Phys. Chem. 99 (1995) 17265 - 17268

We apply the methods of equilibrium fluid theory to calculate the distribution of site energies experienced by a diffusing charge carrier in a polar molecular glass. The Mean Spherical Approximation is used to express the distribution of ion - dipole interaction energies of a hard-sphere ion at infinite dilution in a hard-sphere dipolar solvent in terms of the medium's dielectric constant. The resulting distribution is compared to that extracted from experimental charge transport data with the assumption that in the non-ergodic regime for  $T < T_g$  the medium is characterized by its equilibrium structure at  $T_g$ .

53. *Field Induced Structural Ordering in Electrorheological Fluids*

P. Placke, V. Edel, L. Reversat, R. Richert, E.W. Fischer, *Colloid Polym. Sci.* 273 (1995) 1156 - 1162

Structural relaxations of an electrorheological fluid (ERF) due to changes in the applied electrical field strength or shear rate are observed on time scales  $1 \text{ s} < t < 40000 \text{ s}$ . Commercial ERFs consisting of mesoscopic polyurethane particles in a silicone oil matrix were studied by three different experimental techniques in order to obtain and compare the characteristic relaxation times. It is demonstrated that dielectric spectroscopy, viscosimetry and light transmission experiments represent the same results concerning the structural relaxation phenomena of ERFs when electrical fields are applied. The tendency of strong induced dipoles to align the particles in the direction of the field increases the effective dipole moment and therefore  $\Delta\epsilon$ , the shear viscosity  $\eta$  and the amount of light transmitted along the field direction in an ITO/glass sandwich cell. The optical experiment is capable of resolving fast processes within the first 1 ms if large electrical fields are applied. The effects of electrophoresis and shearing, which both counteract the field induced structures, are also addressed.

52. *Dielectric Relaxation of Liquids at the Surface of a Porous Glass*

J. Schüller, R. Richert, E.W. Fischer, *Phys. Rev. B* 52 (1995) 15232 - 15238

We have measured the dielectric relaxation of the glass-forming liquid *N*-methyl- $\epsilon$ -caprolactam (as a representative of non-associating liquids of low molecular weight) confined to the mesopores of a controlled porous glass with 102 Å pore diameter. Three distinct relaxation peaks within  $\epsilon^*(\omega)$  are found for the confined liquid: a broadened  $\alpha$ -process with slightly modified temperature dependence compared to the bulk relaxation, an intermediate peak which originates from Maxwell-Wagner polarization of the heterogeneous system, and an extremely slow process ascribed to the layer associated with the pore surface. Our assignment of the three features are supported by the results of surface modification using trimethylchlorosilane, Maxwell-Wagner-Sillars calculations, and supplementary experiments where the pores are only partially filled with the liquid under study. By analysing  $-\left[\partial \log(\tau_m) / \partial T\right]^{-1/2}$ , where  $\tau_m$  is the peak relaxation time, we find that the variations of  $\tau_m$  with  $T$  are virtually identical for the three processes.

51. *Dynamics of Glass-Forming Liquids. II. Detailed Comparison of Dielectric Relaxation, DC-Conductivity and Viscosity Data*

F. Stickel, E.W. Fischer, R. Richert, *J. Chem. Phys.* 104 (1996) 2043 - 2055

We have studied the temperature dependence of dielectric relaxation times in terms of the peak frequency  $f_{\max}(T)$  of dielectric loss  $\epsilon''(\omega)$  and the dc-conductivity  $\sigma_{\text{dc}}(T)$  of several glass-forming liquids, covering 12 decades in the peak frequency  $f_{\max}$  and 9 decades in  $\sigma_{\text{dc}}$ . Although dc-conductivity samples the mobility of ionic tracers, its variation with temperature is similar to that of  $f_{\max}(T)$ . The  $f_{\max}(T)$  and  $\sigma_{\text{dc}}(T)$  are analysed using the temperature-derivative method and compared to the viscosity data  $\eta^{-1}(T)$ . While most liquids reveal a common Vogel-Fulcher-Tammann (VFT) behaviour for  $f_{\max}$ ,  $\sigma_{\text{dc}}$  and  $\eta^{-1}$  in an extended temperature range  $T \geq T_m$ , some liquids deviate from this behaviour by displaying a crossover at  $T = T_A$  to an Arrhenius regime. In these cases the quantity  $f_{\max}(T)$  decouples from the common curves for  $\sigma_{\text{dc}}(T)$  and  $\eta^{-1}(T)$  and attains activation energies in excess (~40% for alcohols) of those related to translational processes. For many samples a departure from the VFT behaviour occurs at lower temperatures  $T_B < T_m$  which tends to retard the glass transition. The onset of this qualitative change in the temperature dependence at  $T_B$  turns out to be a characteristic temperature also in other experiments.

50. *Rheodielectric Spectroscopy on Heterogeneous Polymer Systems - Electrorheological Fluids*

P. Placke, R. Richert, E.W. Fischer, *Colloid Polym. Sci.* 273 (1995) 848 - 856

The technique of rheodielectric spectroscopy is used to investigate the dielectric behaviour of electrorheological fluids (ERF) as a function of external electrical DC-field and/or shear rate. Commercial ERF's consisting of

mesoscopic polyurethane particles in a silicone oil matrix were studied. The particles contain a salt which leads to strong dipole moments via the Maxwell-Wagner-Polarization (MWP) if subjected to an external electrical field. In an electrical field the dipoles and, concomitantly, the particles motion become correlated leading to the formation of solid-like structures and significant changes in the viscosity. We demonstrate that dielectric spectroscopy is capable of monitoring the field and shear rate effects in terms of relaxation strength and relaxation time of the MWP. In electrical or shear fields dipole-dipole correlations increase the MWP's relaxation strength, so that we are able to observe structure formation with dielectric spectroscopy, especially the time resolved response of the ERF to changes in the electrical field or the shear rate.

49. *Dynamics of Hydrogen-Bonded Liquids Confined to Mesopores: A Dielectric and Neutron Spectroscopy Study*

Yu.B. Mel'nichenko, J. Schüller, R. Richert, B. Ewen, C.-K. Loong, J. Chem. Phys. 103 (1995) 2016 - 2024

In this paper we present and discuss experimental results on molecular mobility in propylene glycol and its three oligomers confined to the  $\sim 100$  Å pores of a controlled porous glass. The objective is to elucidate the finite size effects on the dynamics of hydrogen-bonded liquids of different molecular weights but identical chemical composition. The methods of dielectric and neutron spectroscopy have been employed to investigate both the low- and high-frequency features as a function of temperature. We find that all fluids in pores separate into two distinct liquid phases: i) molecules physisorbed at the surface which exhibit a dramatic frustration of their mobility related to a substantial *positive* shift of the glass transition temperature  $T_g$  by up to  $\Delta T_g \approx +47$  K, and ii) relatively "free" molecules in the inner pore space subject to only moderate retardation of the  $\alpha$ - and normal mode relaxation and substantial broadening of the distribution of relaxation times. The shift in  $T_g$  for the  $\alpha$ -process with  $\Delta T_g \approx +5$  K is maximal for the monomer liquid and gradually diminishes with increasing molecular weight or decreasing intermolecular hydrogen bonding. The inelastic neutron spectrum of confined propylene glycol shows the boson peak as expected in bulk strong and intermediate glass formers in the vicinity of  $T_g$ . This effect can be attributed to the finite - size induced crossover from long wave vibrations characteristic of a continuous medium to localized vibrations in a confined geometry.

48. *Polarization Response of a Dielectric Continuum to a Motion of Charge*

R. Richert, H. Wagner, J. Phys. Chem. 99 (1995) 10948 - 10951

In cases where dielectric relaxation dominates the time scale of molecular processes which involve the motion of charge (e.g. solvation dynamics, electron transfer reactions, or chemical reactions), the relevant time scale is the longitudinal relaxation time  $\tau_L$ , which is generally faster than the dielectric relaxation time  $\tau_D$ . Numerical calculations of the polarizations  $P_D(t)$  with  $dE(t)/dt = 0$  and  $P_E(t)$  with  $dD(t)/dt = 0$  for an electrical RC network equivalent to an arbitrary dielectric function  $\epsilon^*(\omega)$  are performed in order to generalize the relation between  $\tau_L$  and  $\tau_D$  which only for the Debye case reads  $\tau_L = \tau_D \epsilon_\infty/\epsilon_s$ . The results for non-Debye systems as a function of relaxation time dispersion and relaxation strength are that  $\langle \tau_L \rangle \ll \langle \tau_D \rangle \epsilon_\infty/\epsilon_s$  whereas the decay profiles for  $P_D(t)$  and  $P_E(t)$  are similar. The normalized field decay  $P_E(t)$  represents a continuum model prediction for the Stokes-shift correlation function  $C(t)$  observed in solvation dynamics experiments.

47. *Dynamics of Glass-Forming Liquids. I. Temperature-Derivative Analysis of Dielectric Relaxation Data*

F. Stickel, E.W. Fischer, R. Richert, J. Chem. Phys. 102 (1995) 6251 - 6257

We have measured the dielectric relaxation times of the  $\alpha$ -process of phenyl salicylate (salol) covering 11 decades in frequency. Being representative for the class of low molecular weight organic glass forming materials, the highly resolved temperature dependence of the dynamics in salol does not follow a particular function like the Vogel-Fulcher-Tammann (VFT) law over the entire accessible range of temperatures. In order to conduct a detailed and unambiguous analysis of the temperature dependence we take advantage of the derivatives of the experimental  $\log(f_{\max})$  values with respect to temperature, which allow us to either linearize the frequently used temperature laws or to resolve subtle changes in  $f_{\max}(T)$  by decreasing the number of free parameters. In this manner we observe that none of the common routes for rationalizing the dynamics like Arrhenius, VFT, Souletie scaling, and idealized mode-coupling theory account for the experimental findings properly. However, we do observe a VFT behaviour within the limits  $265 \text{ K} \leq T \leq 320 \text{ K}$ , i.e. for temperatures ranging from significantly above the glass-transition at  $T_g = 220 \text{ K}$  to far above the melting point.

46. *Mechanisms of Second Harmonic Generation Efficiency Relaxation in Poled Guest/Host Polymers*

S. Schüssler, R. Richert, H. Bässler, *Macromol.* 28 (1995) 2429 - 2438

We have investigated the second harmonic generation (SHG) signals of a guest/host system based on 4-(dimethylamino)-4'-nitrostilbene dissolved at 1 wt % in poly-(isobutylmethacrylate) and poled in a sandwich configuration of ITO-electrodes. By blocking the injection from the ITO-surfaces with SiO coatings a significant impact of charge carriers on the SHG decay pattern can be excluded. Using chloroform as a solvent an additional contribution to the SHG decay kinetics is observed which is also active in the presence of the external electric poling field. Separating this effect from the pure orientational relaxation of the dopants leads to a highly improved reproducibility. Due to its weak temperature dependence we tentatively ascribe this solvent specific effect to the diffusion of dipolar impurities which may affect the local field factors and hyperpolarizability tensors. The resulting corrected SHG time constants related to the pure orientational relaxation still appear to be strongly decoupled from the  $\alpha$ -process of the matrix as inferred from dielectric relaxation data of the bulk polymer. This basic discrepancy between SHG decay and  $\alpha$ -process is found not to depend on film preparation, sample conductivity, sample geometry and residual solvent content.

45. *Solvation Dynamics and the Dielectric Response in a Glass-Forming Solvent: From Picoseconds to Seconds*

R. Richert, F. Stickel, R.S. Fee, M. Maroncelli, *Chem. Phys. Lett.* 229 (1994) 302 - 308

We have measured the response times of solvation dynamics in the range 100 ps to 100 s and the dielectric relaxation covering 10 decades in frequency for the glass-forming solvent 2-methyltetrahydrofuran. In this wide range of solvent viscosities, from the glass transition to beyond the melting point, the mean relaxation times for the two techniques which monitor dipolar orientation are identical within our resolution. For two characteristic decay traces recorded on the time scales of 10ns and 1s we compare the observed Stokes-shift dynamics with various theoretical approaches. It turns out that the decay pattern is reproduced by the dipolar dynamic-mean-spherical-approximation, whereas the absolute time scale of the solvation is mapped by the dielectric polarization itself. For the solvent under study we find almost perfect agreement between experiment and the dipolar DMSA theory if the time scale of the predicted curve is rescaled by a factor of  $(\epsilon_\infty/\epsilon_s)^{1/2}$ .

44. *Dielectric Studies of the Glass Transition in Porous Media*

J. Schüller, Y.B. Mel'nichenko, R. Richert, E.W. Fischer, *Phys. Rev. Lett.* 73 (1994) 2224 - 2227

Dynamic processes in liquid propylene glycol and two of its oligomers inside the  $\approx 100$  Å pores of controlled porous glasses have been investigated as a function of temperature by dielectric spectroscopy. We find that geometrical restriction results in retardation and broadening of the inherent  $\alpha$  relaxation. The retardation is most pronounced for the monomer liquid and gives rise to an *increase* in the glass transition temperature by  $\Delta T_g = +4.5$  K. We also observe a second slower relaxation process for all liquids, ascribed to the hindered dynamics of molecules affected by the surface.

43. *Relaxation of Second-Harmonic Generation in Guest/Host Polymers Poled by Indium-Tin Oxide Sandwich Electrodes*

S. Schüssler, R. Richert, H. Bässler, *Macromol.* 27 (1994) 4318 - 4326

Second harmonic generation (SHG) is used to monitor reorientation dynamics of 4-(dimethylamino)-4'-nitrostilbene doped at 1 wt % in poly-(ethylmethacrylate) within a temperature range of  $T_g \pm 30$  K. Special emphasis is put on a systematic analysis of experimental conditions and their severe impact on SHG data for samples which are poled in an ITO-sandwich-electrode configuration. These effects include thermal history, local heating effects due to laser-focus, importance of dopant concentration, physical aging, details of the poling procedure, as well as charge-injection effects. The fast initial response of the SHG-signal upon field switching is attributed to space charge effects. We show how the problem of SHG reproducibility can be overcome with appropriate experimental conditions. Analysis of the reliable data is based on a Gaussian distribution of energy barriers for the dopant relaxation which yields superior fits compared to a stretched exponential function. The Arrhenius-like behaviour of the mean SHG decay rate points towards a decoupling of the dopant motion from the bulk  $\alpha$ -process of the polymer host. Additionally, a novel re-poling technique and its implications are discussed.

42. *The Relation of Solvatochromism and Thermo-chromism to the Solvent Dielectric Constant: The Basis of the  $E_T$  and  $E'_T$  Polarity Scales*

C. Streck, R. Richert, Ber. Bunsenges. Phys. Chem. 98 (1994) 619 - 625

We have measured the thermo-chromism of pyridinium-*N*-phenoxide betain and its penta-*tert*-butyl substituted derivative dissolved in MTHF together with the solvent dielectric properties in order to relate polarity scales to the dielectric constants of the solvent. Both thermo-chromic and solvatochromic shifts of the absorption band of the dyes can be rationalized on the basis of the MSA theory for relating the solvation free energy to the static dielectric constant. Deviations between theory and experiment in the regime of higher viscosities can be attributed to changes in the offset between absorption maximum and electronic transition energy.

41. *Dispersive First-Order Reactions II: Photochromic Model System*

U. Albrecht, H. Schäfer, R. Richert, Chem. Phys. 182 (1994) 61 - 68

The photochromic reactions spiropyran - merocyanine in polymeric matrices has been analysed with respect to their distributions of rates in order to understand the matrix effects on the kinetics in the transition range from a static to fluid environment. Employing the technique of part I we find a static matrix situation only below the Vogel-Fulcher temperature  $T_{VF}$  of the polymer where different species are identified in terms of distinct but distributed decolouration rates. Above the glass transtion  $T_g$  the ensemble averaged reaction approaches an exponential decay pattern, due to the fluctuations of site specific barriers and exchange mechanisms among the set of merocyanine isomers.

40. *Dispersive First-Order Reactions I: Data Analysis*

H. Schäfer, U. Albrecht, R. Richert, Chem. Phys. 182 (1994) 53 - 59

We present an algorithm which is capable of resolving the spectrum of rates for decay kinetics whose elementary processes follow the first-order law. The stability of the results are illustrated via Monte-Carlo analysis of the statistics when trying to reconstruct complex multi-modal distributions of the rates. Additionally, we document the succesful application to experimental data for a photochromic isomerization reaction in a polymeric matrix, which allows for acquiring several 1000 points in time at a noise level of  $\leq 0.1\%$  for the normalized absorption signal. For the first time, different cis-trans conformations of the transient merocyanine species are show to have distinct kinetic behaviours regarding the decolouration process without biasing the decay analysis.

39. *Transient Polarization Four-Photon "Non-Condon" Spectroscopy of Electronic Transitions in Complex Molecules*

B. Fainberg, R. Richert, S.Y. Goldberg, D. Huppert, J. Luminescence 60-61 (1994) 709 - 712

We show both theoretically and experimentally that resonance transient grating spectroscopy (RTGS) is a good method for the investigation of ultrafast solvation dynamics of large probe molecules in solutions. We have studied the solvation dynamics of LDS 750 in many solvents in a broad time range by RTGS and by induced optical Kerr effect spectroscopy. We propose a new method for the investigation of non-Condon effects in solvation: transient polarization four-photon spectroscopy.

38. *Ultrafast Solvation Dynamics by Degenerate Four Wave Mixing: A Theoretical and Experimental Study*

R. Richert, S.Y. Goldberg, B. Fainberg, D. Huppert, in "Reaction Dynamics in Clusters and Condensed Phases", B. Pullman, J. Jortner (Eds.), Kluwer, Dordrecht, 1994, p.227 - 244

We developed theoretically and experimentally the principles of a new spectroscopical method based on four-wave mixing for quantitative description of solvation dynamics of excited large molecules in liquid solutions. We have found that the solvation dynamics of LDS 750 in methanol, ethanol and propanol solutions on a time scale of 1 ps is almost identical. The solvation dynamics in these solvents is biphasic where the long component decays exponentially with a 400 fs decay time. The fast solvation process is followed by the longitudinal solvent relaxation with relaxation times of 5, 10 and 20 fs for methanol ethanol and propanol respectively.

37. *Homogeneous Dispersion of Dielectric Responses in a Simple Glass*

R. Richert, J. Non-Cryst. Solids 172-174 (1994) 209 - 213

Non-exponential patterns are well known characteristics of relaxations in glassy systems, however, the origin of dispersion is a matter of debate in many cases. We compare dielectric relaxation and solvation dynamic data along the lines of the MSA theory for discriminating between homogeneous and heterogeneous nature of dispersion for a low molecular weight glass at 3K above  $T_g$ . From the theoretical point of view the necessary spatial component stems from the dependence of solvation dynamics on  $\epsilon(\omega, k)$ , rather than the macroscopic limit  $\epsilon(\omega, k=0)$ . We show that the two origins of dispersion can be distinguished in terms of solvation data which agrees with the homogeneous limit.

36. *Disordered Systems and Relaxation*

R. Richert, A. Blumen, in "Disorder Effects on Relaxational Processes", R. Richert, A. Blumen (Eds.), Springer, Berlin, 1994, p.1 - 7

It is a widespread experience that the properties of materials do not depend on the chemical constitution only, but also on the mutual arrangement and on the dynamics of the molecules involved. The standard classification of the equilibrium thermodynamic phases into gaseous, liquid, and solid leaves no room for media which combine an irregular structure with extremely high values of the viscosity. However, many materials maintain their disordered liquid-like structure upon cooling, rather than to crystallize and to form a state of high regularity. Hence such glassy systems combine the irregular structure of a liquid with the rigidity of the solid state below the melting temperature  $T_m$ . Irrespective of their chemical nature, most glasses display unique features which are absent in their counterpart crystalline materials. Therefore, disorder itself appears to be the dominant factor which leads to such characteristic properties.

35. *Origin of Dispersion in Dipolar Relaxations of Glasses*

R. Richert, Chem. Phys. Lett. 216 (1993) 223 - 227

Dispersive relaxations typically found in glassy systems stem from a distribution of response times, spread either heterogeneously or homogeneously within the ensemble of sites. To distinguish between these two possibilities we follow the dynamics of dipole solvation, a technique which provides valuable insight on relaxation in both, the liquid and the glassy regime. Employing the dynamic Mean Spherical Approximation (MSA) theory, with  $\epsilon(\omega)$  as an input, we calculate the solvation time evolution in the homogeneous and heterogeneous limits. Due to the remarkable agreement between the homogeneous MSA and the observed solvation in MTHF at  $T_g + 3$  K = 94 K we conclude on the homogeneous nature of dispersion for dipolar relaxations.

34. *Dielectric Aspects of Dipolar Solvation at the Glass-Transition*

R. Richert, in "Disorder Effects on Relaxational Processes", R. Richert, A. Blumen (Eds.), Springer, Berlin, 1994, p.333 - 358

Optical spectroscopy has been employed successively for characterizing and quantifying material properties. In the context of disordered systems the broadening of emission and absorption profiles is often quoted as evidence for the irregularity of an amorphous matrix surrounding a chromophoric guest molecule, albeit without stressing quantitative statements. The qualitative argument is that spatial fluctuations of intermolecular distances and mutual arrangements will modulate interaction energies thus giving rise to an energetic distribution of electronic transitions seen as inhomogeneous linewidth. More precisely, the energy level of an electronic transition differs from that in the gas phase by the energy engaged in polarizing the medium. This site specific polarization energy will not only cause line broadening but also results in a shift of the line position relative to the gas phase value. In the general case, the dipolar coupling to the medium is characterized by the frequency dependent dielectric constant  $\epsilon(\omega)$  implying that the polarization and concomitantly the spectral shift is a function of time.

33. *Spectroscopic Line Shapes in Polar Supercooled Liquids*

R. Richert, A. Wagener, J. Phys. Chem. 97 (1993) 3146 - 3150

We have measured the inhomogeneously broadened  $T_1 \rightarrow S_0$  (0-0) emission spectra of quinoxaline in a series of organic glass-forming solvents, which are characterized in terms of their optical and static dielectric constants. The experimental results regarding Stokes shift and inhomogeneous line width are compared with the predictions of a statistical mechanical line shape theory (R.F.Loring, *J.Phys.Chem.* **1990**, *94*, 513), whose relevant input parameters are known. Using the MSA approach for delineating the solvation free energy, a good agreement between prediction and observation is achieved, indicative of a clear improvement over Onsager's continuum calculation. As a conclusion, spectroscopic line shapes in these systems are completely determined

by electrostatic interaction and, therefore, can be rationalized quantitatively in terms of the solvent dielectric constant. The relation to empirical polarity scales is briefly discussed.

32. *Progress Towards Processible Materials for Light-Emitting Devices Using Poly(p-phenylphenylenevinylene)*

H. Vestweber, A. Greiner, U. Lemmer, R.F. Mahrt, R. Richert, W. Heitz, H. Bässler, *Adv. Mater.* 4 (1992) 661 - 662

In modern electrophotography inorganic photoreceptors have been widely replaced by molecularly doped polymers. These are inexpensive, easily processible and combine the mechanical properties of the polymer binder with the photoelectronic properties of the transport material which can both be optimized according to special requirements. The success of this strategy could lead to the replacement of inorganic materials in light-emitting diodes (LEDs) by polymers. The discovery of yellowish electroluminescence in a conjugated polymer, poly(p-phenylenevinylene), (PPV), marked a breakthrough in this direction. Unfortunately, PPV is insoluble and infusible. Therefore, synthesis, analysis, and processing are quite limited. In order to fully exploit the potential offered by polymers the device material has to be processible in its polymeric form. A promising candidate is poly(p-phenylphenylenevinylene), (PPPV), an analogue of PPV with improved solubility, which can be cast from solution to form high-quality bulk films.

31. *Molecular Probing of Dielectric Relaxation in the Glass-Transition Region*

R. Richert, *Chem. Phys. Lett.* 199 (1992) 355 - 359

Conventional dielectric  $\epsilon^*(\omega)$  data and solvation dynamic  $C(t)$  data are recorded simultaneously, assuring perfect coincidence of experimental conditions for the two relaxation phenomena in the glass-former 2-MTHF doped with quinoxaline. The dynamic MSA theory for dipolar solvation turns out to relate the observed Stokes-shift dynamics to the dielectric data in a quantitative fashion. The agreement between theory and experiment facilitates access to 'microscopic' dielectric relaxation via spectroscopy of appropriate molecular probes in supercooled liquids.

30. *Dispersive and Nondispersive Charge Transport in a Molecularly Doped Polymer with Superimposed Energetic and Positional Disorder*

P.M. Borsenberger, R. Richert, H. Bässler, *Phys. Rev. B* 47 (1993) 4289 - 4295

Time-of-flight photocurrent measurements of 1,1-bis(di-4-tolylaminophenyl)cyclohexane doped bisphenol-A-polycarbonate show dispersive features at low temperatures. Within the nondispersive regime, transients show anomalously broad tails of universal shape. Their relative width is in quantitative accord with Monte Carlo simulations of a material characterized by degrees of energetic and positional disorder that have previously been determined from the temperature and field dependencies of the mobility. The transition to dispersive transport, delineated by a change of the temperature dependence of the carrier mean transition time, occurs at a critical energetic disorder parameter as predicted by simulation. The effect of positional disorder is to decrease the slope of the trailing edge of the photocurrent transient.

29. *Solvation in Glassy Materials*

R. Richert, A. Wagener, *Mol. Cryst. Liq. Cryst.* 216-218 (1992) 61 - 66

Time resolved phosphorescence spectroscopy of molecular probes in organic supercooled liquids indicates solvation dynamics active on the ms-s time scale. A detailed analysis of the positive solvatochromism of quinoxaline allows for experimentally quantifying the change in dipole moment upon  $T_1 \leftarrow S_0$  excitation and the polarity of supercooled liquids. Solvation in macroscopically unpolar solvents indicates the important role of microscopic polarity for rationalizing the local dielectric responses governing the solvation dynamics.

28. *Dipolar Solvation as a Signature of Dielectric Responses in Supercooled Liquids*

R. Richert, A. Wagener, *J. Phys. Chem.* 95 (1991) 10115 - 10123

Time resolved Stokes shifts of phosphorescence bands are investigated monitoring the solvation dynamics of electronically excited probe molecules embedded at low concentrations in organic supercooled liquids of varying polarities. The long lived  $T_1$  states of the solutes give access to dipolar equilibration of the glassy medium near  $T_g$  on a ms to s time scale. Coincidence of solvation and glass transition temperatures over a large  $T_g$  range relates the spectral shift to the  $\alpha$ -process of the glass with only minor sensitivities to the specific probe

molecule. Emission energy data for the Franck-Condon and equilibrated solvent configurations allows determining the change in dipole moment upon  $T_1 \leftarrow S_0$  excitation in agreement with theoretical predictions. Relative polarities of the glasses as quantified by the positive solvatochromism of quinoxaline are highly correlated to the corresponding values for the liquid state at 20°C. The observed solvation dynamics map the dielectric response to a motion of charge and can be rationalized in terms of dielectric dispersion, importance of microscopic solvent behaviour and an excess cooperativity of longitudinal relaxations.

27. *Hole Transport in 1,1-bis(di-4-tolylaminophenyl)cyclohexane*

P.M. Borsenberger, L. Pautmeier, R. Richert, H. Bässler, J. Chem. Phys. 94 (1991) 8276 - 8281

Hole mobilities have been measured in vapor deposited films of 1,1-bis(di-4-tolylaminophenyl)cyclohexane over an extended range of fields and temperatures. At 295 K, the mobility is approximately  $10^{-2}$  cm<sup>2</sup>/Vs, the highest value for a disordered molecular solid reported thus far. Monte Carlo simulations of random walk in a geometrically and energetically disordered medium demonstrate that the time dependence of the photocurrent and the field and temperature dependencies of the mobility can be described quantitatively in terms of the inherent disorder and its effect on charge transport. No polaronic or trapping phenomena need to be invoked to reproduce even subtle features of the experimental results.

26. *Solvation Dynamics versus Inhomogeneity of Decay-Rates as the Origin of Spectral Shifts in Supercooled Liquids*

A. Wagener, R. Richert, Chem. Phys. Lett. 176 (1991) 329 - 334

The recent discussion on the origin of spectral shifts observed for the luminescence of sensor molecules in fluid solution has guided us to reinvestigate solvation dynamics data in glassy matrices. It is demonstrated that the Stokes shift of a phosphorescent probe in a supercooled liquid is of pure relaxational origin and, thus, directly reflects the dynamics of solvation. At lower temperatures, anti-Stokes shifts are observed due to site specific  $S_0 \leftarrow T_1$  rate relating to the emission energy by means of external heavy atoms which increase both the decay rate and local polarizability. This inhomogeneity differs phenomenologically from solvation effects and is found to be effective only at temperatures below the onset of solvation.

25. *Anomalous Time-Independent Diffusion of Charge Carriers in a Random Potential under a Bias Field*

L. Pautmeier, R. Richert, H. Bässler, Philos. Mag. B 63 (1991) 587 - 601

We present Monte Carlo simulation results for time-independent drift and spatial spreading of a packet of charge carriers executing a random walk within a manifold of hopping sites under a bias field. The shape of the density-of-states profile is assumed to be Gaussian (width  $\sigma$ ). The ratio  $eD/\mu kT$ , equal to unity for ordinary diffusion, is found to increase dramatically with increasing disorder and bias field. For  $\sigma/kT = 3.5$  and fields of order  $10^6$  V cm<sup>-1</sup>,  $eD/\mu kT$  reaches values of order  $10^3$ . The effect accounts for the anomalous spreading of time-of-flight profiles often seen in photocarrier transit time studies on various polymeric systems. The role of disorder in charge-carrier transport is emphasized.

24. *Solvation Dynamics of Triplet Excitations*  
(INVITED PAPER)

R. Richert, in "Dynamical Processes in Condensed Molecular Systems", A. Blumen, J. Klafter, D. Haarer (Eds.), World Scientific, Singapore, 1990, p.348 - 358

Solvation dynamics data for the triplet state of quinoxaline in an 2-MTHF glass are presented. In the vicinity of the glass transition temperature of the solvent the solvation times range from ms to s within several K. The relation of these results to the solvation in liquids and to the nature of the glassy state will be discussed.

23. *Simulation of Excitation Transport in Disordered Media*

R. Richert, L. Pautmeier, H. Bässler, in "Large-Scale Molecular Systems: Quantum and Stochastic Aspects - Beyond the Simple Molecular Picture", W. Gans, A. Blumen, A. Amann (Eds.), Plenum Press, New York, 1991, p.471 - 476

Diffusivity and mobility are characteristic quantities of transport phenomena easily correlated to the transition rates and the biasing force in regular systems. In the absence of regularity any quantification in terms of a rate is obscured by the disorder induced distribution of rates or waiting times. It is this characteristic property of random media together with the stochastic and often hierarchical nature of relaxational processes which prevents a straightforward analytical approach to rate controlled quantities in these systems. If a model for the underlying microscopic individual transition is at hand computer simulations yield a powerful tool for quantitatively accessing a wide spectrum of observables.

22. *Solvation Dynamics in Supercooled Liquids: The Quinoxaline Triplet State in 2-MTHF at the Glass Transition*

R. Richert, *Chem. Phys. Lett.* 171 (1990) 222 - 228

The phosphorescence of quinoxaline as dopant in 2-MTHF is investigated at temperatures near the glass-transition of the host solution. Within the accessed time range from 500  $\mu$ s to 1 s the emission band is subject to a temporally resolved Stokes shift of  $\approx 250$   $\text{cm}^{-1}$  monitoring the solvation dynamics of the excited probe molecule. The non-exponential Stokes shift correlation functions indicate that microscopic aspects of the solvation process have to be regarded for rationalizing the experimental data. The results are discussed in the context of solvations dynamics of singlet excitations and the dielectric behaviour of supercooled liquids.

21. *Line Narrowing Effects in Kinetics of Dispersive First Order Reactions*

R. Richert, *Mol. Cryst. Liq. Cryst.* 183 (1990) 283 - 290

The onset of thermally induced configurational fluctuations in a polymer near the glass transition can be monitored by the ensemble averaged isomerization reaction of probe molecules subject to a significant sterical hindrance. The decay patterns can be rationalized in terms of a distribution of activation barriers together with a temperature dependent correlation time for the matrix cages. Experimental support is given by data of a spiropyran/PBMA system investigated in the temperature range near  $T_g$ .

20. *Poole-Frenkel Behavior of Charge Transport in Organic Solids with Off-Diagonal Disorder Studied by Monte Carlo Simulation*

L. Pautmeier, R. Richert, H. Bässler, *Synth. Met.* 37 (1990) 271 -281

By use of Monte Carlo simulation techniques it has been shown that inclusion of random variations of the wavefunction overlap parameter ('off-diagonal' disorder) generates Poole-Frenkel behavior of the charge-carrier mobility ( $\mu$ ) in random organic solids within an experimentally relevant range. The results are in quantitative agreement with experimental data, notably the work of Peled and Schein (*Chem. Phys. Lett.*, 153 (1988) 422) reporting on a temperature-induced change of sign of the field dependence of  $\mu$ .

19. *Glass Dynamics Probed by Motional Line Narrowing of Reactions in Polymers*

R. Richert, in "Optical Techniques to Characterize Polymer Systems", H. Bässler (Ed.), Elsevier, Amsterdam, 1989, p.71 - 114

The challenge in the study of amorphous materials is raised by two important aspects encountered at glasses or supercooled liquids. One is the recognition that the amorphous state leads to new material qualities not found in the ordered counterpart system. This holds especially for polymers where tailoring of desired features meanwhile is a routine technique. The second aspect is the aim of understanding how the absence of regularity affects the unique nature of glasses. Upon investigating a specific quality of a glassy system one is readily confronted with the problem of how the configurational statistics of the glass constituents can be quantified and how does microscopic motion affect the behaviour.

18. *Hopping in a Gaussian Distribution of Energy States: Transition from Dispersive to Non-Dispersive Transport*

L. Pautmeier, R. Richert, H. Bässler, *Philos. Mag. Lett.* 59 (1989) 325 - 331

By means of Monte Carlo simulation techniques the relaxation of a packet of charge carriers migrating in a Gaussian density of states of width  $\sigma$  has been studied. The relaxation time determines the transition from dispersive to non-dispersive transport seen in a time-of-flight signal. For a 10  $\mu$ m thick sample under a bias field of  $10^5$   $\text{V cm}^{-1}$  the critical disorder parameter  $\sigma/kT$  turns out to be 4.4. Consistency with experimental results from polymers is found.

17. *Dynamics of Supercooled Melts Treated in Terms of the Random Walk Concept*  
R. Richert, H. Bässler, J. Phys.: Condens. Matter 2 (1990) 2273 - 2288

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

16. *Diffusion and Drift of Charge Carriers in a Random Potential: Deviation from Einstein's Law*  
R. Richert, L. Pautmeier, H. Bässler, Phys. Rev. Lett. 63 (1989) 547 - 550

Employing Monte Carlo techniques, the diffusion and drift of charge carriers within an array of hopping sites subject to a Gaussian distribution of site energies of width  $\sigma$  has been studied as a function of  $\sigma/kT$  and electric field. With increasing disorder and field, significant deviations from Einstein's law are noted. They are shown to be the consequence of anomalous, field-assisted diffusion while the mobility remains constant. The effect can account for anomalous transit-time dispersion observed in polymeric photoconductors exhibiting time-independent transport.

15. *Frustrated Energy Relaxation in an Organic Glass*  
R. Richert, H. Bässler, B. Ries, B. Movaghar, M. Grünwald, Philos. Mag. Lett. 59 (1989) 95 - 102

Time-dependent transport of triplet excitons in amorphous benzophenone has been investigated in the low-temperature range down to 6 K. The data exhibit some remarkable features associated with the freezing-in of excitations in energy-disordered glasses. The relaxation process is investigated and explained using Monte Carlo simulations and analytical random-walk techniques. The inadequacy of mean-field type methods is demonstrated for the low-temperature domain, where exact averaging techniques can be applied.

14. *Dynamics of a Polymer Matrix Probed by the Ring-Closure of Merocyanine*  
R. Richert, Chem. Phys. 122 (1988) 455 - 462

Decolouration kinetics of the merocyanine-spiropyran transformation in a PBMA matrix near  $T_g$  are followed for both thermal and photoinduced reaction. The barrier of steric hindrance to the intramolecular rotation of the chromophore is approximated to be 22 kJ/mol with significant inhomogeneous fluctuation ( $\pm 3$  kJ/mol) giving rise to the dispersive nature of the decay. The thermal course of the deviation from exponential behavior indicates a temperature dependent rate at which local configurations reorganize. A quantitative description of these matrix dynamics is given, extending the static model to temperatures where the steric hindrance due to the polymer matrix can no longer be expected to be static on the timescale of the reaction. Experimental findings are quantitatively mapped by the model without the need of discontinuities near  $T_g$ .

13. *Disorder-Enhanced Triplet Exciton Diffusion in Condensed Aromatic Systems*  
L. Pautmeier, B. Ries, R. Richert, H. Bässler, Chem. Phys. Lett. 143 (1988) 459 - 462

Employing the Monte Carlo simulation technique it is shown that moderate orientational disorder in condensed random phases of planar aromatic molecules can enhance the diffusivity of triplet excitations by orders of magnitude. This explains earlier experimental results on aromatic melts and on anthracene-doped polystyrene.

12. *Kinetics of Photophysical Hole-Burning in Tetracene Doped MTHF Glasses*  
A. Elschner, R. Richert, H. Bässler, Proc. Acad. Sci. Estonian SSR, Phys., Math. 37 (1988) 154 - 165

Experimental data for growth and spontaneous recovery of photophysical holes burnt into the  $S_1 \leftarrow S_0$  0-0 - band of tetracene doped into a methyltetrahydrofuran (MTHF) glass are analysed in terms of the concept of a

dispersive reaction, whose rate parameter is subject to a Gaussian distribution. The inherent dispersion resulting from the finite homogeneous spectral width of the absorbers as well as the random orientation of their transition moments has been evaluated explicitly. It turns out that hole-burning and recovery are kinetically correlated processes indicating that the photoactive guest-host configurations are well represented by bistable systems.

11. *The Merocyanine - Spiropyran Photochemical Transformation in Polymers Probing Effects of Random Matrices*

R. Richert, *Macromol.* 21 (1988) 923 - 929

Isomerization kinetics of the merocyanine-spiropyran transformation in several poly(alkylacrylates) are detected by time-resolved absorption spectroscopy. The decay of the colored merocyanine exhibits significant deviations from first-order patterns. The energy of activation can be separated into a stabilization energy for the isomer and an activation inherent to the amorphous matrix by observing the decoloration patterns for the corresponding photoisomerization. These observations can be explained by matrix effects in the isomerization modeled by statistics and fluctuations of matrix-site energies. Quantification of matrix effects is based on the concept of transport theories in random media applied to reflect the dynamics of potential energies. The gradual decrease of dispersion of reaction rates with rising temperature is correlated to the time a chromophore remembers its initial matrix cage, thereby extending the kinetic model to the range above the glass transition.

10. *Interpretation of Dispersive Hole-Burning Kinetics*

R. Richert, *J. Chem. Phys.* 86 (1987) 1743 - 1747

Nonexponential decay of an ensemble of first-order processes are modeled assuming distributions of rate-controlling parameters to be responsible for dispersive kinetics. Some problems of deriving microscopic properties from experimental decay data are illustrated focusing on hole-burning kinetics on the basis of the two-level system model. This approach is compared with reasonings leading to the logarithmic decay law.

9. *Temperature Dependent Kinetics of Photophysical Hole-Burning in a Tetracene Doped MTHF Glass*

A. Elschner, R. Richert, H. Bässler, *Chem. Phys. Lett.* 127 (1986) 105 - 110

Kinetics of photophysical hole burning in a MTHF(TC) glass follows the concept of decoupled first-order reactions with Gaussian distribution of the tunneling parameter. The decrease of the hole-burning yield with increasing temperature signals thermally activated hole refilling in the excited state. The ratio of TLS states responsible for dephasing and hole burning, respectively, is estimated to be  $\approx 10^7$ .

8. *Experimental Study of Non-Exponential Relaxation Processes in Random Organic Solids*

R. Richert, A. Elschner, H. Bässler, *Z. Phys. Chem. N. F.* 149 (1986) 63 - 75

We compare experimental results on (i) thermally induced merocyanine  $\rightarrow$  spiropyran transformation of a dye molecule substitutionally doped into a polymer (PMMA) matrix; (ii) growth of a photophysical hole burnt into the inhomogeneously broadened  $S_1 \leftarrow S_0$  0-0 absorption band of tetracene doped into a MTHF glass at low temperature; (iii) diffusion-controlled trapping of a triplet excitation in a benzophenone glass. A common feature is the time-dependence of the observed, i.e. averaged event rate. While in each case a stretched exponential  $\{\exp[-(t/t_0)^{\alpha}]\}$  provides a reasonably good fit to experimental data if restricted to a limited time domain, analysis of the shorter time behavior indicates its failure for modelling the cases (i) and (ii). Instead, it is shown that in these cases the concept of uncoupled parallel relaxations whose rate controlling parameter, an activation energy or a tunnelling matrix element, is subject to a Gaussian distribution provides an appropriate description. Comparison with results of case (iii) demonstrates the possibility of distinguishing between parallel and serial relaxation mechanisms if experimental data span a sufficiently large time interval.

7. *Dispersive Triplet Excitation Transport in Organic Glasses*

R. Richert, H. Bässler, *J. Chem. Phys.* 84 (1986) 3567 - 3572

Time dependent transport of triplet excitations in amorphous benzophenone, anthracinone, and phenanthrene has been investigated in the temperature range  $4.2 \text{ K} \leq T \leq 100 \text{ K}$  by monitoring diffusion-controlled decay of the inhomogeneously broadened 0-0 phosphorescence band of bulk states. The results are in excellent agreement with both the analytic theory of Grünwald et al. and computer simulation of nonequilibrium transport. They indicate the applicability of a stochastic transport model based on asymmetric hopping rates with unrestricted

energy relaxation. The time dependence of the ensemble averaged hopping frequency has been determined within three decades of time. It can be approximated by a  $\nu(t) \sim (t/t_0)^{\alpha-1}$  law with time dependent dispersion parameter  $\alpha$ .

6. *Non-Exponential Hole-Burning Kinetics in Organic Glasses*

R. Jankowiak, R. Richert, H. Bässler, J. Phys. Chem. 89 (1985) 4569 - 4574

The time evolution of nonphotochemical holes in the absorption profile of tetracene doped into amorphous layers of 2,3-dimethylantracene and 9,10-diphenylantracene has been investigated and compared with literature results on tetracene in an alcohol glass. The kinetics can be described in terms of a dispersive first-order reaction of noninteracting reaction centers assuming that site relaxation is a tunnel process, the tunnel parameter  $\lambda$  being subject to a Gaussian distribution. Data of hole burning rates have been evaluated via model fits. Successful application of the concept to analysis of literature data for the recovery of photochemical holes suggest that a Gaussian distribution function for the rate-controlling parameter is superior to the conventionally constant distribution function with cutoff condition.

5. *Energetic Relaxation of Triplet Excitations in Vitreous Benzophenone*

R. Richert, H. Bässler, Chem. Phys. Lett. 118 (1985) 235 - 239

Time-resolved phosphorescence spectra of vitreous benzophenone have been recorded at 4.2, 77, 120 and 140 K within the time domain 2  $\mu$ s to 20 ms for sampling times between 2 and 500  $\mu$ s. They show energetic relaxation of triplet excitons within the inhomogeneous distribution of bulk states at a rate of  $\approx 100 \text{ cm}^{-1}$  per decade time as predicted by computer simulation.

4. *Analysis of Non-Exponential First-Order Reactions*

R. Richert, Chem. Phys. Lett. 118 (1985) 534 - 538

Kinetics determined by an ensemble of time-independent but statistically distributed rates have been investigated mathematically. Some analytically resolved properties of the corresponding decay function are stated with respect to their application to experimental results. This approach to dispersive processes is briefly compared to the well known  $\exp(-t^\alpha)$  law.

3. *Merocyanine - Spiropyran Transformation in a Polymer Matrix: An Example for a Dispersive Chemical Reaction*

R. Richert, H. Bässler, Chem. Phys. Lett. 116 (1985) 302 - 306

The non-exponential time dependence of spiropyran  $\leftrightarrow$  merocyanine transformation in a co-polymer has been reinvestigated experimentally and analysed in terms of a dispersive first-order chemical reaction. Non-exponential dependence can be accounted for by a Gaussian distribution of activation energies whose width decreases with increasing temperature.

2. *Time-Dependent Non-Equilibrium Exciton Diffusion in an Organic Glass*

R. Richert, B. Ries, H. Bässler, Philos. Mag. B 49 (1984) L25 - L30

Decay of donor phosphorescence is used as a sensor for time-dependent diffusion of triplet excitons in an amorphous organic solid (benzophenone) where diagonal disorder of the hopping sites prevails. The exciton jump rate is found to follow a  $t^{\alpha-1}$  law. Between 4.2 K and 100 K the dispersion parameter  $\alpha$  increases from 0.25 to 0.55. The results are compared with computer simulations based on experimental data for the density-of-states distribution.

1. *Monomer and Excimer Triplet States in Glassy Phenanthrene*

R. Richert, H. Bässler, Chem. Phys. Lett. 95 (1983) 13 - 17

Phosphorescence spectra recorded with vapor-deposited glassy phenanthrene layers reveal the existence of several inhomogeneously broadened monomeric triplet traps of structural origin and two excimeric triplet traps. Temperature-dependent studies yield estimates for both the triplet excimer binding energies and the parameters governing triplet trapping kinetics.

*Disorder Effects on Relaxational Processes: Glasses, Polymers, Proteins*

R. Richert, A. Blumen (Eds.), Springer, Berlin, 1994, p.1 - 754

The field of non-crystalline materials has seen the emergence of many challenging problems during its long history. In recent years, the interest in polymeric and biological disordered matter has stimulated new activities which in turn have enlarged the organic and inorganic glass community. The current research fields and recent progress have extended our knowledge of the rich phenomenology of glassy systems, where the role of disorder is fundamental for the underlying microscopic dynamics. In addition, despite the lack of a unified theory, many interesting theoretical models have recently evolved. The present volume offers the reader a collection of topics representing the current state in the understanding of disorder effects as well as a survey of the basic problems and phenomena involved.