Fluctuation dissipation relation and scaling behavior during aging in polymer glasses

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ABSTRACT OF DISSERTATION

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ABSTRACT

The goal of this work is to study the validity of the fluctuation dissipation relation (FDR) during aging in a glassy polymer and in general glassy dynamics, through probing aging dynamics, in thin films of polyvinyl acetate (PVAc). We use a rapid quench process by applying local radiation heating to a thin layer capacitor. The time evolution of polarization noise and dielectric susceptibility are analyzed in the frequency range 0.0259 Hz-13.307 Hz following quenches from above to below the glass transition temperature ($T_g$). It is found that understanding and eliminating various artifacts such as signal drift, non-stationary responses, extraneous noise spikes due to differential thermal contractions, also reducing the effect of spectral leakage due to the finite Fourier transform artifacts and a careful background signal subtraction are very important for accurately determining effective temperature. We find moderate FDR violations, which remain clearly above the bath temperature for more than 100s after quench for frequencies < 0.4159 Hz. This corresponds to $f t_w$ > 10, much larger than for spin glasses. However, we also detect a very strong violations which rapidly decay, with $T_{eff}$ > $10^3$, for the lowest frequencies and shortest aging times, $t_w$. Our measurements of the dielectric response in glassy polymers at the equilibrium and aging regime in frequency range of $10^{-3}$ to $10^5$ Hz provide a direct analogy with the magnetic-susceptibility aging studies in spin glasses. We can then examine if the theories proposed for spin glasses have relevance for glassy polymers. The results of these experimental studies are important in understanding the relaxation dynamics of glassy systems and in testing the validity and the relevance of the effective temperature concepts and also distinguishing between different theoretical models.
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CHAPTER 1

INTRODUCTION

Glasses have been known to humans for ages, but still we lack the very understanding of this state of matter, as well as the transition from liquid to glass on cooling. This transition is considered to be one of the important unsolved problems in condensed matter physics [24]. Glassy systems serve and represent a good prototype to understand slowly and non-exponentially relaxing complex dynamical systems such as protein structures, neural networks, superconductors and granular assemblies [25-27].

Their slow response makes them the most ideal for the study of non-equilibrium statistical mechanics. Despite the importance of the glassy state and glass transition in our life, the nature of this state is enigmatic and still largely in dispute. Although important work continues to be done in this field [28], there is not yet a unified theory that explain the complex nature of glassy dynamics.

Glassy materials play an important role in many technologies and the understanding of their physical properties has become a major research subject. They are characterized by the absence of structural long-range translational order and slow relaxation to equilibrium after rapid quench from the liquid phase to any temperature below their glass transition temperature $T_g$ [29]. This latter phenomenon, which is known as aging, is one of the most enigmatic properties of these materials. More precisely, aging is a dependence of some observables on the age of the system characterized by the study of the time evolution of the response functions, such as mechanical, magnetic, or dielectric properties following a temperature quench. The scaling behavior of the
response curves vs. time of the measurement, t, or frequency, f, with the age of the system since the quench, $t_w$, suggest that the faster modes equilibrate first and faster [30, 31]. This together with the contribution of the memory and rejuvenation effects [32-34], may indicate the presence of a hierarchically structured energy landscape, at least in spin glasses. Because the relaxation to equilibrium is slow, aging glasses are also ideal models for studying non-equilibrium statistical mechanics. For example, the recent development of a non-equilibrium Fluctuation Dissipation Relation (FDR), which relates the thermal fluctuations to response functions, is being largely studied in hopes of generalizing it to weakly out of equilibrium systems [35-37].

Recent theoretical work, which focused on non-equilibrium system evolving slowly, has shown the FDR violations by various mean-field spin glass [38] and structural glass [39] models. This violation can be used to define an effective temperature $T_{\text{eff}}$, which behaves as a real temperature and deviates from the bath temperature. This deviation is a strong indication of FDR violation. Also, computer simulations found FDR violations in finite range spin glasses [41, 42], kinetically constrained lattice gases [43], and domain growth processes [12]. In all cases, The $T_{\text{eff}}$ has been model-dependent, but the violations are found only for $t_w$ that are of the same order or short compared to the measurement time scale, t, i.e. for $t_w/t = ft_w \leq 1$, where f is a measurement frequency.

For these reasons, in the last years, there has been a growing interest to the study of the thermal noise of glassy materials during the aging process. However, there are a large number of theoretical studies dedicated to this subject but only a few experiments have been done in order to test the validity of those models [18-23]. This gap between
theory and experiment may be due to the fact that the regime $f \tau_w \sim 1$ is very difficult to reach. So, new experiments are necessary to understand the FDR in aging glasses.

The first experiment testing these ideas, from our group, showed a weak violation of the FDR in a super-cooled liquid, glycerol [44], following a temperature quench below its glass transition temperature at a single frequency. Long lived violations are observed even with $f \tau_w >> 1$. Recently, we studied the FDR violation on a glassy polymer, Polyvinyl Acetate (PVAc) [45], and we reported the initial results of 15 runs of 1 hour duration which allow us to see the large initial FDR violations. There have been also a handful of other experiments polymers, complex fluids [15, 17], and spin glasses [5]. Electrical thermal noise experiments on Laponite complex fluids and polymers [17] found a huge value of $T_{\text{eff}} \sim 10^6$ K for low enough frequencies at the early time after quench and long-lived violations. Although this has been interpreted as evidence for coarsening dynamics (where $T_{\text{eff}} \to \infty$) a conclusive explanation of the origin of these high values is still unknown. However, these experiments demonstrate very large delta-function-like noise spikes, which were often superior to 5 $\sigma$ in height of the standard deviation of the background noise signal measured in a two decade frequency window near equilibrium. Their sample volumes were of order 10 cm$^3$. We can estimate approximately the total equilibrium noise integrated over all frequencies from dielectric susceptibility data, would give $\sim 5\sigma$. If all of dipoles involved were cooperatively to reorient simultaneously, we would get a single spike, $\sim 5\sigma$ in altitude or perhaps a little higher due to a higher effective temperature. Thus the observed spikes would require nearly the entire 10 cm$^3$ sample volume to coherently fluctuate in terms of strong coupling between electrical dipoles. Therefore the spikes cannot be from the same dipolar
degrees of freedom as those which produce the rest of the noise signal, and are likely extrinsic, e.g. due to differential contractions and macroscopic strain release of amplifier surge power.

Another experiment testing the Einstein relation [15] showed FDR violations in Laponite only after considerable aging time. Whereas the spin glass [5] experiments qualitatively fit the theory in that FDR violations were found for $t_w / t = f t_w \leq 1$.

Recently, an experiment was performed on epoxy glassy former Triphenylolmethane triglycidyl ether (TPMTGE) [46]. At the thermodynamic equilibrium the polarization noise agreed with the predictions if the Fluctuation dissipation theorem (FDT) linking noise spectral density to susceptibility. On the contrary, a strong violation of the theorem was observed after a fast cooling below $T_g$: an intense polarization noise was detected, with a power spectral density following an inverse power law frequency behavior, whose intensity was decreasing with aging time. At the lowest frequency 0.2 Hz, a strong deviation from FDT prediction occurs just few degrees above $T_g$ and $T_{\text{eff}}$ reaches huge values ($> 10^5$ K) at low temperatures. At the same time, the amplitude of polarization fluctuations showed a non-Gaussian distribution, with their widths reduced during the aging process, up to recover the Gaussian statistics on approaching the equilibrium. As an interpretation to their large $T_{\text{eff}}$ at low frequency, they related their founding to the prediction of domains growth [12, 40] and activated dynamics models [47, 48] where the evolution of the system close to $T_g$ in deeper and deeper valleys of the energy landscape was associated to rare jumps between traps, giving rise to intermittent dynamics. The intermittency could cause the strong violation of FDT at low frequency and could be accountable for the huge values of $T_{\text{eff}}$. Their sample
volume was of the order of 2.826 cm$^3$. It is a bulky system where those large and rare peaks or bursts can not be attributed to the system dipoles. They are likely extrinsic noise as explained above for the Laponite experiment [17].

The still puzzling feature of the structural glass experiments is the fact that violations decayed much slower ($f_{tw} > 100$) than predicted by simple models. These results suggest that the excess in energy flows from slower to faster relaxing modes [44]. This may relate to slow structural recovery in glasses [49], but suggests to us highly cooperative relaxation mechanisms such as those found in series kinetics [50] models.

The present work of this thesis is conducted in this direction, focusing on dielectric fluctuations during the aging of a glassy polymer Polyvinyl Acetate (PVAc). The time evolution of noise and dielectric susceptibility is analyzed in the frequency range 0.0259 Hz-13.307 Hz following quenches to below the glass transition temperature ($T_g$). The results of these studies are very important in understanding the relaxation dynamics of glassy systems and in testing the validity and relevance of effective temperature concepts. The origin of aging time $t_w$ is defined as the instant when the quench start, the sample transition temperature is found to $T_g = 308.2$ K, which may depend on the cooling rate. The system falls out of equilibrium when it passes $T_g$. However adjustment of $T_g$ of a few degrees will shift the time reference by at most 0.33s, which has negligible effect on our results.

In addition to noise measurement, we will characterize the time dependence of frequency-dependent dielectric susceptibility of PVAc following quenches to below and above transition temperature $T_g$ in frequency range of $10^{-3}$ to $10^5$ Hz. We also illustrate equilibrium data at different temperature and frequencies in order to study the $\alpha$-
relaxation process. These measurements of response function in glassy polymer PVAc provide a direct analogy with the magnetic susceptibility aging studies in spin glasses. We can thus examine if the theories proposed for spin glasses have relevance for glassy polymer systems [31].

This thesis is organized as follows. A brief introduction to the glassy system and glass transition, basic notions and definitions, open question and references to recent experiments and simulations is discussed in chapter 2. A justification of why noise was chosen as tools for studying glassy systems with some basics of dielectric response in glasses that motivate the experiments presented in this work are given in chapter 3. The fluctuation dissipation relation (FDR) and its application to glassy systems during aging process are discussed in chapter 4. The experimental setup, apparatus and measuring techniques are described in chapter 5. The explanations of the time dependence of the frequency-dependent dielectric susceptibility of PVAc within the equilibrium and aging regimes, also their comparisons with spin glass experiments are described in chapter 6. FDR experimental results and analysis with their interpretation are shown in chapter 7. Further discussion, conclusions and perspectives are presented in chapter 9.
2.1 Glassy state

Structural glasses can be defined as non-crystalline solids which are characterized by the absence of structural long-range translational order while on short ranges the structure may be similar to a crystal. In these materials structural relaxation times become extremely long and diverge for any practical purposes when the temperature is decreased well below the glass transition temperature $T_g$. Glassy materials are therefore never in equilibrium on laboratory or even on geological time scales. Common examples of structural glasses include rapidly quenched simple liquids, polymers, ceramics and amorphous metals. The common method of producing glasses is a cooling process from a liquid or melt phase while suppressing crystallization to maintain the isotropic state of the melt. This kind of suppression can be accomplished with sufficiently fast cooling rates, which freeze the system in the amorphous state of the liquid before any molecular reorganization is possible. The glass transition plays an important role in life. Many microorganisms and insects preserve themselves by freezing their body systems and transforming into a glassy state for survival [50] while the life time of some protein-based medicines has a direct relation to their glassy dynamics [51]. Many polymer products (such as plastics) are amorphous. Injection molded plastics undergo gradual contraction and maintain their shape well when cooled through the glass transition.
Regardless of the importance of glassy state and glass transition in our daily lives, this state of matter remains one of the most fascinating phenomena in condensed matter physics and is far from being well understood. The transition from liquid to glassy state is considered as one of the greatest unsolved problems in condensed matter physics [24]. The understanding of structural relaxation and physical aging phenomena in glassy material is also technologically important for components that are polymer-based such as CD and DVD. The lifetime of the data on these digital storage devices are mostly determined by the structural relaxation times of their molecules.

A general understanding of the glassy state of matter will also be relevant to a number of other poorly understood systems, including proteins, granular assemblies, and spin glasses, soft materials such as gels, foams, and colloids. This topic is still of intense interest [24]. Although there have been many attempts to understand the nature of the glass transition, no theory has yet been proposed that captures all salient features of this phenomenon.

2.2 Glassy dynamics and glass transition

In many liquids systems, cooling slowly below the freezing temperature would cause crystallization. This can be avoided if the cooling rate is rather fast enough to escape any possible molecular reorganization by freezing of motion within the amorphous structure of the substance. More complex molecules have an easier time avoiding crystallization. As the liquid substance cools further below the glass transition temperature, \( T_g \), its viscosity would rapidly increase and that would cause the super cooled molecules to
become more and more sluggish which means molecular mobility decreases. Finally, the viscosity approaches that of a solid state.

Figure 2.1 Volume, enthalpy vs. temperature at constant pressure [1].

The glass transition has thermodynamic signatures, like a sudden drop in the heat capacity of the substances. Even though thermodynamic quantities such as volume, entropy, and enthalpy exhibit a change in slope, the process is still continuous [Figure 2.1]. On the other hand, the first derivatives of those thermodynamic variables such as thermal expansion, compressibility and heat capacity show a discontinuity at $T_g$. This resembles a second order phase transition. However, since there isn’t any obvious order parameter observed below the glass transition, this is inconsistent with such a transition.
In figure 2.1, in the temperature region of $T_{ga}$ to $T_{gb}$, the cooling rate is faster than the critical value. In that region the physical quantities such as volume and enthalpy gradually change. This is also defined as the glass transition region. The temperature at which the substance passes through the glass transition exhibits sensitivity to the rate of cooling process.

When a glass forming liquid is cooled, its viscosity increases, or on the contrary its mobility decreases, this defines the glass transition temperature. As the liquid attains a certain viscosity ($10^{13}$ poise) [26] then that temperature is defined as $T_g$ and it is said to be in the glassy state. This correlates to a molecular relaxation time $\tau$ of about 100 seconds.

The most noticeable feature of the glass transition upon cooling a liquid slowly into the glassy state is its rapid increase of the characteristic relaxation time. This increase is more rapid for some liquids, the so-called fragile liquids.

![Figure 2.2 The plot of viscosity changes vs. temperature ratio $T_g/T$ [1].](image)
Figure 2.2 shows Angell plot of the viscosity (or relaxation time) as a function of inverse temperature (Arrhenius form) scaled by $T_g$. The strong and fragile pattern of the liquid behavior is shown. Strong liquids exhibit approximate logarithmic linearity (Arrhenius) while fragile liquids exhibit non-Arrhenius behavior that is well described by [26] Vogel-Fulcher-Tammann (VFT) law (Equation 2.1). Angell [52] first proposed a useful method to quantify fragility by introducing a term called the fragility index $m$ (a dynamic property). Silica (SiO$_2$) and germanium dioxide (GeO$_2$) are strong glass formers and the viscosity and relaxation time of those glass formers can be well fitted by the Arrhenius equation [2.1].

$$\eta = A \exp\left(\frac{E}{k_B T}\right)$$

2.1

Where, $A$ and $E$ are temperature independent constants and $k_B$ is Boltzmann’s constant, and $T$ is the temperature. Relaxation times are found to follow a similar form.

The fragility factor, $m$, is determined by measuring the local slope of the viscosity curve at the temperature equal to the glass transition temperature $T_g$ [53].

$$m = \left. \frac{\partial \log(\eta)}{\partial \left(\frac{T}{T_g}\right)} \right|_{T=T_g}$$

2.2

Where, $\eta$ is the viscosity of the super-cooled material.
In the figure 2.2, the viscosity of the fragile liquids exhibits a deviation from the Arrhenius behavior. Additionally in the glass transition region, the relaxation time increases faster than activated energy or Arrhenius dependence. This non-Arrhenius behavior is well fitted with the Vogel-Fulcher-Tammann (VFT) law [Equation 2.3].

\[
\tau(T) = \tau_0 \exp\left(\frac{A}{(T - T_0)^\gamma}\right)
\]

Where \(\tau_0\) and \(A (=E/k_B)\) are temperature independent constants and \(\gamma=1\). Note that the Arrhenius relation (equation 2.1) can be obtained from VFT law (equation 2.3) by simply setting \(T_0 = 0\).

This equation further suggests that the relaxation time diverges at a temperature \(T_0 < T_g\) which is a possible indicator of a phase transition at \(T_0\).

The origin of this non-Arrhenius behavior near to \(T_g\) that is described by the Vogel-Fulcher-Tammann law (equation 2.3) is still not fully understood even though it has been shown to be quite experimentally accurate. In the next section, previous theoretical and experimental works and explanations of Vogel-Fulcher-Tammann law are described briefly.

The complex dynamical nature of the glassy dynamics can be explained in terms of a complex energy landscape [2]. The strong and the fragile behavior of the glass formers can also be distinguished from the potential energy landscape diagram.
The activation energy of the strong glass former is almost constant. The landscape of this strong glass former may consist of a single mega basin (single energy scale). In contrast, the activation energy of the fragile glass former increases near to the glass transition. Because of this non-Arrhenius behavior, the landscape of the fragile glass may contain multiple well-separated mega basins [1] as shown in the following figure 2.3. The small barriers inside the deeper (less frequent) wells allow the fragile liquids to have a glass structure that can be reorganized so that their structure fluctuates over a wide variety of different orientations.

Figure 2.3 Schematic representations of the energy landscapes of strong and fragile substances. The potential energy increases vertically, and the horizontal direction represents collective configurational coordinates [2].
Several phenomenological and theoretical approaches have been developed to describe the diverging relaxation time near to the glass transition. Adam and Gibbs [54] first proposed that the relaxation in glasses occurs via the cooperative relaxation of small domains. This idea stated that the rearrangement of the glass constituents required that a certain number of them change their position simultaneously, i.e. relaxation of a certain molecule needs the rearrangement of neighboring molecules (cooperative relaxation).

In a previous work Gibbs and DiMarzio [55] proposed that a second order phase transition takes place when the configurational entropy vanishes (at $T=T_K$). The configurational entropy, which is related to the number of minima in the system’s energy landscape, is that part of the entropy which is due to configurational rather than vibrational degrees of freedom. It can be calculated by subtracting the entropy of the crystal from that of the super-cooled liquid. This phase transition solves the Kauzmann paradox (which is the apparent result that it is possible to obtain a super-cooled liquid with entropy lower than that of its corresponding crystal. This is viewed as a paradox, since the disordered liquid must have higher entropy than the ordered crystal.) [27], by introducing the “ideal glass” concept with configurational entropy $S_c=0$.

The Adams and Gibbs theory explains the temperature dependence of relaxation behavior in glasses in terms of the temperature variation of the size of the cooperative relaxing domains. The ideal glass would have only one macroscopic cooperative region (the whole sample) with $S_c=0$. The temperature dependence for the relaxation time proposed is:

$$\tau(T) = \tau_0 \exp\left(\frac{A}{TS_c}\right)$$

2.4
Where, $\tau_0$ and $A$ are temperature independent constants.

If $S_c$ goes to zero at a finite temperature the VFT law (equation 2.3) is recovered, provided that $T_K \equiv T_0$. In many glass formers the temperature of structural arrest is very close to $T_K$ obtained from calorimetric measurements, typically $0.9 < T_K/T_0 < 1.1$ [56].

According to this picture, the origin of the viscous slow-down close to $T_g$ is the decrease in the number of configurations that the system is able to sample. At $T=T_K$ a kinetic structural arrest is predicted since $S_c = 0$ and no other configuration is available to the system, reaching the ideal glass state.

If we consider a system far below $T_g$ in which the configuration entropy is frozen and the relaxation time to a certain perturbation can still be measured, Equation 2.4 predicts that an Arrhenius law should apply. Furthermore, the activation energy will depend on the frozen-in entropy. If the system is only slightly below $T_g$, then the configurational entropy will change with time as the system evolves toward equilibrium. In this case non-linear relaxation is expected since $S_c$ itself will change with time as given by Equation 2.4 because it is a structural relaxation governed quantity.

2.3 Non-exponential relaxation functions

Viscous liquids near to the glass transition temperature exhibit non-exponential decay in response functions. If the temperature of a fragile glass former is suddenly dropped, the volume does not approach the new volume exponentially. The same response
is observed when applying an electrical field; the molecules of the glass will not arrange to the equilibrium average orientation exponentially. These response functions can often be very well approximated by a stretched exponential or Kohlrausch-Williams-Watts (KWW) function.

\[ \varphi(t) = \varphi_o \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \]  

2.5

Where \( \beta \) (the stretching exponent) is a phenomenological shape parameter measuring the deviation from single exponential decay (\( \beta=1 \)) and \( \tau \) is a parameter with time units (or the usual relaxation time in the case \( \beta=1 \)). The smaller the value of \( \beta \), the less exponential the response function. Although KWW functions are usually used as an empirical two-parameter fitting function, a theoretical derivation can be obtained in statistical mechanics context [57]. Typical \( \beta \) values for fragile glass formers are around 0.5 near \( T_g \) and usually decrease with decreasing temperature.

This non-exponential behavior can be explained in two fundamentally different ways. One way is to think of a glass as composed of many independent domains. In this heterogeneous picture [Figure 2.4], the domains would each relax in an exponential way, but their relaxation time would vary significantly among domains. The resulting average correlation function observed in macroscopic sample, averaging over the ensemble would be a stretched exponential response. On the other hand, one can think that the domains relax nearly identically in an intrinsically non-exponential manner. This would give the
same kind of response in a macroscopic sample indistinguishable from the first scenario. This thought of a glass as composed of different domains that relax cooperatively has long been postulated by Adam and Gibbs [58] in their entropy theory for relaxation.

Recently, a number of experiments [59-65] and simulations [66-68] have found evidence for dynamical heterogeneity in relaxation time. Several of those experiments are using different techniques like NMR [69, 70], light scattering [71], dielectric relaxation [72], and dielectric hole burning [73, 74] show an agreement with the heterogeneous picture. Other experiments using neutron scattering [75] showed that the homogeneous scenario would be a better description of the non-exponential relaxation process in glasses.

![Figure 2.4 Dynamical heterogeneity: molecules with similar relaxation times are clustered.](image)

In the diagram 2.4 the glassy region is divided into a number of small clusters and those clusters have very different relaxation times. In addition it shows that the molecular
clusters in region A move rather faster than those in regions B and C. Experiments using confocal microscopy on glassy phases of colloidal particles [3] have also demonstrated cooperativity and heterogeneity near to glass transition $T_g$. In figure 2.5 even though all colloidal particles have the same size, in order to clarify and visualize the heterogeneities, those colloidal particles with higher mobility were represented by a larger size. The apparent heterogeneity in the clustering of high and low dynamical mobility seems to support the idea of spatial non-homogeneity of dynamics [3].

Figure 2.5 The evidence for the cooperative and heterogeneous picture of the dynamics near to glass transition is shown from the glassy phase of the colloidal particles [3].

2.4 Physical aging in glassy systems
When a glassy system is quenched from above to below the glass transition temperature $T_g$, any response function of the material depends on the time $t_w$ elapsed from the quench [76]. For example, the dielectric and elastic constants of polymers continue to evolve several years after the quench [76]. Similarly, the magnetic susceptibility of spin-glasses depends on the time spent at low temperature [77]. Another example of aging is given by colloidal-glasses, whose properties evolve during the sol-gel transition which may last a few days [78]. For obvious reasons related to the applications, aging has been mainly characterized by the study of the slow time evolution of response functions, such as the dielectric and elastic properties of these materials. It has been observed that these systems may present very complex effects, such as memory and rejuvenation [76, 79-81], in other words their physical properties depend on the detailed thermal history of the sample.

Figure 2.6 Plot for TRM decay (first column) with four cooling protocols. It should be noted that the magnetization (y-axis) is scaled by the field cooled magnetization [31].
The figure 2.6 shows an example of physical aging in a magnetic system, which described that the thermoremanent magnetization decays with the waiting time, $t_w$, and can sometimes be scaled by functions of $t/t_w$. By employing a series of cooling protocols, they demonstrated that the rate at which the sample is cooled to the measuring temperature plays a major role in the determination of scaling procedure.

Understanding physical aging properties of the amorphous materials have tremendous economic implications in long-term usage of industrial applications. For example, the properties and applications affected by aging in design, manufacture and performance of polymer-based composites, automotive applications of polymers, adhesives and permeability of packaging materials, curling of photographic film supports, non-linear optic materials, curling of epoxies, the optical, electrical and mechanical properties of graphic materials and glass to metal seals.

The aging properties of the glassy polymers are strongly influencing the industrial usage of these materials in devices. In most devices glassy polymers are selected in order to delay the polymer aging effect compare to device lifetime. One such example is the life times of the digital data in storage devices such as CD’s, DVD’s. The compact disk (CD) pits are subject to physical aging. Structural relaxation in the sub-micron holes in a polymer layer which represent the information on a CD or DVD leads to a gradual recovery of the pitted material. This diminishes the quality of the data imprint, or can be used intentionally to limit the disc to a certain effective lifetime.

In order to slow down the physical aging effects in digital devices, the glassy polymers substance are nicely selected such that the glass transition temperatures of them
are relatively higher than room temperature which give them some resistance to the aging process and long lifetime.

In recent times, new types of CD’s and DVD’s are being introduced to the market so that the lifetimes of those digital storage devices are much shorter (in weeks) than usual storage devices. Those devices are being used in the entertainment industry (movie rental stores). In order to have shorter lifetime in them, the glassy polymers are chosen such that the glass transition temperatures of those polymers are closer to room temperature of regular usage.

2.5 Fluctuation-dissipation relation

The FDR relates the linear response of a system [susceptibility] to an applied field to the fluctuation properties of the thermal equilibrium of the system [82]. In 1928, Nyquist [83] introduced the FDR for electrical circuits from classical statistics. His work was prompted by Johnson’s experiments on electrical noise. The Nyquist formula has a widespread application in equilibrium systems. In linear electrical networks, it relates the voltage noise spectral density, $S_V$, to the network resistance or real part of the impedance, $Z$, by equation 2.7.

$$S_V(T) = 4K_B T(\text{Re}(Z))$$  \hspace{1cm} 2.7
Earlier in 1905, specific FDRs were derived for the Brownian motion and pressure fluctuations in gas. In Brownian motion, the Stokes-Einstein relation [equation 2.8] states that diffusion constant scales inversely with viscosity.

$$D = \frac{k_B T}{6\pi \eta_0 R}$$

Where $D$ is the diffusion constant, $\eta_0$ is the viscosity and $R$ is the radius.

The FDR has been derived for specific cases, but Kubo [82] derived the FDR as a general theorem, the fluctuation-dissipation theorem in 1966.

In general when a system is in thermodynamic equilibrium, FDR relates the system’s linear response function to its equilibrium fluctuations. However, if the system is out of equilibrium, the linear response may not be proportional to the fluctuations. This so-called FDR violation has been found for a mean field theory of spin glass models below some critical temperature [38, 40]. Weak FDR violations were also observed in experiments on structural glasses after a quench from just above and just below $T_g$ [44], as well as in experiments on spin glasses [32].

Since the time dependent properties of a glassy system after the quench from $T_g$ are accessible for measurement due to relatively long response times, this can yield an interesting insight into non-equilibrium dynamics by exploitation of non-equilibrium
fluctuation-dissipation relations in general. This can be used to test and explain out of equilibrium FDR for complex systems.

Glassy systems represent an ideal environment for studying non-equilibrium statistical mechanics. However, insight from glass model systems such as glassy colloidal systems and computer simulation models are somewhat useful, but are not clearly connected with experimental measurements on molecular glasses. Colloidal and molecular dynamics simulations are incapable to access the important regimes of glassy dynamics on long time scales and at low temperature scales due primarily to size scaling.

As an example, figure 2.7 [5] illustrates direct measurements of FDT violations in the time domain have been reported for insulating spin glasses [5]. FDT violations have been measured beyond the quasi-stationary regime and experimental FD plots have been found to be consistent with results obtained by numerical simulations in spin-glass models. However, the value of the effective temperature obtained in these experiments is much larger than the annealing temperature at which the system is equilibrated before the quenching takes place, casting doubts on the meaning of the effective temperature as a thermodynamic temperature in these experiments. Moreover, these measurements reveal that, within the experimentally accessible time window, FD curves $\chi(C)$ are time dependent and quite far from the expected asymptotic curve.
Figure 2.7 FD plot obtained by measuring voltage autocorrelations and relaxation susceptibility in the insulating spin glass CdCr$_{1.7}$In$_{0.3}$S$_4$ quenched from $T = 1.2T_g$ down to $T = 0.8T_g$ ($T_g = 16.2$ K). Effective temperatures are around 30 K and much larger than the annealing temperature $19.4$ K [5].

2.6 Questions related to the dynamics of glassy systems

Even though recent results from experiments, molecular dynamics simulations and model theories have demonstrated the cooperative and spatially heterogeneous nature of the dynamics near the glass transition, still much remains to be understood in these aspects.

One of the most mystifying properties of these glassy systems is the very slow relaxation behavior towards equilibrium, named *aging*, which represents an interesting and unusual phenomenology. Many models and theories have been constructed in order to enlighten the observed phenomenon, which is not yet completely understood. These models either predict or assume very different dynamical behaviors of the systems during
aging. This dynamical behavior can be directly connected to the thermal noise features of these aging systems and the study of the response functions alone is incapable to give ultimate answer or elucidation on the approach that are the most tailored to explain aging of a specific materials. Thus it is important to combine the measurements of thermal noise with that of response functions. This measured fluctuations are also related to another very important aspect of aging dynamics, that is the definition of an effective temperature in these systems which are weakly, but strongly, out off equilibrium. In fact recent theories [38] based on the picture of spin glasses by mean field approach proposed to broaden the concept of temperature using a Fluctuation Dissipation Relation (FDR) which generalizes the Fluctuation Dissipation Theorem (FDT) for a weakly out off equilibrium system [11, 35, 40, 84].

For all of these reasons, in the current years, the study of the thermal noise of aging materials has received a rising interest. Conversely in spite of the large amount of theoretical studies there are only a small number of experiments devoted to this problem [5, 14, 15, 17, 44, 45, 59, 85-90]. The existing experimental results are in some way in disagreement and they are incapable to give definitive answers. Hence, new experiments are needed and essential to increase our knowledge on the thermal noise properties of the aging materials and to fill in the remaining gap for true understanding of their complex dynamics. So, the present work of this thesis is conducted to follow this path, focusing on electrical fluctuations during aging of glassy polymer Polyvinyl Acetate (PVAc).
CHAPTER 3

NOISE AS A TOOL FOR STUDYING GLASSY SYSTEMS

Fluctuations have a long history as an essential tool for investigating materials, going back to 1909 when Perrin tried to confirm the Einstein’s theory of Brownian motion through his demonstration of the molecular picture of matter. From that time to today, the range of problems for which the fluctuations can be more enlightening continues to grow as attention shifts from fundamental issues to the numerous problems connected with complex systems. For some period of time, one of the most flourishing areas for noise research has been the study of glasses and other disordered materials. For such systems, ordinary macroscopic response functions have a tendency to miss some, if not all, of the information on the heterogeneity of a system. It is beneficial to look at small samples, for which individual domains start to become very significant, and for which fluctuations become significant compared to responses.

3.1 Fluctuation and noise sources

Fluctuations, or noise, like any other natural phenomena, are related to the internal dynamics physically, representing a response within the system. They can be described by physical laws. Therefore noise can also be used as a signal to study the dynamics of a system. The fluctuation can be caused by diverse mechanisms. The source of the noise determines how the noise reflects on the internal dynamics.
We can split the variety of studies in this field into two wide categories: those for which the properties measured are present in thermal equilibrium or quasi-equilibrium and those which are off equilibrium. Most of the fluctuation measurements of the first sort basically used a weak non equilibrium field probe to study the thermal equilibrium behavior of complicated mixed phases; i.e., fluctuations that were taking place whether or not the field was applied. This is what was done in the study of magneto-resistance of some materials[91]. On the other hand, many studies of the dynamics in glassy systems are looking at fundamentally non-equilibrium effects since most such dynamics vanish in equilibrium state. We normally suppose that the equilibrium-like measurements are explained by the Fluctuation-Dissipation Theorem [35, 38], even when the materials described, like most materials, have been unsuccessful to attain true thermal equilibrium in some respects, e.g., having more crystal defects than the equilibrium state would have. One of the most fascinating new developments to be investigated concerns the possible breakdown of the FDT in glasses. Theoretical arguments and some experimental data show that the slow approach to equilibrium continues to influence even fluctuations whose time scale is much shorter that the time for which the glass has aged [12, 38, 40, 92, 93].

One way that the noise can be probed is by gathering the time dependent response continuously from a noise source as a time series measurements. Then the time series are analyzed by Fourier transform, which yield insight into the frequency domain of the signal, to obtain its power spectra. The later can be statistically analyzed to study the dynamics of a system.
The physical origin of noise is not a unique source. In conductors there exist at least four kinds of fluctuations or noise observed. They are thermal noise, shot noise, 1/f noise (which has several mechanisms), and generation-recombination noise (this is one source of 1/f).

- **Thermal noise**, called Johnson noise or Nyquist noise, can be detected by measuring the *voltage or current fluctuations* across a conductor due to thermal agitation of electrons.

- **Shot noise** is detected by measuring the *current fluctuations* due to discreteness of the electrical charges (electrons) in electronic devices. This occurs not only in p-n junctions but as well in any conductors, and even in the case where the charge is not well localized. In the quantum optics, shot noise is caused by fluctuations of detected photons, and this the consequence of discretization of energy in electromagnetic field.

- **1/f noise** arises from the random motion of impurities or defects and can be detected by measuring low frequency *conductance fluctuations*. It can occur also in many other physical, biological and economic systems.

- **The generation-recombination** noise can be measured in the *fluctuations of the number of carriers* in the conductance and valence bands of a semiconductor due to the continuous trapping and de-trapping of charge carriers. Carrier generation and recombination processes are fundamental to the operation of many optoelectronic semiconductor devices, such as photodiodes, LEDs and laser diodes.
The common two forms of fluctuations that are of most concern in glassy systems are the thermal and 1/f noise. The thermal fluctuations are generated by the thermal agitation of electrons, ions, or dipoles in conductors or dielectrics. The maximum noise power $P$ in watts that can be delivered is given by [94]:

$$P = k_B T (\Delta f)$$  \hspace{1cm} 3.1

Where $k_B$ is the Boltzmann’s constant, $T$ is the conductor temperature and $\Delta f$ is the frequency bandwidth. The thermal noise power spectral density, $S$, of white noise, is constant throughout the frequency spectrum. The thermal noise spectral density in resistor, which often named as Nyquist relation, can be described as:

$$S = 4k_B TR$$  \hspace{1cm} 3.2

The defining characteristic of 1/f noise is that, in contrast of the flat or ‘white’ spectrum of thermal noise, its power spectral density, $S$, varies inversely with frequency as:
Where $\alpha$ is the spectral exponent ($\alpha \sim 1$).

1/f noise was first observed in vacuum tubes in 1925 [83]. It is not restricted to electronic devices but is everywhere in nature due to different mechanisms. In conductors, 1/f noise is only observed in the presence of a current since it is a resistance fluctuation. In semiconductor devices, it is caused by fluctuation in the mobility or number of electrons or charge carriers. In metals it is associated with defect motion. 1/f fluctuations were found in biological systems like human heart rates and other systems from DNA to organ cells. It is also measured in geophysical, meteorological and ecological systems [95].

1/f noise can be a valuable tool to investigate slowly evolving complex dynamical systems. Systems that exhibit a slow dielectric or magnetization relaxation after application of a small external field also often have 1/f thermal fluctuations, which could be probed even in equilibrium without excitation field.

**3.2 1/f$^\alpha$ noise characteristic in condensed matter**

One exceptional feature of 1/f noise is that it is self-similar, e.g. the signal time series looks similar in any time decade. This scale invariant characteristic is an intrinsic property of a **power-law spectrum**. Figure 3.1 shows an example of 1/f noise from our data measured at equilibrium and at temperature of 300K.
Figure 3.1 Plot of 1/f noise power spectrum, as calculated from the polarization noise response of a PVAc glassy polymer at equilibrium with T=300K.

In order to deeply study a complex dynamical system, we need examine the time and temperature dependence of spectral exponent in different frequency windows.

The spectral exponent $\alpha$ is defined as:

$$\alpha = -\left(\frac{d(\ln S)}{d(\ln f)}\right)$$

Where $S$ is the noise power spectrum and $f$ is the frequency.
The value of spectral exponent $\alpha$ in the time averaged 1/f noise power spectrum is practically equal to 1. Conversely, it is equal 2 for Brownian motion. In some special cases, such as the thermal drift caused by various mechanisms during the signal acquisition can raise the spectral exponent $\alpha$ to a value of 2. Figure 3.2 and 3.3 demonstrate an example of simulated 1/f and 1/f$^2$ noise signal. Their power spectral density is shown in Figure 3.4 which illustrated the scale invariant characteristic of power law spectrum.

Figure 3.2 Plot exhibits the aspects of simulated 1/f noise signal.
Figure 3.3 Plot exhibits the aspects of simulated $1/f^2$ noise signal.

Figure 3.4 Plot exhibits the aspects of simulated $1/f$ and $1/f^2$ noise power spectrum, the dashed line represent the fitting function.
1/f noise can be exploited to understand the kinetics of amorphous systems. Noise studies have continued from electronic devices, where they first were detected, to be extended to circuits, metallic conductors, semiconductors, diodes, photo diodes, bipolar transistors, quartz crystals, SQUIDs, piezoresistive cantilevers and carbon nanotubes, among others. In the field of biophysics the 1/f noise power spectral exponent has been analyzed in order to investigate the interaction between biological molecules and water [96]. Noise techniques have been employed in condensed matter as an essential tool to study low frequency dynamics in structural glasses [6] and spin glass systems [97].

3.3 Macroscopic scale thermal noise of a glassy system

![Diagram](image)

**Figure 3.5** Current or voltage fluctuations across a capacitor cell filled with a glassy polymer sample are measured in order to investigate the bulk glassy dynamics [6].

A capacitor circuit [figure 3.5] filled with an organic glass former can used to investigate the macroscopic dynamics of a glassy system [6]. The dielectric polarization noise of a glassy material can be collected by probing its current or voltage noise across the capacitor. The dynamics of the equilibrium glassy system are studied by investigating temperature and frequency dependence of the thermal polarization noise of a glass former.
near its glass transition temperature. The Nyquist formula can be used to relate the spectral density of the fluctuations to the dielectric susceptibility of the sample.

In the general form of the Nyquist relation (equation 2.7), we can relate the spectral density of voltage fluctuations $S_v$ to the real part of the sample impedance, $Z$.

\[ S_v = 4k_B T \text{Re}(Z) \]

The impedance $Z$ can be written in terms of the complex capacitance, $C^* = C' - iC''$, by using its real ($C'$) and imaginary ($C''$) parts.

\[
Z = \frac{1}{iC^* \omega} = \frac{1}{i(C' - iC'') \omega} = \frac{1}{\omega (C' + iC'')} = \frac{1}{\omega (C' + iC') (C' - iC')}
\]

\[ Z = \frac{1}{\omega \frac{C'' - iC'}{C''^2 + C'^2}} \]
And so, the real part the impedance \( Z \), can be:

\[
\text{Re}(Z) = \frac{1}{\frac{1}{\omega} \left( \frac{C'}{C} \right)^2 + \left( \frac{C''}{C} \right)^2}
\]  

3.7

Therefore from the equation 3.5, we can define the power spectral density of voltage fluctuations as:

\[
S_V = \frac{4k_B T}{\omega} \left( \frac{C''}{C'} \right) \left( \frac{C'}{C} \right)^2 + \left( \frac{C''}{C} \right)^2
\]  

3.8

Since \( C'' \) is much smaller than \( C' \), we can approximate and write \( S_V \) in its reduced form as:

\[
S_V \approx \frac{4k_B T}{\omega} \left( \frac{C''}{C'} \right) \left( \frac{C'}{C} \right)^2 \quad \text{for} \quad C'' \ll C'
\]  

3.9

Therefore, by using the definition of the tan\( \delta \) with \( \varepsilon' = \frac{C}{C_0} \) and \( \varepsilon'' = \frac{C''}{C_0} \) where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the dielectric constant of the system, \( S_V \) can be written in the following form:
\[ \tan(\delta) = \frac{C^*}{C'} = \frac{\varepsilon^*}{\varepsilon'} \]  \hspace{1cm} (3.10)

\[ S_V \approx \frac{4k_B T \tan(\delta)}{\omega C} \]  \hspace{1cm} (3.11)

In similar way, the spectral density of current noise can be related to the real part of the sample admittance \( Y \).

\[ Y = \frac{1}{Z} \]  \hspace{1cm} (3.12)

\[ S_I = 4k_B T \text{Re}(Y) = 4k_B T \text{Re}\left(\frac{1}{Z}\right) \]  \hspace{1cm} (3.13)

So, from equation 3.6 we get the real part of the sample admittance as:
\[ \frac{1}{Z} = \omega (C' + iC') \quad 3.14 \]

\[ \text{Re} \left( \frac{1}{Z} \right) = \omega C'' \quad 3.15 \]

By inserting equation 3.15 in equation 3.13, we get the finale form of \( S_I \) as:

\[ S_I = 4k_B T \omega C'' \quad 3.16 \]

Where \( C''(\omega, T) \) is a function of frequency \( \omega \) and temperature \( T \), and can be written in terms of the imaginary component of dielectric susceptibility \( \varepsilon'' \) as:

\[ C'' = \varepsilon'' C_0 \quad 3.17 \]

\[ S_I = 4k_B T \omega \varepsilon''(\omega, T)C_0 \quad 3.18 \]

Where, \( C_0 \) is the empty plat or geometrical capacitance.
The power spectral density $S_v$ and $S_i$ are examples of fluctuation dissipation relations (FDR), where the linear response function of the system is related to the fluctuation properties of system dynamics.

Figure 3.6 shows the temperature dependence of the current noise measured in a capacitor filled with glassy polymer glycerol at different frequencies [6]. The response function of the system reveals at certain temperature range measured the existence of a distinct peak. The magnitude of the noise peaks and the imaginary component of the dielectric susceptibility $\varepsilon''(\omega, T)$ measurements of glycerol [98] at those temperature and frequency were fitted with equation 3.16 [6]. The experimental results confirmed the FDR
in quasi-equilibrium state, but whether the FDR is satisfied in non-equilibrium state of the system continues to be investigated [44].

Low noise is not only restricted to electronic devices but is also widespread in nature due to the slow kinetics of different systems. So, as a powerful tool, it is used to probe the material properties at different state of existence in equilibrium or off-equilibrium. The time series of fluctuation, the noise power spectral density, and the statistical properties of the time series signal and the noise power are some of the quantities that are very significant to investigate in order to gain an insight into the dynamics of complex systems. Also, the temperature, time and frequency dependence of these quantities are studied.

Using this technique of noise measurement and its statistical properties, we study the aging process in glassy polymer (PVAc) and we try to probe the early stage of aging of the system where it suppose to be a huge violation of Fluctuation Dissipation Relation (FDR) and also in order to quantify the smaller and longer-lived violation. Further noise techniques and measurements will be discussed in chapter 5 and 7.
CHAPTER 4:
FLUCTUATION DISSIPATION RELATION (FDR) IN GLASSY SYSTEMS

In this chapter, we will concentrate our effort on proposed modifications to the fluctuation dissipation relation (FDR) in aging glassy system. For this reason, we will give a brief preamble on the fluctuation dissipation theorem (FDT) in systems in thermodynamic equilibrium. Afterward, we will discuss an approach based on mean field theory in which an effective temperature is defined for glasses out of equilibrium. Then we will discuss some numerical and experimental studies that have tested this approach.

4.1 Introduction

The search for a general theory of non-equilibrium processes has been a principal objective in modern statistical physics. In spite of many efforts in this direction, we have an incomplete understanding of the basic principles behind non-equilibrium theories. Evaluated with ensemble equilibrium theory, a general principle such as the equal probability Boltzmann principle (that forms the basis of equilibrium statistical mechanics and provides a statistical foundation of thermodynamics) is still lacking. During the last century, the field of non-equilibrium phenomena has grown-up in two main directions. One has been the development of new statistical models as an inspiring source of productive new concepts and ideas and second by establishing partial links among different, apparently disconnected, non-equilibrium phenomena.
Even though a large amount progress has been made in the first direction; the second one remains less investigated. Despite the fact that a general principle governing non-equilibrium systems probably does not exist at all, so, considerable progress could be made following the second route in the search for basic principles governing a constrained category or class of systems. The relevant applications of such basic principles may be very important because many different systems can fall into the same category type. Therefore the concern in the research on the existence of such restricted formulations.

Throughout the past years it has become gradually more apparent that glassy systems may represent one of these large categories where their physical behavior can be restructured within a constrained formulation. Glassy systems are rather common in nature and many systems such as spin glasses, structural glasses, granular materials, colloids, or proteins present what is called glassy behavior. This means a remarkable slowing down of relaxation processes when some control parameters are varied. A typical signature of glassy behavior is a power law or stretched exponential behavior of correlation functions, as opposed to exponential decay. As the characteristic relaxation time may change by several orders of magnitude it can easily exceed the observation time. As a consequence the system ages: the observed static and dynamic properties depend on the age of the system defined as the time since the system was prepared (also called waiting time). For this reason, this residual very slow non-equilibrium phenomenon is commonly known as aging.

Aging systems consist of a large range of materials. In reality, nearly all physical systems, within a suitable set of conditions and observed during a definite time window,
exhibit glassy properties. However, the origin of glassy behavior can differ from system to system. The most essential category of glassy systems, which contain typical window glasses that we deal with in every day life, are glasses forming liquids where glassy behavior is due to the appearance, as some external factor is changed or evolving with time, of a long-lived complex pattern of interacting bonds between their microscopic constituents which strongly slows down relaxation towards equilibrium. Aging follows from the very slow motion of such a complex pattern of interacting bonds which provokes a slow change of the atomic structure of the liquid. For this reason glass forming liquids are usually called structural glasses. Our present understanding of the slow glassy relaxation dynamics is greatly restricted by the lack of a general non-equilibrium theory that takes account these phenomena.

Glasses can be produced by the fast cooling of a liquid. Upon the cooling process from high temperatures down to the melting transition temperature $T_M$, sometimes crystallization does not take place and the liquid continues its way down in temperature beyond $T_M$ by following a line (called the super-cooled liquid line) which is the continuation of the liquid line. As the liquid line is thermodynamically stable only above $T_M$, the super-cooled liquid line is meta-stable with locally equilibrated properties, therefore its lifetime can be enormously large. As the cooling proceeds it is seen that the super-cooled liquid falls out of equilibrium (i.e. departs from the super-cooled liquid line), below a temperature $T^*(r)$ which depends on the cooling rate $r$. The state reached below $T^*(r)$ is called a glass and the corresponding relaxation regime is indistinctly termed as aging or glassy. For small values of $r$ a sharp transition is observed at $T^*(r)$, usually referred to as structural arrest, where the heat capacity jumps down,
demonstrating the freezing of degrees of freedom. The equilibration process may take an extremely long time being inaccessible from any practical point of view. Beneath some conditions the equilibration time can be larger than the age of the universe! In these conditions the glass state is the only observable state.

Long equilibration times mean that the glass state is characterized by very low energy dissipation rates, also called entropy production. This may give the false impression that the glass is in a stationary state. For example, a piece of silica glass at room temperature looks pretty stable; in fact its mechanical, electrical and optical properties seem constant in time. Though, a more cautious examination shows that the physical properties are constant only if observed on timescales much smaller than the time elapsed since the glass was prepared or formed. Beyond that timescale, the physical properties change revealing that the glass is aging.

Even though aging was identified a long time ago in the study of polymers [29] it has received new interest in connection with the study of spin-glasses. Measurements of the magnetization in spin glasses have shown that aging is a general property of the low temperature spin-glass phase. There are several types of spin-glass materials, the most common ones are metallic spin glasses. These are random diluted magnetic systems where glassy behavior arises from the disordered pattern of exchange interactions, rather than being self-generated as in structural glasses. Indeed random dilution generates exchange interactions with random competing signs; the system is then frustrated since a finite fraction of bonds cannot be satisfied. Aging is a consequence of the slow evolution of the pattern of satisfied bonds which becomes strongly inhibited as the temperature is lowered.
Another class of systems with glassy properties is *driven systems* which, under certain conditions, achieve a stationary state distinguished by non-Gibbsian probability distributions. After applying a time-dependent perturbation of frequency $\omega > 1/t_{eq}$, upon an initially equilibrated system of relaxation time $t_{eq}$, a new stationary state is reached which for many aspects is similar to the aging state of the relaxation system of age $\sim 1/\omega$.

An additional important feature of glassy systems that has received significant attention for a long time [99] is the idea of the existence of an effective temperature (sometimes also called fictive temperature) describing the non-equilibrium properties of the glassy state. Throughout the last decades, it has appeared that a possible way to rationalize the existence of an effective temperature is by measuring violations of the fluctuation–dissipation theorem (FDT). In glassy systems, a new modified relation between correlations and responses that goes under the name of FDR (fluctuation-dissipation relation) provides a description of the dynamics in the glassy state by quantifying the violations of the FDR. In this new theorem the effective temperature plays the role of the temperature of the bath. Related to the concept of the effective temperature is the idea of the existence of a heat flow from the glass to the thermal bath put in contact with the system. As the glass has an effective temperature higher than that of the bath, the heat flows from the glass to the bath. However, the energy dissipation rate from the glass towards the bath is extremely low (hardly quantifiable) and, in general, this flow can also be understood in terms of an effective very low thermal conductivity. In general, other definitions which use a generalization of different equilibrium relations to the non-equilibrium regime are possible. This gives rise to the problem of the
equivalence of all possible definitions. In this discussion, we will stick only to the FDR definition of an effective temperature.

In this work, we will concentrate on the existence of a FDR, its physical meaning, in what conditions it can emerge and the numerical and experimental evidence reported in favor of its validity. This is a rapidly growing area of research which is attracting new condensed matter and statistical physicists.

### 4.2 Fluctuation dissipation theorem

The fluctuation-dissipation theorem (FDT) relates the correlations of spontaneous fluctuations to the induced fluctuations in equilibrium. It is a model independent relation between the linear response and its associated correlation function that takes different forms for classical and quantum system. The later reduces to the former when quantum fluctuations become irrelevant. When the equilibration hypothesis is not justified, this relation does not necessarily hold.

Let’s consider \( O \) is an observable of a physical system and \( h \) its conjugate variable in the Hamiltonian function. In the absence of the external perturbation (\( h = 0 \)), we suppose the observable \( O \) have zero mean for simplicity [40]. So, we define the fluctuation autocorrelation function of the \( O(t) \) by:

\[
C(t,t_w) = \langle O(t)O(t_w) \rangle \quad 4.1
\]

Where \(<...> \) represent the mean of the ensemble.
The associated response function can be defined as:

\[ R(t,t_w) = \left. \frac{\delta \langle O(t) \rangle}{\delta \langle h(t_w) \rangle} \right|_{h=0} \]  \hspace{1cm} (4.2)

Which gives the linear response of the observable \( O(t) \) for an infinitesimal field \( h \) acting at time \( t_w \). Let us integrate the response function over a time interval going from awaiting time \( t_w \) to a final time \( t \):

\[ \chi(t,t_w) = \int_{t_w}^{t} dt' R(t,t') \]  \hspace{1cm} (4.3)

This yields a time integrated susceptibility that is exactly what is measured experimentally and which characterizes how the observable \( O \) responds to infinitesimal field step \( h(t) \) with:

\[ h(t) = h\Theta(t-t_w) \]  \hspace{1cm} (4.4)

With:

\[ \Theta(t-t_w) = 0 \quad \text{for } t \leq 0 \]  \hspace{1cm} (4.5)

\[ \Theta(t-t_w) = 1 \quad \text{for } t > 0 \]

Where \( \Theta \) is the Heaviside function.
In equilibrium thermodynamics, by using the time invariance translation:

\[ C(t, t_w) = C(t - t_w) \]  \hspace{1cm} 4.6

One can use FDT to show that:

\[ \frac{-\partial \chi(t-t_w)}{\partial t_w} = R(t, t_w) = \frac{1}{kT} \frac{\partial C(t-t_w)}{\partial t_w} \]  \hspace{1cm} 4.7

Where \( T \) is the thermodynamic temperature and \( k_B \) is the Boltzmann constant. In integral form:

\[ \chi(\tau) = \begin{cases} 
0 & \text{for } \tau < 0 \\
-\frac{1}{k_B T}[C(\tau) - C(0)] & \text{for } \tau > 0 
\end{cases} \]  \hspace{1cm} 4.8

Where \( \tau = t - t_w \). Hence if one draws a plot of \( \chi \) against \( C \), for increasing \( t_w \), in the large \( t_w \) limit the plot will approach a straight line of slope \(-1/k_BT\).

In the frequency domain, we start from expression of Wiener-Khinchin [100], relating the power spectral density \( S_\theta(f) \) of the signal \( O(t) \) and its autocorrelation function \( C(\tau) \) by the equation:
The factor 2 in the above expression can be explained by considering only the positive frequencies (we will add power density of frequency mode $f$ and $-f$). Then we will transform the equation 4.9 using that $C(\tau)$ is a real function:

$$S_o(f) = 2\int_{-\infty}^{+\infty} C(\tau) e^{i\omega \tau} d\tau$$

4.9

We introduce the value of $\partial_\tau C(\tau)$ given by FDT in the time domain (Equation 4.8), then we get:
\[ S_0(f) = \frac{4}{\omega} \text{Im} \int_0^{+\infty} k_B T \chi(\tau)e^{i\omega\tau} d\tau \]
\[ = \frac{4k_B T}{\omega} \text{Im} \int_0^{+\infty} \chi(\tau)e^{i\omega\tau} d\tau \]
\[ = \frac{4k_B T}{\omega} \text{Im} (\tilde{\chi}(f)) \]

Where \( \omega = 2 \pi f \) is the angular frequency and \( \tilde{\chi}(f) \) is the Fourier transform of the response function. This last equation is the frequency expression of FDT.

The experimental applications of FDT are numerous. We will cite for example the Einstein formula \( D = \mu k_B T \) relating the diffusion coefficient \( D \) of a particle in a fluid to its mobility factor \( \mu \) [101], and the Nyquist formula \( S_v = 4k_B TR \) expressing the spectral density of thermal fluctuation of a resistance \( R \) [83]. In the case of a magnetic system, we can choose coupled variables, magnetization \( M \) – field \( H \), and we get a relation of fluctuation of \( M \) and its magnetic susceptibility.

For systems out of equilibrium, we lose the time invariance translation and also the FDT validity. So, in the next section, we will discuss the generalization of fluctuation dissipation relation taking in consideration two-time functions which will ignite the glassy system thermodynamics.

4.3 Fluctuation dissipation relation in mean field theory

Generalization of FDR for glassy systems comes from the community of spin glasses. Microscopic models for spin glasses have been in the scene for thirty years now.
In 1975, Edwards and Anderson model was introduced [102]. It is composed of spin vectors on a network, their Hamiltonian is:

\[ H = - \sum_{<ij>} J_{ij} s_i s_j \quad 4.12 \]

Where \( \sum_{<ij>} \) is the sum on the neighboring spins, \( J_{ij} \) is randomly independent coupling with Gaussian distribution, and \( s_i \) is Ising spin ± 1. Because of the random characteristic of \( J_{ij} \), the total magnetization density Equation 4.13 equals zero low temperature:

\[ \frac{1}{N} \sum_{i=1}^{N} m_i = 0 \quad 4.13 \]

Where \( m_i = <s_i> \) is the local magnetization at site \( i \), \( N \) is the number of spins, and \(<..>\) represents the mean. They proposed the following order parameter:

\[ q_{EA} \equiv \lim_{t \to \infty} \lim_{t',w \to \infty} C(t,t') = \lim_{t \to \infty} \lim_{t',w \to \infty} <s_i(0)s_i(t)> \quad 4.14 \]

With \(<...>\) is the average on the disorder.

Sherrington and Kirkpatrick works [103] give a new version to the mean field for this model, the starting Hamiltonian is that all spins interact with the ensemble spins of the system, so the summation will be extended to all other pairs in the system (SK model).
In 1980, Derrida considered a system with interaction of p-spins (p>2) (p-spins model) [104] whose Hamiltonian is:

\[
H = -\sum_{1 \leq i_1 < i_2 \ldots < i_p \leq N} J_{i_1 i_2 \ldots i_p} s_{i_1} s_{i_2} \ldots s_{i_p}
\]

The dynamic of this kind of system related to a thermal bath of temperature \( T \) is given by the Langevin equation:

\[
\frac{ds_i(t)}{dt} = -\frac{\partial H[s]}{\partial s_i(t)} + \eta_i(t)
\]

Where \( \eta_i \) is a Gaussian noise, has zero mean and variance of \( 2k_B T \). In this case, we are interested in the autocorrelation function with two times:

\[
C(t, t_w) = \frac{1}{N} \sum_{i=1}^{N} \langle s_i(t) s_i(t_w) \rangle
\]

The response function, which expresses the influence on the system at time \( t \) caused by a perturbation or a modification at time \( t_w \), is:

\[
R(t, t_w) = \frac{1}{N} \sum_{i=1}^{N} \frac{\partial s_i(t)}{\partial h_i(t_w)}
\]
Where $h_i(t_w)$ is local magnetic time-dependent field coupled to $s_i$, and the over-line means the average over disorder.

The mean field approximation is the only method to resolve equations on energy loss and dimensionality: each spin becomes equivalent and interacts only with the mean field. The equations still vary on the whole temperatures interval. A dynamical transition temperature $T_c$ appears when the system cooled down. So, a number of metastable exponential states exist: the energetic structure becomes more complicated. The numerous equilibrium states are organized in kind of clusters, etc. forming a hierarchical structure. At temperature $T_c$, the system is trapped in one of the minima of metastable free energy. Below $T_c$, aging dynamic appears and shows the existence of separation between time scales of fast relaxation (analogy with $\beta$-relaxation), i.e. stationary states, and slow relaxation (analogy with $\alpha$-relaxation) which depend on the age of the system. This suggested a dynamic evolution in phase space with superposition of two processes fast and slow one. The value of the correlation on plateau separating the two regimes is the Edwards-Anderson parameter $q_{EA}$ defined in Equation 4.14.

In 1993, Cugliandolo and Kurchan [38] resolved the off equilibrium dynamic of $p$-spins system in its spherical case for low temperature at thermodynamic limit with taking into account the initial time of the quench. The system is not reaching the equilibrium state whatever is the aging time $t_w$: the dynamics is not stationary (not time invariance by translation) and FDT is violated. Therefore, it is necessary to modify FDT to FDR relating the linear response function $R(t, t_w)$ with spontaneous autocorrelation function $C(t, t_w)$. The equation 4.7 is no longer satisfied in the aging regime. So, it should be replaced by:
\[
R_{\text{aging}}(t, t_w) = \frac{X(t, t_w)}{k_B T} \frac{\partial C_{\text{aging}}(t, t_w)}{\partial t_w}, t > t_w \tag{4.19}
\]

It turns out that the effective temperature:

\[
T_{\text{eff}}(t, t_w) \equiv \frac{T}{X(t, t_w)} \tag{4.20}
\]

In equilibrium, we used time-translation invariance; the derivative operator \( \partial/\partial t_w \) in equation 4.7 can be replaced by \( \partial/\partial t \). So, it is possible to argue that similar substitution in Equation 4.19 give different definition to \( X(t, t_w) \). For values of \( X(t, t_w) \) different than 1, FDT is violated. In glassy system, this can be persisted for a long time limit, which indicates strongly out of equilibrium behavior even thought the quantities at one time like the mean energy or system entropy already relaxed toward stationary values.

In analytic studies of mean-field systems, one can furthermore show that for large times \( X \) depends on \( t, t_w \) only through the value of the correlation function[105] as \( X(t, t_w) = X[C(t, t_w)] \). In particular, when \( C > q_{E_A} \), \( X = 1 \), and the FDT is recovered. Graphically, the FDR out of equilibrium limit can be obtained by plotting the integrated response function \( \chi(t, t_w) \) vs. its correlation function \( C(t, t_w) \), with \( t \) used as time parameter and \( t_w \) a fixed time, as shown in Figure 4.1.
Figure 4.1 the asymptotic behavior of the integrated linear response against the correlation in a parametric plot, for fixed waiting time and using $t$ as a parameter [7]. The right part of the graph corresponds to quasi-stationary regime. The left part corresponds to the aging regime, where it is the FDT violation. The asymptotic regime of violation depends on the model considered, from the top to the bottom: (-.-) SK model (continues line for $T_{\text{eff}}$), (-) p-spins model (single $T_{\text{eff}}$) and (--) domain growth model (infinite $T_{\text{eff}}$).

The curves in the bottom part represent $\chi(C)$ for two different aging time $t_w$ with from the bottom to the upper $t_{w1} < t_{w2}$. We can define an effective temperature $T_{\text{eff}}$ [38], given by inverse of the curves slope. This result is just an asymptotic study. We see that the two curves, $t_{w1}$ and $t_{w2}$, tend toward curve limit. For fast modes, as $C > q_{\text{EA}}$, $T_{\text{eff}}$ will be already equilibrated at the thermal bath temperature $T$. In other hand, for slow modes, as $C < q_{\text{EA}}$, $T_{\text{eff}}$ is larger than $T$. When the system is in an equilibrium state with its environment, the parametric curve $\chi(C)$ approaches a straight line with slop of $-1/k_B T$ (FDT), it is the linear part of the graph. On the contrary, for systems far from equilibrium
with weak entropy, $\chi(C)$ tend to an asymptotic curve different than the simple straight line. As illustrated in this Figure 4.1, there exist three distinct slopes for this asymptotic curve following the mean field model considered:

- 0 for domains growth (Spherical p-spins model, with $p=2$)[92].
- $-1/(k_B T^*)$ with $T^*$ is a constant and $T^* > T$ (p-spins model, with $p \geq 3$)[38].
- $-1/(k_B T_{\text{eff}})$ for Sherrington-Kirkpatrick (SK) model, i.e., solid line [106].

Cugliandolo, Kurchan and Peliti [40] works demonstrate that $T_{\text{eff}}$ had the sense of thermodynamic temperature which described the thermal exchanges in the system, indeed deserve the name of temperature, because:

- The effective temperature associated with a time scale is the one measured on the system by a thermometer, in contact with the system, whose reaction time is equal to the time scale.
- It determines the direction of heat flows within a time scale.
- It acts as a criterion for thermalization.

In the framework of the mean field theory, these results are exact but outside this approximation, $X(t, t_w)$ is no more a function of correlation only and its thermodynamic context is not clear any more. In order for understanding, how the observable is chosen is important in this theory, should we first verify this property? And what are about non mean-field theory models?
4.4 Other theoretical approaches to aging dynamics

In the following, we will discuss in some detail the theoretical approaches introduced to explain the aging dynamics. We will focus only on some well known models.

4.4.1 Trap Model

The trap model for aging dynamics has been introduced by Bouchaud in [107] and broadly developed since then [108-110]. The trap model is not a microscopic model. It is however very fascinating because on the one hand it has been used and it is still used a lot on a phenomenological level to interpret results of experiments and simulation and, on the other hand, it provides a coarse grained description of different microscopic models. The simplest version [107] is defined as follows: there are \( N \) possible states plotted as wells in Figure 4.2. The dynamical evolution is determined by stochastic jumps: each well acts as a trap for the system. The trapping time is determined by the Arrhenius law:

\[
\tau_\alpha = \tau_0 \exp\left( \frac{F_0 - F_\alpha}{k_B T} \right) \tag{4.21}
\]

Where \( F_\alpha \) is the free energy of the “state” (or well, trap) \( \alpha \) and \( F_0 \) is a threshold free-energy state, see Figure 4.2.
Figure 4.2 Schematic representation of the configuration space for trap model.

Once the system is escaped from a trap, it falls completely at random into another trap. The rationale behind these rules is that generically for disordered systems there exist many different metastable states which, at least in some regimes, are surrounded by large energy barriers. The complete absence of geometry is of course the simpler assumption one can do. More complicated structures of the configuration space have been considered. The other essential ingredient of the model is the distribution of free-energies that is taken exponential with a certain parameter $x$:

$$P(F) = \frac{x}{T} \exp\left(x \frac{(F - F_0)}{k_B T}\right)$$

4.22
This choice is motivated by the presence of a similar distribution in mean-field disordered systems like the Random Energy Model (in which $x = T/T_g$) [108] and, on general grounds, by the extreme value statistics for deep free-energy states [108]. The resulting distribution of trapping times $\psi(\tau)$ is:

$$\psi(\tau) = x\frac{\tau^x_0}{\tau^{1+x}}$$  \hfill (4.23)

The important feature of this law is that the average trapping time $<\tau>$ is infinite for $x<1$, i.e., for $T < T_g$ if we take $x$ as proportional to the temperature. In this regime the system, taken at time zero uniformly distributed over the traps, never reaches equilibrium and ages forever. In this case the nature of the aging dynamics is particularly clear [107]: the time $t_w$ after $n$ jumps equals:

$$t_w = \sum_{i}^{n} \tau_i$$  \hfill (4.24)

Where, $\tau_i$ are independent variables with probability law $\psi(\tau)$. It is a well-known result that since the first moment is infinite the central limit theorem does not apply, $t_w$ is distributed with a Levy Law and its typical value is of the order of the maximum trapping time encountered during the evolution. At a given waiting time $t_w$ the sum $\tau_1 + \tau_2 + \ldots$ is dominated by its largest term which is of the same order of $t_w$. In this case it is very clear that the system ages because the relaxation time is set by the age of the system itself. The Trap Model provides a coarse grained description of the Sinai model in a biased potential.
[111] as well as the aging dynamics (on extremely long times, diverging with the system sizes) of the Random Energy Model [112]. These results suggest that it is not only a phenomenological model and it might play in the future an important role in the description of the finite dimensional extension of the mean-field aging.

In the last few years, this model was used for FDR verification [47, 113]. In the presence of exterior field \( h \) coupled to a magnetization \( m \) of each trap energy \( E \), the time \( \tau \) of the landscape is modified:

\[
\tau(E, h) = \tau_0 \exp\left(\frac{E + mh}{k_B T}\right)
\]

The energy distribution chosen was that given in equation 4.22. In the contrary, the probability distributions \( P(E, m, t) \) were modified; they are also depending on the probability of a well with \( E \) in deep and magnetization \( m \), so:

\[
P(E, m, t) = P(E, t)\sigma(E | m)
\]

Where, \( \sigma(m|E) \) is the probability for a trap with energy deep of \( E \) and magnetization \( m \).

In the case when this probability is a Gaussian, the results from this study show that:

- The FDR and \( T_{\text{eff}} \) dependent on the observable \( m \).
- For a given observable, \( T_{\text{eff}} \) evolves slowly with time
- For all observables, when \( t \rightarrow \infty \), \( T_{\text{eff}} \rightarrow \infty \).
4.4.2 Free energy landscape model

In the free energy landscape (FEL) picture, a thermodynamic potential defined in a configurational space of all constituents plays an essential role. We expect a flat landscape at high temperatures and a rugged one at low temperatures as recently shown by a first principle calculation based on the density functional theory [114]. A schematic behavior of the FEL is illustrated in the Figure 4.3.

![Figure 4.3 a schematic picture of the FEL model at high and low temperature.](image)

Assuming a stochastic motion in the rugged landscape, Tao et al. [6] showed that a rapid change of the specific heat occurs when the representative point begins to be trapped in a basin and that the glass transition can be understood as a transition from annealed to quenched dynamics of the representative point. The theoretical predictions are consistent with experimental observations [115].
In order to take account of the cooperative rearrangement of the regions during the formation of glasses or super-cooled fluid systems while we decrease the temperature, Sastry, Debenety and Stillinger [116] showed how dynamical properties of a system changes in FEL model by numerical simulation on binary mixed system of particles interact via Lennard-Jones potential. The free energy landscape permits a qualitative description of the complex system behavior. The landscape topology controls the dynamic of the system and the minimum energy of traps visited at temperature T, which describes the system thermodynamics.

For a collection of N particles, the system energy is determined by the exact position of all particles. The energy landscape is a hyper-surface of dimension 3N+1, which is impossible to conceptualize. We will implement a partition of the configurational space in basins, so that the local minimization of potential energy cartography each point in the basin to the same minimum. The obtained configuration of minimum energy is named inherent structure. The system properties a given temperature are dictated by the basins shapes and there mutual accessibility. The representation in two dimensions permits an illustration of a distinction between crystal, liquid and glass phases. In the equilibrium at temperature T, the liquid is positioning between 2 minimums energies determined by the temperature T. When the temperature increased, the system spends most of the times above the energy landscape and is accessing all possible states. The perfect crystallization state corresponded only to most deeply well. For temperature less than $T_g$, the system freezes because the vibration energy becomes insufficient for activating the system for local minimum to other one.
Simple model based on energy landscape was created. The system evolution will be controlled by the diffusion process through the energy landscape potential described by order parameter $\gamma$. The system evolved by activated thermal jumps. $\gamma_1$ and $\gamma_2$ describe the maximum and minimum potential. The system dynamic description between the two state levels can be simplified to the evolution in the populations $n_1$ occupied state 1 and $n_2$ occupied state 2. The diffusion process intervenes in two transition rates. The out of equilibrium state was analyzed by introduction of the observable $O(\gamma)$ which is $O(\gamma_1)$ in $\gamma_1$ state and $O(\gamma_2)$ in state $\gamma_2$.

In this case, $T_{\text{eff}}$ depend on the observable $O(\gamma_1)$ and $O(\gamma_2)$. Contrary to mean field model, for a simple phenomenological model, $T_{\text{eff}}$ depend on time $t_w$ and the observation frequency $[48]$ as:

$$T_{\text{eff}} = T \frac{1}{A e^{-t_w/\tau} + (1 - e^{-t_w/\tau})}$$  \hspace{1cm} 4.27

Where, $A$ depends on the diffusion rate between state 1 and 2 for the observables $O_1$ and $O_2$ of the populations’ $n_1$ and $n_2$.

FDT violations become obvious consequence of fast processes elimination and thermal activation related to the slow processes.
4.4.3 Domain growth model

a) Domain growth in pure systems

A simple case where aging effects do become visible is phase ordering in pure systems [117]. Let’s take for example an Ising ferromagnetic abruptly quenched from high temperatures to a temperature below its transition temperature. The system then attempts to order, and has to choose between the up phase and the down phase. Apparently, this takes some time, and the dynamics progresses via domain growth. After some waiting time $t_w$ after the quench, the distinctive distance between domain walls is $\xi(t_w)$, which grows as a power-law of time, i.e. relatively quickly, even for small temperatures. Far from the domain walls, any given spin will have to wait for a time $t$ such that:

$$\xi(t + t_w) \geq 2\xi(t_w)$$ \hspace{1cm} 4.28

This will be required to flip from the up phase to the down phase and de-correlate. For a power-law growth, this means that the effective relaxation time is of the order of $t_w$ itself, corresponding to $\mu = 1$ (The effective relaxation time grows as $t_w^\mu$). This behavior is established by several exactly solvable models of coarsening, such as the Ising model on a chain, or the ‘spherical’ model, where one can calculate explicitly the correlation function to find [117]:

89
We can also derive several other quantities, such as the effect of an external magnetic field \( h \) on the aging properties. One then notices that when \( \xi(t_w)^{-1} \) is smaller than \( h \), the driving force due to the curvature of the domain walls is superseded by the driving force due to the external field [92]. In this situation, the preferential phase quickly occupies the whole system and the aging is stopped. This directs, for very small fields and moderate time scales, to an effective value of the exponent \( \mu < 1 \). The most important quantity of interest to compare with experiments is the response function. The result is that the aging part of the response function vanishes as \( \xi(t_w)^{-1} \) as \( t_w \) becomes large. In terms of the a. c. susceptibility, one finds that [92, 118]:

\[
\chi''(\omega, t_w) = \chi''(\omega) + \xi(t_w)^{-1} \chi'''(\omega t_w)
\]

Instinctively, this result shows that the aging part of the susceptibility only comes from the domain walls, while the spins in the bulk of domains contribute to the stationary part \( \chi''(\omega) \). Since the density of spins belonging to domain walls which decreases as \( \xi^{-d-1}/\xi^{d} = \xi^{-1} \), thus the aging contribution decreases with time as the density of walls.

Domain growth in pure systems is only determined by surface tension and does not necessitate thermal activation; therefore, the aging effects in these systems are hard to identify experimentally, since the typical size of the domains reaches quickly its maximum value [which can be placed either by the size of the system or by magneto-
static or other considerations]. Correspondingly, one does not expect the cooling rate to have a major influence on the coarsening of the system

b) – **Domain growth in random system**

More fascinating situation is the case of ferromagnetic disordered systems (as an example in the presence of quenched random fields or random bonds). In this case, the impurities proceed as pinning sites for the domain walls. The problems of elastic objects such as domain walls, vortices in superconductors, and dislocations, pinned by random impurities have been the subject of intense work in the last decades, both from a static point of view where the typical equilibrium conformation of such objects is investigated or in order to understand their dynamics behavior such as relaxation to equilibrium, response to an external driving force, creep and transition state [8, 119-122]. In fact, these systems represent early studies in spin glasses where frustration is present because of the competition between pinning, which have a tendency to distort the structure, and elasticity which tends to reduce the deformations.

The main outcome of this theory is the appearance of a typical pinning energy $E_p(\ell)$ associated with the linear size $\ell$ of the piece of domain wall that attempts to re-conform. This energy scale grows as a power of $\ell$:

$$E_p(\ell) \square Y(T) \ell^\theta$$

4.31
Where, $\gamma$ is energy scale with temperature dependent, and $\theta$ an exponent which depends on the dimensionality of the structure in the system (1D for dislocations, 2D for domain walls, etc.) and also on the correlations of the pinning field. With the use of a very naïve Arrhenius law for thermal activation, this means that the typical time associated to re-conformation of events that occur on a scale $\ell$ take a time, as:

$$t(\ell) \propto \tau_0 \exp\left(\frac{\gamma(\ell)\ell^\theta}{T}\right)$$  \hspace{1cm} 4.32

Evenly, the size over which the system can be equilibrated after a waiting time $t_w$ only grows logarithmically, as:

$$\ell(t_w) \propto \left[\frac{T}{\gamma(T)}\log\left(\frac{t_w}{\tau_0}\right)\right]^{\frac{1}{\theta}}$$ \hspace{1cm} 4.33

In particular, the typical size of the growing domains is estimated to grow logarithmically with time, that is, extremely very slow. This very slow growth means that the density of domain walls only perishes slowly with time, and consequently that the aging contribution to the susceptibility is still significant even after macroscopic times.

Even though very straightforward, the exponential relation between length scales and time scales specified by Equation 4.32 has far-reaching consequences: the dynamics becomes, in a loose sense, hierarchical. This is demonstrated in Figure 4.4. The object changes between metastable configurations which differ by flips of regions of size $\ell_1$ on a
time $t(\ell_1)$ that, because of the exponential dependence in Equation 4.32, is much shorter than the time needed to flip a region of size $\ell_2 > \ell_1$. Thus, the dynamics of the short wavelengths occurs on a time scale such that long wavelengths are effectively frozen. As we shall explain below, this feature is, in our eyes, a major ingredient to understand the coexistence of rejuvenation and memory. An additional important consequence is the fact that domain growth happens to have a very intermittent process: once an event on the scale of the domain size $\xi$ has taken place, the details of the conformation on scales $\ell < \xi$ start developing between nearby metastable states, while the general pattern formed by the domains on scale $\xi$ hardly change.

In addition, the equation 4.32 permits one to define a very important quantity which called, by analogy with the glass temperature $T_g$, the ‘glass length’ $\ell_g$, through the following equation 4.34:

$$\Upsilon(T)\ell_g^0 = AT$$

This is launched in this context in [122-124]. $A$ is rather an arbitrary factor; the choice $A = 35$ corresponds to a time of 1000 seconds if $\tau_0 = 10^{-12}$ seconds. In analogy with the glass temperature $T_g$, one sees that length scales larger than $\ell_g$ cannot be equilibrated on practical reasonable time scales, whereas length scales smaller than $\ell_g$ are completely equilibrated. Qualitatively speaking, the equilibrated modes contribute to the stationary part of the correlation and/or response function, although the glassy modes $\ell > \ell_g$ contribute to the aging part. As a result, the strong hierarchy of time scales stimulated by
the exponential activation law allows equilibrated modes and aging modes to coexist at the same time.

![Figure 4.4](image)

Figure 4.4 Schematic evolution of a pinned object on well separated time scales. On the scale \( t(\ell_1) \), the object re-adapts by flipping a small portion of size \( \ell_1 \) from one preferred configuration to another \((a \rightarrow b)\). On much longer scale \( t(\ell_2) \gg t(\ell_1) \), the re-adaptation on scale \( \ell_2 \) (dashed line) has developed \((b \rightarrow c)\). The shorts wavelengths dynamics occurs on time scale such that the long wavelengths are effectively frozen \([8]\).

At last, it is straightforward to understand that the logarithmic growth law, Equation 4.33, directs to a strong cooling rate which depends on the typical size of the
domains [125]: since the growth law is fundamentally that of pure systems as long as $\xi \ll \ell_g(T)$, the longer the time spent at higher temperatures (where $\ell_g$ is large) evidently the larger the domains grow before getting pinned at lower temperatures.

### 4.4.4 Mode-coupling theory

A model Hamiltonian or an effective Lagrangian capable of describing the relaxation processes in super-cooled liquids and structural glasses is difficult to obtain. Early studies based on both dynamical mode-coupling theories or equilibrium density-functional theories suggested that there may be a close connection with mean-field spin-glass models [126]. They thus provide a set of microscopical models where glassy dynamics can be studied analytically.

Mode-Coupling Theory (MCT) [127-129] has had essential successes in describing some features of super-cooled liquids [130, 131], in particular the two-step form of the relaxation function or, equivalently, the behavior of the frequency dependent susceptibility $\chi(\omega)$ around its minimum, which splits the low frequency process ($\alpha$-peak) from the high frequency process ($\beta$-peak). Conversely, the Mode-Coupling description is founded on the existence of a true dynamical transition temperature $T_c$ (higher than the glass transition $T_g$) where no singularity is actually observed experimentally. Theoretically, this is assigned to the so-called “activated processes” (or hopping processes), which are not described by the MCT, and which spread out the transition. Correspondingly, the clear-cut predictions of MCT are somewhat weakened and more difficult to test explicitly.
The fundamental quantities in the dynamical MCT are the local particle density correlation functions \( \langle \delta \rho(x, t) \delta \rho(x) \rangle \), where \( \delta \rho(x) = \rho(x) - \rho_0 \), with the local particle density is:

\[
\rho(x) = \sum_{i=1}^{N} \delta(x - x_i)
\]

4.35

Where, \( \rho_0 \) is the uniform fluid density. For the homogenous state:

\[
\langle \rho(x) \rangle = \rho_0
\]

4.36

Where, the angular brackets denote an average of the ensemble. In the case of glassy phase, the system is trapped into metastable states with non-uniform (average) local density field \( \langle \rho(x) \rangle \not= \rho_0 \) and the density fluctuation correlation function do not decay to zero for \( t \to \infty \):

\[
\lim_{t \to \infty} \langle \delta \rho(x,t) \delta \rho(x) \rangle \not= 0
\]

4.37

The full mode-coupling theories lead to the time-evolution equations for the normalized correlation functions:
\[
\phi_q(t) = \frac{\langle \delta p(q,t)^* \delta p(q,0) \rangle}{N S_q}
\]

Where, \( S_q = \langle |\delta \rho(q)|^2 \rangle / N \) is the static structure factor, and \( \rho(q) \) are Fourier components of the density field \( \rho(x) \):

\[
\rho(q) = \int \exp(-iq.x) \rho(x) dx = \sum_{i=1}^{N} \exp(-iq.x_i)
\]

The basic idea of MCT is to obtain the equations of motion for the slow relaxing modes integrating all fast modes. This leads to a set of self-consistent equations involving only slow mode variables in which all information from fast modes are hidden into density-fluctuation memory kernels of the following form:

\[
M_q(t) = iv_q + \Omega_q^2 m_q(t)
\]

Where, \( v_q \) is a (white-noise) frictional term arising from fast modes, \( \Omega_q > 0 \) gives the frequency or timescale of microscopic motion and \( m_q(t) \) accounts for slow modes couplings arising from the integration of the fast modes. The general form of the MCT equations is [132]:

\[
\partial_t^2 \phi_q(t) + v_q \partial_t \phi_q(t) + \Omega_q^2 \phi_q(t) + \Omega_q^2 \int_0^t ds m_q(t-s) \partial_s \phi_q(s) = 0
\]
This must be solved with initial conditions:

\[ \phi_q(t = 0) = 1, \dot{\phi}_q(t = 0) = 0 \]

The essential mechanism for the glass transition in the MCT is the feedback between low densities fluctuations expressed through \( m_q(t) \). The solution of these equations is a difficult task since the kernel \( m_q(t) \) involves higher order correlations between density-fluctuation modes. Thus when these theories are employed, approximations are generally made. The simplest approximation consists of replacing the average of products with products of averages to obtain a set of closed equations. This is some sort of mean-field approximation. Indeed within this scheme the memory-kernel \( m_q(t) \) can be expressed as a functional of the \( \Phi_q \):

\[ m_q(t) = F_q[V,\{\phi_q\}] \]

With some vertex functions \( V \). Regardless of this rather strong approximation, similar to a mean-field approach, the theory contains the basic mechanism of the glass transition. We note that due to this approximation, the MCT is not capable of describing activated processes, in the same way they cannot be discussed within mean-field theories. As a result the appearance of activated-process dominated regimes is indicated in this theory by the divergence of some of system quantities. Activated processes could, in principle,
be included as perturbation terms, on the other hand reliable theories which account for them are not yet available.

The most important properties of the MCT can be best seen using a simplified version of the theory called *schematic mode-coupling theory* in which only one relaxation function is considered [132-134]:

\[
\partial_t^2 \phi(t) + v \partial_t \phi(t) + \Omega^2 \phi(t) + \Omega^2 \int_0^t ds m(t-s) \partial_s \phi(s) = 0
\]

4.44

The simplest model describing an idealized structural glass transition is the one specified by two coupling constants \((v_1, v_2)\):

\[
m(t) = v_1 \phi(t) + v_2 \phi(t)^2
\]

4.45

This theory predicts a transition from an ergodic liquid phase, where \(\Phi(t \to \infty) \to 0\), to a glass phase, where the ergodicity is broken and \(\Phi(t \to \infty) \to f > 0\), as the parameter \((v_1, v_2)\) are varied. Depending on the values of \((v_1, v_2)\) the nature of the transition can be either continuous (type A) with \(f\) growing continuously from zero or discontinuous (type B) with \(f\) jumping from zero to a finite value as the transition line is crossed [135].

### 4.5 Numerical evidence

Numerical simulations are in general based on algorithms of type Monte-carlo or molecular dynamics. Those Computer simulations have the great advantage, over the real
experiment, of direct access to the microscopic level, also the instantaneous quench which can be done at temperature near $T_g$ or far away from it. Even if only relatively small timescales and system sizes can be studied, contrary to the real system that had big sizes and large time scale. Although this can be serious limitations, the true fact is that numerical studies of aging phenomena and FDT violations have been successfully done during the last few years for several systems and permit the observation of early modification of FDR.

### 4.5.1 Structural glasses systems

Using ideas developed in the field of spin glasses, many assumptions have been formulated concerning the structure of the phase space of glassy systems. Though, obtaining direct information, either from experiments or from numerical simulations, is a difficult challenging task. Relaxation times in a glass are so long as to prohibit the equilibration within experimental time scales. Numerical or experimental exploration of the phase space in these systems is therefore necessarily incomplete. The raise in computational power and the recent progresses in the theory of disordered systems have hardly pushed forward an approach which should not suffer from these limitations. The idea, which was actively developed in the study of spin glasses, is that relevant information on the phase space structure should be hard-encoded into the non-equilibrium dynamics of glassy systems.

According to the conjecture of the similarity between structural glasses and some spin glass models, $X(C)$ for structural glasses is a two-valued function with $X(C) = 1$ at
short times, and $X(C) = m < 1$ in the long-time aging regime. This scenario has been largely studied using numerical simulations.

In a numerical investigation of aging effects not only the waiting time must be changed over several orders of magnitude, but for a given waiting time the subsequent dynamics must also be studied over a long time. For these reasons, aging phenomena have been studied for models that are simple enough to be simulated over long times, but at the same time still catch the essential features of real glasses. Moreover, to maintain the systems in a non-equilibrium state for very long times, crystallization must be strongly inhibited. This is obtained either with a particular choice of interaction potential parameters or by adding a (small) extra term in the potential. In the following we will discuss results obtained for some models.

**a) – Mixture of soft particles of different sizes**

In this system, it was considered to be constituted of $N$ particles of which half will be of type A and other half of type B, interacting via the following Hamiltonian:

$$H = \sum_{i<j} \left( \frac{r_i + r_j}{|x_i - x_j|} \right)^{12}$$  \hspace{1cm} (4.46)

Where, the radius $r_i$ depends on the type of particle. It is known that the choice of two different types of radius such that $r_B/r_A = 1.2$ prevents crystallization and the system can be transported into a glassy state.
Due to the simple scaling of the potential, the thermodynamic quantities depend only on \( \Gamma = \rho \beta^4 \), where \( \rho \) is the density which can be taken equal to 1. This model presents a glass transition at about \( \Gamma_c = 1.45 \) [136]. Figure 4.5 showed the response of the particle to a force of strength \( \epsilon \). This figure shows \( \chi \) versus \( \beta \Delta \) at \( t_w = 2048 \) and \( t_w = 8192 \) for \( \Gamma = 1.6 \) and \( t \leq 4t_w \) at \( N = 66 \). It also shows the data for \( t_w = 2048 \) at \( N = 130 \). It does not illustrate any significant systematic shift in this plot among three data sets. We distinguish two linear regions with different slope as expected from one step replica symmetry breaking. The slope in the first region is compatible with 1, as expected from the FDT theorem, while the slope in the second region is near 0.62. Also the data at different temperatures for all values of \( \Gamma \geq 1.5 \) show a similar behavior. The value of \( \chi \) in the region where the FDT relation does not hold can be very well fitted by a linear function of \( \Delta \). The region where a linear fit (with \( m < 1 \)) is quite good corresponds to \( t/t_w = 0.2 \) [9], with:

\[
\chi(t_w + \tau, t_w) \square \frac{1}{N} \sum_{i=1}^{N} < f_i \cdot x_i(t_w + \tau) >
\]

Where, \( f_i \) is a random Gaussian vector of squared length equal to the space dimension \( d \), versus the self-diffusion function, as:

\[
\Delta(t_w + \tau, t_w) = \frac{1}{N} \sum_{i=1}^{N} |x_i(t_w + \tau) - x_i(t_w)|^2
\]
The average is over different initial states at \( t_w \) and realization of \( f \). It is clearly seen two linear regions with different slopes, one with \( X(C) = 1 \) and one with \( X(C) = m < 1 \), and they are in good agreement with the two-timescale scenario. The temperature \( T \) dependence of \( m \) is well fitted by the spin-glass model prediction \( m(T) = T/T_c \). The fitted value of \( m = \partial \chi / \partial (\beta \Delta) \) is displayed in Figure 4.6 using the data at \( t_w = 2048 \). When \( m \) becomes equal to 1, the fluctuation dissipation theorem holds in the whole region and this is what happens at higher temperatures. The straight line is the prediction of the approximation \( m(T) = T/T_c \), using \( \Gamma_c = 1.45 \). Similar, result have been found in monatomic Lennard-jones glasses [137, 138].

![Graph](image)

**Figure 4.5** \( \chi \) versus \( \beta \Delta \) at \( \Gamma = 1.6 \) for \( t_w = 8192 \) and \( t_w = 2048 \) at \( N = 66 \) and for \( t_w = 2048 \) at \( N = 130 \). The two straight lines have slope 1 and 0.62, respectively [9].
Figure 4.6 The quantity $m = \partial \chi / \partial (\beta \Delta)$ as $t_w = 2048$ as function of temperature. The straight line is the prediction of the approximation $m(T) = T/T_c [9]$. 

b) - Lennard-Jones binary-mixtures

The system is created of a mixture of particles of type A and B with equal mass $m$ and interacting via a 12-6 Lennard-Jones potential of the following form:

$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right]$$

4.49

Where, $\varepsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ depend on the particle type and are chosen to prevent crystallization. For a mixture of 80:20, and using $\varepsilon_{AA}$ and $\sigma_{AA}$ as units of energy and length and $(m\sigma_{AA}^2/48\varepsilon_{AA})^{1/2}$ as the unit of time, these are $\varepsilon_{AA} = 1$, $\sigma_{AA} = 1$, $\varepsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\varepsilon_{BB}$
\[ = 0.5 \text{ and } \sigma_{BB} = 0.88. \text{ The atomic dynamics of this model is well described by the mode-coupling theory with a critical temperature of } T_c = 0.435 \text{ in reduced units.} \]

Typical FDR plots numerically obtained by Barrat and Kob[10, 139, 140] are shown in figure 4.7. The correlation is given by the incoherent scattering function for a wave vector \( \mathbf{k} \) as:

\[
C_k(t_w + \tau, t_w) = \frac{1}{N} \sum_{j} e^{ik \cdot [r_j(t_w + \tau) - r_j(t_w)]} \tag{4.50}
\]

While the response is measured by adding to the potential a term of the form:

\[
\delta V = V_0 \sum_j \varepsilon_j \cos(k \cdot r_j) \tag{4.51}
\]

Where, \( \varepsilon_j = \pm 1 \) with equal probability and \( V_0 < T \). Again a two-timescale scenario is clearly seen. Furthermore, the effective temperature in the slow regime, where \( m < 1 \), is in reasonable agreement with the glass transition temperature \( T_g \) of the system, which is defined as the temperature below which the system fails to equilibrate on the experimental timescale. For structural glasses \( T_g \) is defined as the temperature at which the viscosity is equal to \( 10^{13} \) Poise or, equivalently, a relaxation time of 100 seconds.

Therefore, the FDT is violated as the system fails of the equilibrium state, as predicted from spin glass models.
Figure 4.7 Parameter plot of the integrated response function $M(t_w + \tau, t_w)$ and the correlation function $C(t_w + \tau, t_w)$ for $k = 7.25$. Final quench temperature $T_f = 0.3$, $t_w = 1000$. Circle: $t_w = 10000$. The straight lines have slopes -1, and -0.45 [10].

Another case, using molecular dynamics simulations, J. L. Barrat and W. Kob study the out of equilibrium dynamic correlations in a model glass-forming liquid. The system was quenched from a high temperature to a temperature below its glass transition temperature and the decay of the two-time intermediate scattering function $C(t_w, t+t_w)$ is monitored for several values of the waiting time $t_w$ after the quench. $C(t_w, t+t_w)$ showed a strong dependence on the waiting time, i.e., aging, depends on the temperature before the quench, and, similar to the case of spin glasses, can be scaled onto a master curve [93].
4.5.2 Spin glasses systems

As we have explained in the mean field theory, the spin glasses represent the most important motif of many results regarding FDT violations. Particularly, numerical simulations have been the most widespread tools to investigate many aspects of equilibrium and non-equilibrium behavior of spin glasses that cannot be tackled by analytic means.

a) – Spin glasses

Edwards and Anderson proposed a simplified model for spin-glasses in which one represents the magnetic impurities with Ising spins placed on the vertices of a three-dimensional cubic lattice.

Through her work, L. F. Cugliandolo used as a test model a spherical disordered model with p-spin interactions (Figure 4.8)[84]. The model has been introduced in its purely relaxational version by Crisanti and Sommers [141, 142] as a simple spin-glass model with several advantages, in particular, that exact dynamical equations can be written for it in the thermodynamic limit.
Figure 4.8 Diagram $\chi(C)$ of p-spin in glassy phase. The full curves correspond to different total times $t$, equal, from bottom to top, to 12.5, 25, 37.5, 50, 75 respectively ($t_w > t/4$ throughout). The dots represent the analytical solution when $t_w \to \infty$. Neither $\chi(t, t_w)$ nor $C(t, t_w)$ achieve stationary state. For fast modes ($C > q_{EA}$), FDT is verified. In the other hand, for slow modes ($C < q_{EA}$) are associated to an effective temperature $T_{eff} > T[11]$.

b) – Growth domain systems

A. Barrat, in Monte-Carlo simulation on many growth domain systems, computed the correlation functions at two times and the response functions [12]. The FDT is valid in the quasi-equilibrium regime (fast mode spins within the domains) and $T_{eff}$ is infinite in the aging regime (in the coarsening regimes which correspond to the dynamics of domains edges). Even though, the response at large time was frozen and very weak, the correlation continues decreasing toward zero (Figure 4.9).
Figure 4.9 Susceptibility in function correlation for growth domain model of dimension 2, with from the upper curve to the bottom one, $T = 1.7$ and $t_w = 200, 400, 800, 2000$, $T = 1.3$ and $t_w = 800$, $T = 1$ and $t_w = 800$. The straight line represents the FDT. We see that it is valid at short times but there is a violation at large times and $T_{\text{eff}}$ is infinite [12].

c) – Trap model

After L. Cugliandolo and Kurchan exposed their work of effective temperature $T_{\text{eff}}$, sooner, it is proven by numerical simulations that FDR was modified by 1+1 dimensional directed polymer in random media out of equilibrium [13]. The chosen model was based on trap model. H. Yoshino demonstrated that the response function
didn’t age (the quench located at 0.2 T\text{g}) because the excitation field was applied only at the edges of polymer fiber, whereas the rest of the system is the same with the existence of an excitation field. In the contrary, there is a strong correlation with aging time t\text{w}. The polymer dynamic is governed by two elementary processes:

- Fast fluctuations at the inside trap; in this model, the considered tubes with diameters varied with temperature. These tubes represent the space probability density of finding a polymer in particular configuration. Also, those tubes can be interpreted as activated thermal state levels.

- The thermal jump was active between each tube. In this relaxational dynamic, the thermal jumps between excited stated are observed, as shown in Figure 4.10 (a).

In this system, the FDR is violated in the aging regimes as we can see on Figure 4.10 (b): practically, the response function had no sign of aging opposed to the fluctuations.

Figure 4.10 (a) Time evolution of polymer fiber position. (b) FDR for T = 0.2 T\text{g}. The three curves from the top, represented C(t\text{w} + t, t\text{w} + t) - C(t\text{w} + t, t\text{w}) for different waiting times, t\text{w} = 40, 200, 1000. The bottom three curves were representing the response function for the same waiting times [13].
Those examples of numerical simulation exhibit the importance of experimental studies of fluctuation dissipation relation in glassy systems. The mean filed theory approach give amazing and original results that can be transposed on glassy system models, and seems that can be also applicable to the structural systems in our every day life. Upon its measurement, $T_{\text{eff}}$ can give an insight on the aging dynamic of the system, also supplied us with information on microscopic process during aging behavior by comparison with different theoretical predictions.

4.6 Experimental evidence

Contrary to the numerous theoretical and numerical studies done in last decades on the systems out of equilibrium thermodynamic, it is only few experimental verification of FDR violation during aging process, are done in this field. Actually, it is the experimental experiences that are very difficult to realize, because of the small noise measurement; we reach very quickly the limitations of our experimental techniques. Nerveless, some good work was already done in this context.

4.6.1 Spin glasses

D. Herisson had measured the FDR in spin glass system of CdCr$_{1.7}$In$_{0.3}$S$_4$ [5]. The variables measured are autocorrelation functions of magnetic fluctuations and magnetic susceptibility relaxation (Figure 4.11). With decreasing $C$ (increasing $t - t_w \geq t_w$), the data points depart from the FDT line. Indeed, $C(t_w, t \rightarrow \infty) = 0$ and $\chi_{\text{FC}} = \chi(t_w, t \rightarrow \infty) = 1$. The
mean slope of the FDT data corresponds to a temperature of about 30 K. This value is far above the annealing temperature, ruling out a simple interpretation of a “fictive” temperature [143]. Despite the scatter of the results, a tendency of the data at small \( t_w \) to depart the FDT line a large values of \( C \) is very clear: it is experimentally impossible to fulfill the condition of time scale separation underlying the existing theories. Even if the long \( t_w \) limit for \( \chi(C) \) does exist, it is not reached in the plot of data in Figure 4.11 and a \( t_w \) dependence of the \( \chi(C) \) curves is expected.

![Figure 4.11 FD plot. Relaxation measurements are plotted versus correlation functions for each \( t_w \). The dot-dashed line (FDT line) is calculated for \( T = 0.8 \, T_g = 13.3 \) K, from the calibration obtained with copper sample. The dashed line represents the scaling extrapolation for \( t_w \to \infty \). The branching point with the FDT line, corresponds to \( C = q_{EA} \) (square symbols, with size giving the error range). Inset: the same data in the whole range.](image)
4.6.2 Colloidal glass: Laponite

L. Bellon measured the FDR violation within Laponite gel in course of formation. The $T_{\text{eff}}$ measured was off order of $2 \times 10^5$ K at the beginning of the gel formation at 1 Hz (Figure 4.12). Although this has been interpreted as an evidence for coarsening dynamics (where $T_{\text{eff}} \to \infty$) a conclusive explanation of the origin of these high values is still unknown. Though, the absence of knowledge of $T_g$ due to the technical raisons (If they warm the system, the water vaporized before appearance of any glass transition phase). One interesting aspect of these experiments is the scaling behavior $\omega t^{1/2}$ observed in the power spectrum indicative that FDT violations persist even in the regime $\omega t >> 1$. Contrarily to what be expected, noise in a rheological experiment for Laponite do not detect significant FDT violations [14, 86].

![Figure 4.12 Effective temperature of Laponite as a function of frequency for different aging time [14].](image)
B. Abou and F. Gallet [15] presented a direct experimental measurement of an effective temperature in colloidal glass of Laponite, using a micrometric bead as a thermometer. The non-equilibrium FDR, in the particular form of a modified Einstein relation, was investigated with diffusion and mobility measurements of the bead embedded in the glass. They observe an unusual non-monotonic behavior of the effective temperature (Figure 4.13): starting from the bath temperature, it was found to increase up to a maximum value of 1.8 of the bath temperature, and then decrease back, as the system ages. They showed that the observed deviation from the Einstein relation is related to the relaxation times previously measured in dynamic light scattering experiment performed in colloidal glasses of Laponite [144, 145].

Figure 4.13 Effective temperature of the colloidal glass versus $t_w$, measured at a frequency $f = 1$ Hz. Upon increase on $t_w$, $T_{\text{eff}}$ increases up to 1.8 time the bath temperature and decreases back to $T_{\text{bath}}$. The dashed line is a guide for eyes [15].
These results are in contradiction with electrical measurement of FDR performed in the same system [86], where $T_{\text{eff}}$ is found to decrease with aging time $t_w$ and frequency $f$ and is larger by about 1 order of magnitude. A possible origin of this discrepancy may be the choice of different observables in the two experiments [47].

In another experiment, N. Greinert et al. [16] studied the thermal fluctuations of an optically confined probe particle, suspended in an aging colloidal suspension, as the suspension transforms from a viscous liquid into an elastic glass. The micron-sized bead forms a harmonic oscillator. By monitoring the equal-time fluctuations of the tracer, at two different laser powers, they determined the temperature of the oscillator, $T_o$. In the ergodic liquid the temperature of the oscillator and its environment are equal, while in a non-equilibrium glassy phase, they found that $T_o$ substantially exceed the bath temperature. This is a systematic increase in the oscillator temperature with increasing age, with the ratio $T_o/T_{\text{bath}} \approx 2$ at the longest accessible age of the system (Figure 4.14). The growth evidence in $T_o$ as the glass ages is very surprising and it is in good agreement with the previous results on same system with diffusion and mobility measurements [15], however, it contradicts the electrical measurement done on the same colloidal system [86] as mentioned above in this section. Intuitively, on expect a glass to cool as it ages and $T_{\text{eff}}$ to fall with increasing $t$. In order to interpret their results, they proposed a simple theoretical model for these non-equilibrium experiments, which considers the diffusion of a harmonically bound particle coupled to two thermal baths. The two baths are kept at different temperature to mimic the effects of the fast and slow modes of the glass on probe diffusion [146]. This model reveals that, at high elasticities, the probe thermalizes to the effective temperature of the slow modes of the glass.
Figure 4.14 Effective temperature as a function of sample age. The circles and squares depict the results of measurements using similarly sized particles in two physically distinct Laponite samples. The scatter illustrates the typical level of reproducibility achieved. Errors bars, which are estimated from the variability in $\langle \delta x^2 \rangle$ for $t < 100$ min where the asymptotic mean-square displacement (MSD) is constant, are only shown on few representative points for clarity [16].

Recently, S. Jabbari-Farouji et al. [23] provided a direct experimental test of the fluctuation-dissipation theorem (FDT) in an aging colloidal glass. The use of combined active and passive microrheology allows them to independently measure both the correlation and response functions in this none-equilibrium situation. Contrary to previous reported experiments on the colloidal glass [14-16, 86]; they find no deviations from the FDT over several decades in frequency (1 Hz–10 kHz) and for all aging times (Table 4.1). In addition, they find two distinct viscoelastic contributions in the aging
glass, including a nearly elastic response at low frequencies that grows during aging which appears to be the main characteristic of the aging in this system.

\[
\begin{array}{cccccc}
 t_a & 7.5 \text{ rad/s} & 68 \text{ rad/s} & 728 \text{ rad/s} & 6.5 \text{ rad/s} & 75 \text{ rad/s} \\
 0-2 \text{ h} & 0.75 \pm 0.3 & 1 \pm 0.1 & 0.95 \pm 0.1 & 0.85 \pm 0.1 & 1.0 \pm 0.1 \\
 2-4 \text{ h} & 1.2 \pm 0.3 & 1 \pm 0.1 & 1 \pm 0.1 & 0.9 \pm 0.1 & 1.0 \pm 0.1 \\
 4-6 \text{ h} & 1.4 \pm 0.3 & 1 \pm 0.1 & 1.1 \pm 0.1 & 1.1 \pm 0.1 & 1.1 \pm 0.1 \\
 6-8 \text{ h} & 0.85 \pm 0.1 & 1.0 \pm 0.1 & 1.1 \pm 0.1 & 1.0 \pm 0.1 & 1.0 \pm 0.1 \\
\end{array}
\]

Table 4.1 the effective temperature obtained for different frequencies averaged over 2 h time intervals. Within the uncertainty in the experiments, \( T_{\text{eff}}/T_{\text{bath}} = 1 \) [23].

**4.6.3 Glassy polymer**

L. Buisson and S. Ciliberto had measured the electrical thermal noise in a polymer polycarbonate [17]. They observed that the electrical noise is characterized by strong intermittency, which induces a large violation of FDT during aging time, and may persist for several hours at low frequency. However, this experiment exhibited large delta-function-like noise spikes, which can not be from the same dipolar degrees of freedom as those which produce the rest of the noise signal, and are likely extrinsic, e. g. due to differential contractions in the sample. Figure 4.15 shows the effective temperature \( T_{\text{eff}} \) as a function of frequency at different aging time \( t_w \). We clearly see that after quench \( T_{\text{eff}} \) is much larger than \( T_{\text{final}} \) in all frequency intervals. High frequencies rapidly decay towards the FDT prediction whereas at the smallest frequencies \( T_{\text{eff}} \approx 10^5 \) K. Moreover, the low frequencies decay very slowly than high frequencies and that the evolution of \( T_{\text{eff}} \)
toward the equilibrium value is very slow. They interpreted their founding in the framework of the trap model which is based on phase space description of the aging dynamics. Its basic ingredient is an activation process and aging is associated to the fact that deeper and deeper valleys are reached as the system evolves [47, 48, 147]. The dynamics in this model has to be intermittent because either nothing moves or there is a jump between two traps[47].

Figure 4.15 Effective temperatures vs. frequency at different aging time $t_w$ (Form the top to the bottom: $t_w = 200$ s, 260 s, 2580 s, 6542 s and 24h. The horizontal straight line is the FDT prediction. The dot dashed line corresponds to the limit where the FDT violation can be detected [17].
4.6.4 Structural glass: Glycerol

N. E. Israeloff and T. S. Grigera have studied the fluctuation-dissipation theorem (FDT) [44], connecting dielectric susceptibility and polarization noise, in glycerol below its glass transition temperature \( T_g \). Weak FDT violations were observed after a quench from just above to just below \( T_g \), for frequencies above the \( \alpha \) peak (Figure 4.16). Violations persisted up to \( 10^5 \) times the thermal equilibration time of the configurational degrees of freedom under study, but comparable to the average relaxation time of the material. These results suggest that excess energy flows from slower to faster relaxing modes. These FDT violations which appear in the range \( \omega t \gg 1 \) seem to in good agreement with later results on Laponite [86]. Those results seem to be in contradiction with previous results from theory and simulation. The origin of this discrepancy is presently unclear.

![Graph](image)

Figure 4.16 Effective temperature \( T_{\text{eff}} \) vs. waiting time for \( T = 179.8 \text{ K} \). Points: experimental data; solid line: fit to exponential decay.
The current accumulated experimental knowledge is still too poor. The contradictions found in the experiments of colloidal glass Laponite [14-16, 23, 86] with different measurements techniques and analysis and also the disagreements of those experiences with theoretical models and simulation, mark a numerous open questions in the field. The origin of these discrepancies and contradictions is presently unclear. More experiments that successfully and clearly demonstrate the existence of effective temperature related to FDT violation are certainly needed for this field of research to grow.
CHAPTER 5

APPARATUS AND EXPERIMENTAL TECHNIQUES

We present in this chapter the principal of FDR measurement through the noise and dielectric measurements in order to obtain and explain FDR deviations during aging processes. The measurements seem very straight-forward and feasible, in principle, but are very difficult in practice.

5.1 Sample preparation

A glassy polymer, poly-vinyl-acetate (PVAc) (Pellets from Aldrich Chemical (Figure 5.1)), was used for these experiments.

Figure 5.1. Poly-vinyl-acetate (PVAc) polymer pellets.
The average molecular weight (relative molar mass) used was 167,000. Where, the term relative molecular mass is defined as the sum of the relative atomic masses of the constituent atoms of a molecule. The glass transition temperature of this polymer is in the range of 305-308K dependent on the sample thickness [148]. This molecular weight is considered low to moderate for this polymer which is important in thin film samples to reduce confinement effects that can affect the transition temperature and dynamics[148]. Figure 5.2 shows the chemical formula of the PVAc.

![Chemical formula of PVAc](image)

**Figure 5.2. Poly-vinyl-acetate (PVAc) polymer structure.**

PVAc was selected as the main sample for our experiments because it is a well studied polymer [18]. In addition, the fact that PVAc has a convenient glass transition temperature, a low vapor pressure required for high vacuum experiments and that is solid at room temperature made this a good selection. Moreover PVAc is a quite fragile glass former as early experimental studies revealed (with a fragility index m=95 [149]) and has a stretching exponent for response function of $\beta =0.43$ at $T_g$ [18]. The non-exponential relaxation features measured in the macroscopic samples are another reason for this choice. This makes PVAc a good sample candidate to study non-exponential relaxation dynamics. PVAc exhibits besides that the commonly studied \(\alpha\)-relaxation process also a \(\beta\)-relaxation at temperature around 220K that arises from the motion of side groups [18, 148, 150]. The
dielectric properties of PVAc can be found in figures 5.3 and 5.4. Although PVAc gets contaminated with water (3 to 6 % at room temperature[151]) which considerably lowers the glass transition temperature.

Figure 5.3. Frequency dependence of $\varepsilon'$ the real part component of dielectric susceptibility, at various temperatures for glassy polymer PVAc in the $\alpha$-relaxation region [18].
The samples were prepared by dissolving PVAc pellets in toluene and spin coating the solution of PVAc onto AuPd-deposited Alumina substrate at 2000 RMP (Figure 5.5 and 5.6). The AuPd bottom electrodes are patterned in four dumbbell shaped patterns by sputtering through a stainless steel physical mask. The film thickness was 0.5 to 1 µm. The sample thickness is ~ 1 µm based on the plate dimension and capacitance measurement. The samples are annealed near $T_g \sim 308$ K for 48 hours in a vacuum, and a second pair of crossed electrodes of AuPd are sputtered on top to form an array of 8 parallel-plate capacitors with 0.3 cm in length and $C \sim 200$ pF. Some capacitors end up with pinholes and
metallic short-circuits thus the redundancy is helpful. The annealing process reduces and minimize the water contamination and also relax the sample from residual strains and polarization from spinning process.

Figure 5.5 Spin Coating apparatus.

Figure 5.6 PVAc sample on Alumina substrate showing an array of 8 capacitors.

It should be mentioned that there was no polymerization during sample preparation. The raw material was obtain already in polymer form and the sample preparation process
only dissolved the material (solid like) for film preparation. This kind of polymer is polymerized by free radical vinyl polymerization, which involves the breakage of the carbon-carbon double bond (vinyl group) to create a free radical used for building the polymer chain from stand alone monomers [18]. The temperature used for polymerization is much higher than the maximum temperature that the sample is ever subjected to. As reference, the degradation temperature at which PVAc looses 50 % of its weight when heated in vacuum for 30 minutes is 542 K [151]. The thickness of the samples is enough that the samples are bulk-like, i.e. thick enough to avoid dynamical effects that might affect the glass transition due to confinement [152]. These effects start to become apparent when the thickness is less than 100 nm, which is well below our thicknesses. The $T_g$ that we determined for our samples are nominal glass transition temperatures specified by the manufacturer, and agree with determinations found in the literature [151].

5.2 Thermal noise in a Capacitor

A capacitor permits the storage of electrostatic energy between its electrodes separated by dielectric material. Its properties depend on the nature of the material used. Usually, a glassy polymer is used as a dielectric substance. The expression for the capacitance is:

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \] 5.1
Where C is the value of the global capacitance in Farads, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant, A is the sample area and d is the sample thickness. The dielectric susceptibility can be described as a complex quantity, $\varepsilon_r = \varepsilon' + i\varepsilon''$.

A simplified electrical model describes a real capacitor by a capacitance C in parallel with a resistance R which represents the dissipative part in it (Figure 5.7). This is what we are going to measure in the experiment. It is related to loss factor by:

$$\tan(\delta) = \frac{1}{RC\omega}$$  \hspace{1cm} (5.2)

The dissipative angle, $\delta$, depends on the nature of the dielectric material, the frequency and the temperature. It shows the ratio of the imaginary part to the real part of the dielectric permittivity.

$$\tan(\delta) = \frac{\varepsilon''}{\varepsilon}$$  \hspace{1cm} (5.3)

The total impedance is given by:

$$\frac{1}{Z} = \frac{1}{R} + i\omega C$$  \hspace{1cm} (5.4)
Fluctuation Dissipation Relation in a Capacitor

From the famous Nyquist relation, the electrical charge distribution in an impedance is not perfectly isotropic in equilibrium. The random agitation of electrons with time due to the temperature, induces weak electrical charge fluctuation in the resistance.

In the case of dielectric polymer systems, as in our case, the response to an electrical field is related to the motion of charges and dipoles. In general, since the macromolecular degrees of freedom have permanent dipole moments, their motions are correlated to the dielectric response, which explains why the dielectric relaxation phenomenon has the same origin as mechanical relaxation. Precisely, the changes in the dielectric behavior are related to the thermal activation of some molecular motions which allow an escape over an energetic barrier separating two configurations.

The microscopic fluctuation dissipation theorem provides an expression for the average change of certain observable of a system under the action of a perturbation. Lets consider an observable $V$ and it conjugate variable $q$ for this system which is in a
thermodynamic equilibrium. The response function $\chi(\omega)$ at frequency $f = \omega/2\pi$, describes the variation $\delta V(\omega)$ of $V$ induced by a perturbation $\delta q(\omega)$ of $q$ which defined by:

$$\chi(\omega) = \frac{\delta V(\omega)}{\delta q(\omega)}$$

The FDR relates the fluctuation spectral density of $V$ to the response function $\chi$ and the temperature of the system as [38]:

$$S(\omega) = \frac{2k_B T}{\pi \omega} \text{Im}[\chi(\omega)]$$

Where $S(\omega) = \langle |V(\omega)|^2 \rangle$ is the fluctuation spectral density of $V$, $k_B$ is the Boltzmann constant, $\text{Im}[\chi(\omega)]$ is the imaginary part of $\chi(\omega)$. In the literature, examples of FDR are Nyquist’s formula which relate the voltage noise to the electrical resistance of the system, and the Einstein’s relation for Brownian motion which relates the particle diffusion to coefficient of the fluid viscosity [100].

In the studied model, we observe that $\chi(\omega) = i\omega Z$, the spectral density of our impedance is:

- **In the case of voltage spectral density:**

$$S_V(\omega) = 4k_B T \text{Re}[Z(\omega)]$$
-In the case of current spectral density:

\[
S_1(\omega) = 4k_B T \text{Re}\left[\frac{1}{Z(\omega)}\right]
\]

When the system is not in equilibrium, FDR represented in equation 5.6 may fail and it is not longer valuable. We need to consider the age of the system, \(t_\omega\). The FDR generalization introducing the effective temperature which takes account of the age, \(t_\omega\), and frequency \(\omega\), becomes:

\[
T_{\text{eff}}(t_\omega, \omega) = \frac{S(t_\omega, \omega)\pi\omega}{2k_B \text{Im}[\chi(t_\omega, \omega)]}
\]

In our case:

\[
T_{\text{eff}}(t_\omega, \omega) = \frac{S_V(t_\omega, \omega)}{4k_B \text{Re}[Z(t_\omega, \omega)]} = \frac{S_1(t_\omega, \omega)}{4k_B \text{Re}\left[\frac{1}{Z(t_\omega, \omega)}\right]}
\]

It is very clear that if equation 4.6 is satisfied \(T_{\text{eff}} = T\), otherwise \(T_{\text{eff}}\) turns out to be a decreasing function of \(t_\omega\) and \(\omega\). At out of equilibrium state, the system demonstrates separated modes, the fast processes from the slow ones. In other words, the low
frequency modes relax towards the equilibrium state much slower than the high
frequency ones which rapidly relax to the value of the temperature of the thermal bath.
Therefore it is believable that the slow frequency modes keep memory of the higher
temperatures for long time and for this reason their temperature should be higher than
that of high frequencies. It is now necessary to measure \( S(t_\omega,\omega) \) and \( Z(t_\omega,\omega) \) in function of
aging time \( t_\omega \) and frequency \( f=\omega/2\pi \) in order to get \( T_{\text{eff}} \).

5.3 Experimental apparatus

In this part, we will discuss different techniques used for dielectric and noise
measurements, their advantages and disadvantages and which methods give the best results.

5.3.1 Dielectric measurements

5.3.1.1 Novocontrol Broadband Dielectric measurement technique

The real and imaginary components of the dielectric susceptibility \( \varepsilon'(f, t_\omega) \) and \( \varepsilon''(f, t_\omega) \) were separately, from noise experiment, measured after identical temperature quenches
using a Novocontrol Broadband Dielectric Converter system which uses a Stanford SR830
Research lock-in amplifier (Figure 5.8). Novocontrol spectrometers for dielectric,
conductivity and impedance material analysis have a world wide reputation for highest
quality and flexibility [19]. The sample is inside the cryostat which is inside a Faraday cage
for an extra electromagnetic shield and the whole system is mounted on an air table in order
to reduce and eliminate mechanical vibrations coming through the building floor. The
temperature of the system was controlled by an Oxford ITC512 Temperature controller. During the aging process, we locally heat the sample radiatively by passing a current through a resistance underneath the sample (Figure 5.12). The heater voltage and current was controlled by HP E3632A DC Power Supply. The whole setup is powered through an Isolator Transformer IS1000 which cleans the building power line from 60Hz noise and also voltage surges. The most important characteristic of this isolator, is it provides a very clean reference ground for the whole system.

Figure 5.8 Dielectric susceptibility measurement setup using Novocontrol Broadband Dielectric Converter Analyzer
The ac voltage from the generator is applied to the sample and measured in amplitude and phase. The sample current is converted into voltage from which the sample impedance is evaluated and converted to complex permittivity or conductivity by internal firmware (Figure 5.10). All system functions are controlled by the BDC mainframe via high level GPIB commands which can be easily integrated in own programs. Optional turnkey operation is provided by Novocontrol WinDETA/WinFIT software including data evaluation, visualization and export [19]. This system uses also a technique of reference measurement. In this mode, for each impedance point first the sample is measured, $Z_s$. From this value, the reference capacity with the lowest difference of the impedance of the sample is selected and $Z_s$ is recalculated with the good precision. This mode enables the highest precision for $\tan(\delta)$. 

Figure 5.9 Connection of analog and digital units of BDC [19]
This kind of instrument has a very high precision for equilibrium measurements but it is less flexible when it comes to the measurement during aging process where time-resolution is important. The firmware software takes too much time to process data, 5.6 seconds for high frequency and 85 seconds for a low frequency of 0.1 Hz, even with minimum time settings, so we lose track of the value of dielectric susceptibility at early times after quench which roughly correspond to 1/f for the measured frequency. It is acceptable for high frequencies but it is much worse for low frequencies. For these reasons, we try to measure the dielectric constant with only the Stanford SR830 lock-in Amplifier using mono-frequency measurement technique.

![Figure 5.10 principles of impedance and material measurement](image)
5.3.1.2 Lock-in Amplifier Dielectric measurement technique

In order to measure the real $\varepsilon'$ and imaginary $\varepsilon''$ parts of dielectric constant of the system, we collect the in phase and out phase current signal when a sinusoidal voltage is applied to the sample using the Stanford SR830 lock-in Amplifier (Figure 5.11). The frequency will be fixed to a desired value and the voltage amplitude is a 1.0 volt rms which is a fixed value through the measurement process.

Figure 5.11 Dielectric susceptibility measurement setup using Stanford SR830 lock-in Amplifier
What does really the SR830 measure?

The Stanford Lock-in amplifier SR830 (Figure 5.12) multiplies the signal by a pure sine wave at the reference frequency. All components of the input signal are multiplied by the reference simultaneously. Mathematically speaking, sine waves of different frequencies are orthogonal, i.e. the average of the product of two sine wave is zero unless the frequencies are exactly the same. In the SR830, the product of this multiplication yields a DC output signal proportional to the component of the signal whose frequency is exactly locked to the reference frequency. It gives the amplitude and phase of the signal relative to the reference, or alternatively x (in-phase) and y (out-of-phase) components of the signal. The low pass filter which follow the multiplier provides the averaging which removes the products of the reference with components at all other frequencies.

Figure 5.12 Stanford DSP lock-in Amplifier SR830.
The signals, which are collected and saved in a computer through a Labview interface program, are the current $I_x$ and $I_y$, which are related to the imaginary and real parts of the system dielectric constant $\varepsilon'$ and $\varepsilon''$ by the following equations:

\[
\frac{1}{Z} = -iC\omega = \omega\varepsilon_0 (-\varepsilon'' + i\varepsilon') \tag{5.11}
\]

\[
\frac{I_x}{V} = \text{Re}(\frac{1}{Z}) = -\omega\varepsilon_0 \varepsilon'' \iff \varepsilon'' = -\frac{I_x}{\omega\varepsilon_0 V} \tag{5.12}
\]

\[
\frac{I_y}{V} = \text{Im}(\frac{1}{Z}) = \omega\varepsilon_0 \varepsilon' \iff \varepsilon' = \frac{I_y}{\omega\varepsilon_0 V} \tag{5.13}
\]

Where $\varepsilon_0$ is the vacuum permittivity, $\omega = 2\pi f$ is the frequency, $Z$ the impedance of the system and $V$ is the applied voltage which is 1 volt.

With this technique, we can collect the signal quite fast with a sampling rate of 18ms which is very adequate for following the system evolution during aging process. But the result still not adequate when signals are changing rapidly for low frequencies. The Lock-in Amplifier has an issue of time constant. In this case the measured signal is obstructed by $2\omega$ signal which shows some wiggling shape in the data, because the response is no longer a single frequency sine wave. Indeed, we want to record the information and follow the system progression with both speed and accuracy in order to follow the early-time aging in detail.
In order to resolve these issues, we adopted another technique which used white noise for dielectric measurement that we will discuss in more detail in the next paragraph.

5.3.1.3 White noise dielectric measurement technique

The white noise dielectric measurement technique is very simple in principle but somewhat complicated in practice which required careful programming and statistical processing. The setup used in this measurement was shown in figure 5.13.

Figure 5.13 Dielectric susceptibility measurement setup using white noise.
The details of the technique are as the following: the sinusoidal excitation voltage is replaced by a white noise signal generated from an HP 3561A Dynamic Signal Analyzer. The signal is amplified and filtered by a Stanford 560 Low noise amplifier with amplitude of 10 µV RMS, the cutoff frequency is 10Hz, then the output signal is sent through the sample impedance which is in the cryostat. The current signal from the other electrode of the sample is amplified by a LCD-30-1T low-noise current amplifier and filtered by a Stanford SR640 low noise filter, which has very sharp cut-off frequency of 30Hz. Finally, the resulting current signal, I(t), and the input white noise voltage signal, V(t) were both collected by computer with a Labview interface program through a DAQ card. The HP3632A DC Power supply was used again to heat the sample during the aging procedure.

The admittance, \( Y = 1/Z \), of the system is related to the measured current \( I \) and applied white noise voltage \( V \) by the following relation:

\[
Y = \frac{1}{Z} = \frac{I}{V}
\]

By applying a Fourier transform to the both signals \( I \) and \( V \), we get the dielectric susceptibility of the system as shown in the expressions below:

\[
Y = \frac{\tilde{I}}{\tilde{V}}
\]

\[
\text{Re}(Y) = -\omega \varepsilon_o \varepsilon
\]

\[
\text{Im}(Y) = \omega \varepsilon_o \varepsilon
\]
Where \( \varepsilon_0 \) is the vacuum permittivity, \( \omega = 2\pi f \) is the frequency, \( \varepsilon' \) and \( \varepsilon'' \) the real and imaginary parts of the system dielectric constant.

In order to reduce a statistical errors, we repeat the measurement many times (10 times) and we take the average of the runs. The equation 5.15 can be written in the form below:

\[
Y = \frac{\langle \tilde{I} \rangle}{\langle \tilde{V} \rangle}
\]  
5.15

Because, the voltage is a random noise and if the value of it equals a value somewhat near zero, the admittance \( Y \) in equation 5.15 becomes a very large number. So, to reduce the large fluctuation in \( Y \) and to smooth its values, we multiply the denominator and nominator of expression 5.15 by the conjugate value of the voltage \( V^* \) and we average each quantity before the division instead of taking the average of the whole thing. The equation adopted in this analysis is the following:

\[
Y = \frac{\langle \tilde{I} \tilde{V}^* \rangle}{\langle \tilde{V} \tilde{V}^* \rangle}
\]  
5.16

And the question is why we do not choose the following expression as a replacement for of the above:

\[
\]
\[ Y = \left\langle \frac{\tilde{I}\tilde{V}^*}{\tilde{V}\tilde{V}^*} \right\rangle \]  

5.17

In order to answer the above question, we did a computer simulation and compare the results of the three equations 5.15, 5.16 and 5.17. We suppose the admittance is equal to the following value:

\[ Y = 5 + 2i \]  

5.18

Then, we generated a 100 sets of independent random noise for the voltage \( V \). From the given \( Y \) and \( V \), we calculated the current \( I \) and we added some percentage of white noise as a background to the current calculated. So, we computed again the values of \( Y \) from the new current, which include some background in it, using the random voltage noise generated before. The goal of this simulation was to compare the imaginary and real part of \( Y \) and also their errors and standard deviations matched up to to the input \( Y \) of equation 5.18. In addition, we evaluated the influence of the background added to each quantity. The graphs below showed the result of our simulations.
Figure 5.14 Real part of the admittance Y vs. added background noise.

Figure 5.15 Imaginary part of the admittance Y Vs. The added background noise.
From the graphs (Figure 5.14 and 5.15) above of real and imaginary part of the admittance $Y$, we can clearly see that the adopted equation 5.16 in our analysis is the best choice. It shows smallest error bars compared with the other two equations 5.15 and 5.17, and also shows a small amplitude variation with add background noise if compared to the values calculated from the two equations. The maximum error on Re($Y$) is 0.4% and for Im($Y$) is 0.5% form the introduced value in equation 5.18.

Figure 5.16 Standard deviation of Real part of the admittance $Y$ vs. the added background noise
Figures 5.16 and 5.17 show similar variation of the standard deviation calculated for Re(Y) and Im(Y). All three equations simulated demonstrate an increase in sigma with the added background noise percentage. But, the difference is the selected equation 5.16 again shows a small amplitude variation compared with the other two equations.

The only problem we faced in this method of dielectric measurements using white noise is there are some small phase and amplitude shifts compared with the data collected from lock-in amplifier measurement method, due to, for example, the filters in the circuit. We calibrated these amplitude and phase corrections by measuring the system in equilibrium with the white noise, comparing to the measurement of Novocontrol and calculating the
(complex) correction factor for each selected frequency studied in this project. So, we multiplied our data by the correction factors and we got the desired results that appear in good agreement with the FDR theory.

5.3.2 Noise measurements

The current noise spectral density, $S_I$, is measured via an ultra-low noise current amplifier (Femto LCA-30-1T) (Figures 5.18, 5.19), in an electromagnetically shielded steel enclosure, mounted on a vibration isolation air table. The current noise is measured as a function of frequency, ($f = 0.0259$ Hz to 30 Hz) and waiting time, $t_\omega = 0.0187$ s to 600 s following the quench, and in equilibrium (Figure 5.20).

Figure 5.18. Ultra Low Noise Current Amplifier LCD-30-1T image.
### Figure 5.19. Low noise current amplifier LCA-30-1T specifications [20].

<table>
<thead>
<tr>
<th>Specifications</th>
<th>Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gain</td>
<td>Transimpedance</td>
</tr>
<tr>
<td></td>
<td>1 x 10^9 WA (&gt;10 kΩ Load)</td>
</tr>
<tr>
<td>Accuracy</td>
<td>±1%</td>
</tr>
<tr>
<td>Frequency Response</td>
<td>Lower Cutoff Frequency</td>
</tr>
<tr>
<td></td>
<td>Upper Cutoff Frequency</td>
</tr>
<tr>
<td></td>
<td>Rise-/Fall-Time</td>
</tr>
<tr>
<td></td>
<td>Gain Flatness</td>
</tr>
<tr>
<td>Input</td>
<td>Eq. Input Noise Current</td>
</tr>
<tr>
<td></td>
<td>Eq. Input Noise Voltage</td>
</tr>
<tr>
<td></td>
<td>Input Bias Current</td>
</tr>
<tr>
<td></td>
<td>Input Bias Current Drift</td>
</tr>
<tr>
<td></td>
<td>Offset Current Compensation</td>
</tr>
<tr>
<td></td>
<td>Max. Input Current</td>
</tr>
<tr>
<td></td>
<td>Input Offset Voltage</td>
</tr>
<tr>
<td></td>
<td>DC Input Impedance</td>
</tr>
<tr>
<td>Output</td>
<td>Output Voltage</td>
</tr>
<tr>
<td></td>
<td>Output Impedance</td>
</tr>
<tr>
<td>Power Supply</td>
<td>Supply Voltage</td>
</tr>
<tr>
<td></td>
<td>Supply Current</td>
</tr>
<tr>
<td>Case</td>
<td>Weight</td>
</tr>
<tr>
<td></td>
<td>Material</td>
</tr>
<tr>
<td>Temperature Range</td>
<td>Storage Temperature</td>
</tr>
<tr>
<td></td>
<td>Operating Temperature</td>
</tr>
</tbody>
</table>

### Figure 5.20 Noise measurement setup using ultra low noise current amplifier LCD-30-1T.
The noise measurement setup is shown in the above Figure (5.20). The technique seems very simple but because the collected signal is very small in amplitude (~$10^{-15}$ A), this makes the measurement very difficult and it can be easily corrupted by the outside noise (mechanical, electromagnetic and acoustic noise). So, in order to reduce or eliminate the electromagnetic and acoustic noise, we placed the system inside a Faraday cage enclosure (metal steel box) and for damping the mechanical vibration coming from the building, we mount the whole system on the top of a vibration isolation table which can damp as low as 1 Hz mechanical frequencies.

The measured signal is amplified by the current amplifier LCD-30-1T ($10^{12}$ V/I Gain), then is filtered through Stanford SR 640 low noise filter. The cutoff frequency is 30 Hz. The temperature of the system is controlled by Oxford ITC 502 temperature controller. The output signal was collected by computer with Labview interface program through a DAQ card which has built-in anti-alias filters. The HP3632A DC Power supply was used to heat the sample during the aging process. All electronic devices used in this setup are powered through an Isolator Transformer IS 1000 which provide a very clean reference ground and clean power from 60 Hz noise and voltage surges. The signal processing and analysis will be discussed in more details in the following paragraph.

5.4 Signal processing and analysis method

We have measured the polarization noise and dielectric susceptibility in macroscopic samples of a polymer (PVAc) during aging in order to study FDR violations. These measurements require great care to eliminate extrinsic noise. It is critical to avoid or
eliminate extrinsic spikes that have plagued some of the other experiments, to be certain that the fluctuations are coming from the microscopic degrees of freedom involved in glassy dynamics. The sample is radiatively heated from below well above $T_g = 308 \, \text{K}$ for 9 seconds, and then quenched to temperatures below $T_g$ (Figure 5.21). The quench time is short, < 10s, because of the small sample mass.

**Figure 5.21 Sample experimental setup.**

### 5.4.1 Signal processing

We collect the noise signal from the sample. One annoying artifact is a transient dc offset which slowly decays following a quench. This produces a background drift in the signal following a quench. To remove this effect, we subtract the average of 120 consecutive quenches (a batch) (Figure 5.22). A second artifact arises from occasional large delta-function-like voltage spikes, some produced by the amplifier and others, we believe, produced by differential thermal contractions following the sudden temperature quench. We have shown that these spikes are much too large [153] to come from the sample, thus
we exclude them from the analysis. This is very important for accurately determining the effective temperature (Figures 5.23 and 5.24). The criteria adopted in this process is deleting the spikes that are greater than 5 standard deviations of the signal and replacing them by the mean value in the region of the spikes. The spikes removal method will be considered as a sufficient analysis because the probability that a measurement will lie outside $5\sigma$ width of the distribution is extremely small in the order of $\approx 1 \times 10^{-3}$ %.

Figure 5.22 Signal drift correction.
Figure 5.23 Signal with spikes.

Figure 5.24 Clean signal with spikes removed
5.4.2 FFT Analysis

We apply a fast Fourier transform to the clean signal in order to get the power spectrum of the system. The sampling time for our signal is usually $t_s = 0.018787$ s. It is limited by the speed of the Mac time-series program. We calculate the FFT of the time series for different batch sizes ($2^n$ data points). For each time series we overlap the batches by a single time step. We want to obtain the best time resolution for the lowest measurement frequency. Thus we save only the lowest non-zero frequency bin of the FFT in order to get a power spectrum evolution with time for a fixed single frequency (Table 5.1).

<table>
<thead>
<tr>
<th>FFT size</th>
<th>1st bin Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>2048</td>
<td>0.02590 Hz</td>
</tr>
<tr>
<td>1024</td>
<td>0.05198 Hz</td>
</tr>
<tr>
<td>512</td>
<td>0.10396 Hz</td>
</tr>
<tr>
<td>256</td>
<td>0.20790 Hz</td>
</tr>
<tr>
<td>128</td>
<td>0.41584 Hz</td>
</tr>
<tr>
<td>64</td>
<td>0.83169 Hz</td>
</tr>
<tr>
<td>32</td>
<td>1.66338 Hz</td>
</tr>
<tr>
<td>16</td>
<td>3.32677 Hz</td>
</tr>
<tr>
<td>8</td>
<td>6.64354 Hz</td>
</tr>
<tr>
<td>4</td>
<td>13.3070 Hz</td>
</tr>
</tbody>
</table>

Table 5.1 FFT size and 1st bin frequency
There are several problems that we worry about in this analysis, which are the effect of small residual DC in the signal, background noise, and also the most vital effect which is the spectral leakage on the first bin spectral frequency. So, to study the effect of those artifacts on our analysis and how to eliminate and reduce their outcomes, we did a signal simulation replicating the way we investigate our signal. Therefore, we will have a big picture of the situation and find the right solutions for those effects.

5.4.2.1 Signal simulation

a)- Spectral Leakage

- Effect of spectral leakage

Spectral leakage occurs when a frequency component of a signal does not slot exactly into one of the frequency channels in the spectrum computed using the Fast Fourier transform. In real life, signals are not simple sine waves, and even periodic signals may not perfectly match the FFT time window size, so it is extremely unlikely that there will be a smooth match at the beginning and end of the sampled signal. These end-effects cause spectral leakage and can therefore almost certainly affect any signal of practical interest.

In order to measure the effect of spectral leakage on our signal analysis, we simulate the situation for different signal power exponent (α) and for different FFT sizes. This spreading out of spectral energy across several frequencies affects any frequency component of a signal which does not exactly coincide with a frequency channel. Since the frequency components of an arbitrary signal are unlikely to satisfy this requirement, spectral leakage is more likely to occur than not with real-life sampled signals.
Figure 5.25 Simulated Power Spectral with exponent 0.6 for different FFT size.

Figure 5.26 Simulated Power Spectral with exponent 0.8 for different FFT size.
Figure 5.27 Simulated power spectral with exponent 1.0 for different FFT size.

Figure 5.28 Simulated Power Spectral with exponent 1.2 for different FFT size.
Figures 5.25, 5.26, 5.27, 5.28 and 5.29 show simulated power spectral for chosen exponent spectral $\alpha = 0.6, 0.8, 1.0, 1.2$ and $1.4$ for different FFT batches size. We clearly see that the first bin in each FFT is corrupted and shows a high amplitude in all different exponent cases caused by leakage of adjacent frequencies.

- **Reducing spectral leakage**

Spectral leakage causes energy (amplitude) from distinct spectral features to leak into adjacent frequency channels, giving rise to spurious components in the frequency spectrum of the signal. The only way to avoid such leakage entirely would be to arrange that all frequency components of the signal being examined coincide exactly with
frequency channels in the computed spectrum. This, however, is impractical for an arbitrary signal containing many unknown frequency components.

While spectral leakage cannot in general be eliminated completely, its effects can be reduced to some acceptable level. This is done by applying a narrowed window function to sampled signal. The sampled values of the signal are multiplied by a function which tapers toward zero at either end, so that the sampled signal, rather than starting and stopping suddenly, weaken in and out like some music CD tracks. This reduces the effect of the discontinuities where the mismatched sections of the signal join up, and hence also the amount of leakage. There is, however, a downside to the use of a tapered window function: lines in the spectrum of a signal become broadened, making it difficult to distinguish separate frequency components, and therefore effectively reducing the spectral resolution. A number of tapered window functions have been devised. Some are more effective in reducing spectral leakage, at the expense of loss of spectral detail, while others to try to achieve a compromise between these conflicting requirements. A popular choice is the **Hanning** (or von Han) window function, which is essentially one cycle of an inverted cosine function, shifted and scaled so that it has maximum value of 1 in the middle and tapered to zero at either end (Equation 5.19).

\[
\omega(n) = 0.5(1 - \cos\left(\frac{2\pi n}{N - 1}\right)) \quad 5.19
\]

Where N represent the width, in samples, of a discrete-time window function. Typically it is an integer power of 2, such as \(2^{11} = 2048\) and \(n\) is an integer, with value \(0 \leq n \leq N-1\).
In our signal processing, we chose the Hanning window as the most common window for its features that compromise between frequency resolution and amplitude accuracy (Figure 5.30).

![Hanning Window](image)

**Figure 5.30** Hanning Window

The graphs below (Figures 5.31 and 5.32) exhibit the effect of applied Hanning window on power spectral simulation compared to the case above in Figures 5.25 to 5.29 which demonstrate the effect of spectral leakage on the first bin frequency before applying the Hanning window. We see clearly that this process damps and reduces this harmful effect. One drawback of this window is loss in amplitude accuracy which we correct by figuring out the correction factor on the first bin before and after the window application where the spectral leakage effect is negligible in a white noise spectral simulation (Figures 5.33 and 5.34). The simulation was averaged $10^6$ time in order to reduce statistical errors to a negligible value. This correction factor is 3.201 which correspond to 2.09 dB amplitude loss.
Figure 5.31 Applied Hanning window to Simulated Power Spectral with exponent 0.8 for different FFT size.

Figure 5.32 Applied Hanning window to Simulated Power Spectral with exponent 1.0 for different FFT size.
Figure 5.33 Power spectral density of White noise simulated and averaged $10^6$ times with and without Hanning window effect for FFT size of 2048.

Figure 5.34 Power spectral ratio of white noise simulated signal before and after applying a Hanning window. The horizontal line is the fit for the other FFT bins which shows a constant value of 2.67.
b)- Constant DC level

- Effect of a constant DC level

In our simulated signal analysis we did add some amount of DC offset to our signal then we calculated the power spectrum in order to see the effect of the DC level on the first frequency bin. Figure 5.35 shows obviously a huge and tremendous amplitude in the first frequency bin for different FFT batch size. In terms of the spectrum of a signal, any constant DC level shows up as a zero frequency component which has a big impact and influence on the first bin frequency through the effect of spectral leakage despite the fact that we did apply a Hanning window to the signal during Fourier analysis. We found that the Hanning window increased the effect of DC offset.

![Figure 5.35 Applied Hanning window to Simulated Power Spectral with exponent 1.0 for different FFT size and with a DC level added.](image)
• **DC offset elimination method**

In order to totally eliminate the residual DC offset in the time series signal, we locally subtracted the mean of each signal batch from the signal itself before FFT calculation, so the zero frequency component due to the DC level is 0 and had no influence on the first bin power spectral frequency.

**c)- Background noise**

• **Effect of adding background noise**

Real life signal often contains appreciable amount of “background noise”, i.e. a randomly-varying voltage superimposed on the signal, arising from various sources. To illustrate the effect of the noise on the spectrum, we will generate a simple signal with added white noise. The spectrum of the noisy simulated signal should consist of the real signal frequencies, together with components of small, randomly varying amplitudes spread across the entire frequency spectrum. When FFT is applied to a signal containing random noise, the noise amplitude tends to be spread more or less evenly across the frequency baseband, giving an approximately flat background level from which the true signal components can be seen emerging.

Figures 5.36, 5.37 and 5.38 show a simulated signal for different power spectral exponent with added white noise which demonstrated the effect of white background noise on the frequency component of the original signal and is shown as a flat background level.
In reality, the signal contain many frequency components. The spectrum of such a signal obtained using FFT will reveal the more important components, while weaker features may be swamped in the noise background.

Figure 5.36 Applied white noise to a Simulated Power Spectral with exponent 0.8 for different FFT size.
Figure 5.37 Applied white noise to a Simulated Power Spectral with exponent 1.0 for different FFT size.

Figure 5.38 Applied white noise to a Simulated Power Spectral with exponent 1.2 for different FFT size.
• **Background noise removal**

In practical environment, the subtraction of white noise background from the intrinsic signal components is very difficult during the analysis. Finding the source of the background noise will really be a big help in characterizing its features then subtracting it from the wanted signal. In our case, the background noise existing in our signal is the current and voltage noise of the current amplifier LCD-30-1T which will be discussed in the next section in more details.

### 5.4.3 Amplifier Background noise subtraction techniques

#### 5.4.3.1 Conventional background subtraction technique

Initially, we used the well known techniques adapted in removing the possible current noise and voltage noise of an amplifier that disguised the sample signal (Equations 4.20 and 4.21).

\[
S_{I}^{m} = S_{I}^{s} + S_{I}^{A} + \frac{S_{V}^{A}}{Z^2} \quad 5.20
\]

\[
S_{I}^{Backg} = S_{I}^{A} + \frac{S_{V}^{A}}{Z^2} \quad 5.21
\]
Where $S_{Im}^m$ is the measured output current noise, $S_I^s$ is the sample intrinsic current noise, $S_I^A$ is the amplifier current noise, $S_V^A$ is the amplifier voltage noise, $Z$ is the sample impedance, and $S_I^{Backg}$ is the total background current noise. From the figure 5.19 which shows the amplifier specifications, the input noise current is $S_I^A = 2.5 \times 10^{-31} A^2/Hz$, and the input noise voltage is $S_V^A = 8.1 \times 10^{-15} V^2/Hz$ at 10 Hz.

In our measurements, we work at low frequencies where the amplifier current and voltage noise are more significant compared to the signal and careful subtraction should be considered. So, we measured the amplifier current noise at the required frequency range by short circuiting the amplifier input. Figure 5.39 shows the current amplifier noise which is almost a constant value in the frequency range studied. The measurement of the amplifier voltage noise is done by connecting a dummy capacitor with a constant value and low loss factor to the amplifier input. We chose a 192 pf capacity which is close to the value of our sample in equilibrium. We carefully measure its real and imaginary components of its capacitance with the Novocontrol system. After subtracting the amplifier current noise $S_I^A$ and the capacitances predicted thermal noise spectrum from (Equations 5.22 and 5.23), we get the amplifier voltage noise (Figure 5.40).

$$S_V^A = \left[ S_{Im}^m (192 \, pF) - S_I^A - S_I^{Thermal} (192 \, pF) \right] Z^2 (192 \, pF) \tag{5.22}$$

$$S_I^{Thermal} (192 \, pF) = 4k_B T \omega C^\prime \tag{5.23}$$
Where $S_{1m}^{(192pF)}$ is the dummy capacitor measured current spectrum, $S_{1A}$ is the amplifier background current noise, $S_{1}^{\text{Thermal}}(192pF)$ is the capacitor thermal current power spectrum, $Z(192pf)$ is the capacitor impedance, $k_B$ is the Boltzmann constant, $T$ is room temperature (295K), $\omega=2 \pi f$ is the angular frequency, and $C''$ is the previously measured imaginary part of the capacitance.

![Figure 5.39 Background amplifier current noise](image)
Figure 5.40 Background amplifier voltage noise.

After a long time of working with this background subtracting technique, we figured out that both the amplifier current and voltage noise vary with the input impedance to the amplifier. So, as we measured the power spectrum of the sample during the aging process, its impedance varies with aging time and this had an impact on the background noise. Therefore, we develop a technique that allows as to know the exact amount of total background that should be subtracted from our measured spectral density and which we will discuss in more detail in the next section.

5.4.3.2 New Background subtracting technique

We choose dummy capacities in the range where our sample impedance varies during the aging process and which are from 192 pF to 990 pF. We measure their power spectral density at equilibrium and at room temperature, then, we subtracted from them the
capacity thermal noise only (Equation 5.21). We fit the results in order to get a smooth data graphs (Figures 5.41 and 5.42).

![Figure 5.41 Total amplifier background noise measured for different input dummy capacities.](image-url)
Figure 5.42 Measured impedance of different dummy capacities used in the new background subtraction technique.

Form the amplifier background noise data for different impedance versus frequency, we plot the $S_{I}^{\text{Backg}}$ versus impedance $Z$ for a fixed frequency (Figure 5.43) and we fit each single frequency case as a function of $1/Z^2$ (as shown in equation 5.21 below), then we get the fitting values of $S_{I}^{A}$ and $S_{V}^{A}$ for different frequencies.

$$S_{I}^{\text{Backg}} = S_{I}^{A} + \frac{S_{V}^{A}}{Z^2}$$

So, we plot again the value of $S_{I}^{A}$ and $S_{V}^{A}$ versus frequency (Figures 5.44 and 5.45) and we come up with empirical equation for each quantity as the following:
\[ S^A_I = b_{IA} f^2 + a_{IA} \quad 5.24 \]

\[ S^A_V = \frac{b_{VA}}{f^2} + a_{VA} \quad 5.25 \]

And from the fitting procedure, we get the constant values of \( a_{IA} \), \( b_{IA} \), \( a_{VA} \), and \( b_{VA} \) as shown in the table below (Table 5.2).

<table>
<thead>
<tr>
<th>( a_{IA} )</th>
<th>( 3.429265 \times 10^{-31} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_{IA} )</td>
<td>( 0.025382 \times 10^{-31} )</td>
</tr>
<tr>
<td>( a_{VA} )</td>
<td>( 2.836766 \times 10^{-15} )</td>
</tr>
<tr>
<td>( b_{VA} )</td>
<td>( 6.739975 \times 10^{-15} )</td>
</tr>
</tbody>
</table>

Table 5.2 Fitting parameters of the background components.
Figure 5.43 The total amplifier background noise versus input impedance for a different fixed frequencies.

Figure 5.44 The Amplifier background voltage noise versus frequency.
Finally, the equations 5.24 and 5.25 are the main and final current and voltage amplifier background noise formulas that will be used in all our analysis process.

### 5.4.4 FDR calculation

Lastly, after a painful and careful signal processing and analysis techniques used in this chapter which we have explained in very specific details, we get the power spectrum of the system, which is related in our case to the Real part of the admittance $\text{Re}(1/Z)$ and effective temperature $T_{\text{eff}}$ by the FDR:

$$ S_I = 4k_B T \frac{1}{\text{Re}(1/Z)} $$

5.26
The real and imaginary components of the dielectric susceptibility \( \varepsilon'(f, t_0) \) and \( \varepsilon''(f, t_0) \) were separately measured after identical temperature quenches using a Stanford Research lock-in amplifier and white noise techniques. We use these to calculate the background current and voltage noise produced by the amplifier acting on the sample impedance (Equations 5.24 and 5.25). Both of these must be carefully measured and subtracted from the measured sample noise.

In equilibrium, the FDR (Nyquist’s relation) is:

\[
S_I = 4k_B T \text{Re}(Y)
\]

Where \( Y = 1/Z \) is the admittance.

Thus we calculate the non-equilibrium effective temperature [40] via:

\[
T_{\text{eff}} = \frac{S_I}{4k_B \text{Re}(Y)} = \frac{S_I}{4k_B C_0 \omega \varepsilon''}
\]

The results reported in this work are for a temperature, 300K. A large number of quenches (~120 runs) followed by measurement runs of short duration (600 second) and 9 measurement sets of 120 runs in each are done in order to reduce the statistical errors and resolve small and long-lived violations.
In this chapter, we will characterize the time dependence of frequency-dependent dielectric susceptibility of PVAc following quenches to below and above transition temperature $T_g$. We also show equilibrium data at different temperature and frequencies in order to study the $\alpha$-relaxation process. Our measurements of the dielectric response in glassy polymer PVAc provide a direct analogy with the magnetic susceptibility aging studies in spin glasses. We can thus examine if the theories proposed for spin glasses have relevance for glassy polymer systems. The dielectric susceptibilities discussed here were collected by the Novocontrol measurement technique.

### 6.1 Dielectric susceptibility in glasses

The frequency dependence dielectric susceptibility is a characteristic response of a given material.

$$\varepsilon^* = \varepsilon'(\omega) + i\varepsilon''(\omega)$$
The dielectric susceptibility can be used as an indicator of the mobility of polar molecules or ions in a sample. It is commonly used to study the complex dynamic nature of glassy system. One advantage of probing the dielectric response over other detecting techniques is that dielectric spectra can be measured over more than 18 decades of frequency [154]. In this work, the temperature dependent dielectric relaxations near to the primary relaxation region are discussed.

The simple classical case of dielectric response can be illustrated a set of identical non-interacting dipoles free to rotate against some viscous resistance or by jumping due to thermal excitation between two favored orientations separated by a potential barrier.

For this simple case, the frequency dependent complex dielectric material can be expressed based on the Debye model [155] is given by,

\[
\varepsilon(\omega) = \varepsilon_\infty + \left( \frac{\varepsilon_0 - \varepsilon_\infty}{1 - i\omega\tau} \right)
\]

Where \(\varepsilon_0\) and \(\varepsilon_\infty\) are low and high frequency limits of \(\varepsilon(\omega)\) and \(\tau\) represents the single relaxation time.

If we plot the dielectric loss \(\varepsilon''\) (imaginary part of the susceptibility) as a function of frequency in a logarithmic plot this yields a symmetric graph. Even though Debye’s theory of relaxation describes qualitatively well many systems, but dense interacting systems such
as glasses more often show asymmetrical loss peaks with low and high frequency tails. As an example of this very different behavior from a Debye response is shown in figure 6.1, where a compilation of dielectric loss for many polymeric glassy systems is shown along with a Debye peak for reference only.

At temperatures greater than the glass transition temperature a sharper $\alpha$-peak is usually found. The response for frequencies higher than the peak is often characterized by a power law of the kind $\varepsilon(\omega) \propto \omega^{n-1}$ with $n < 1$. Sometimes a knee can be observed at high frequencies so that the response is better characterized by superposition of two such functions with higher component having value of $n$ closer to unity. Many polymeric materials demonstrate very flat dielectric losses over many decades of frequency not compatible with Debye approach. Therefore, the tail at high frequencies is projected to contain important information about the dynamics of glass relaxation. In other hand, the dielectric $\beta$-relaxation displays a broad and in the most cases symmetric loss peak with half widths of 4-6 decades. Extracting information on the basic mechanism of motion is difficult from such broad peaks. The width of the $\beta$-peak is often explained in terms of a distribution of both the activation energy and the pre-exponential factor caused by a distribution of molecular environments in which the molecular motion of the $\beta$-relaxation can take place [156]. The width of $\beta$-peak generally decreases with increasing temperature.

The heterogeneous picture could elucidate and clarify the origin of the high frequency tail of the loss peak, by adding the contribution of many independent Debye domains, each relaxing with a single characteristic relaxation constant $\tau_i$ (Equation 6.3) with a proper distribution of relaxation times [59]. This idea is shown in Figure 6.2, where
the imaginary part of the susceptibility is assumed to arise from a superposition of Debye peaks with different characteristic times for each relaxing cluster (Figure 6.3), because of the disorder present in a glass.

\[ \varepsilon''_i(\omega) = (\varepsilon_\infty - \varepsilon_0) \left[ \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \right] \]  

6.3

Also this phenomenological model for dielectric relaxation can explain the Debye peak seen in the low frequency imaginary part of the dielectric susceptibility \( \varepsilon'' \) of the glassy system by the single relaxation time \( \tau_i \) discussed above (equation 6.3). Based on this picture, by summing all the relaxing clusters from equation 6.3, we will obtain the total response for the dielectric susceptibility of the system.

In the experimental data, the primary relaxation peak was detected near to the glass transition temperature. Using this heterogeneous representation [figure 6.2], we could give enlightened explanation to the observed primary relaxation peak by saying that the number of clusters relaxing at the peak area is somewhat higher than number of clusters relaxing at the lower and higher end of frequency tail of the peak.
Figure 6.1 Compilation of dielectric loss data for range of polymeric glass formers. The points marked with different symbols correspond to data taken at different temperatures and transposed laterally to make the loss peaks coincide. Graphs are displaced vertically for different substances for clarity only. The shape of a Debye peak is included for comparison. a)- Low temperature data for polychloroprene; b)-PCTFE 12% crystalline; c)- Polyethylene terephthalate; d)- Polymethyl methacrylate; e)- High temperature data for polychloroprene; f)- Polyethyl methacrylate; g)-Polydian carbonate; h)- Polyvinyl acetate [21].
Figure 6.2. The imaginary component of the dielectric susceptibility is assumed to arise from the superposition of Debye like peaks [22].

6.2 Dielectric spectroscopy measurements in PVAc

The \( \alpha \)-relaxation is related to the glass transition of the system and for that reason this relaxation process is also called dynamic glass transition. The static \( T_g \), was determined by differential scanning calorimetry, and which corresponds to a frequency of approximately \( 10^{-3} \) Hz. Obviously this frequency is dependent on the cooling and heating rate of the system during the experimental procedures. So, a dynamic glass temperature from dielectric experiments can be defined as the temperature of the maximum loss at the selected frequency. In general, the \( \alpha \)-relaxation and the related glass transition phenomenon are not well understood, and the real microscopic description of the relaxation remains an unsolved and current problem of polymer science [157, 158].
For more understanding of this relaxation process in PVAc, the dynamics are investigated in the frequency range of $10^3$Hz to $10^5$Hz, and in the temperature range of 296K to 339.5K. The most remarkable feature in the response is the peak due to $\alpha$ relaxation in the glassy sample. Figures 6.4 and 6.5 clearly illustrate that the location of the $\alpha$-peak in the frequency spectrum shifts with temperature, since the $\alpha$-peak determined by the average relaxation time of molecules in the sample.

Dielectric spectroscopy demonstrates dynamical responses which are of interest in a number of ways. In the plot of $\varepsilon'$ spectrum (Figure 6.3) the characteristic shape of the change in the $\alpha$ relaxation region $\Delta \varepsilon = \varepsilon_\alpha - \varepsilon_\infty$ from slow dielectric susceptibility $\varepsilon_\alpha$ at low frequencies to the fast dielectric susceptibility $\varepsilon_\infty$ at high frequencies is evident.

Figure 6.3 PVAc sample dielectric susceptibility real part $\varepsilon'$ vs. frequency at different temperature.
Figure 6.4 PVAc sample dielectric susceptibility imaginary part $\varepsilon''$ vs. frequency at different temperature.

It is clearly observed that the magnitude of the dielectric $\alpha$ relaxation $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ decreases with increasing temperature, as found for most of other amorphous polymers at temperatures above $T_g$ [18, 159].

The first thing we see from the response functions in our measurements is the shift in the $\alpha$ peak toward high frequencies as the temperature increases (figures 6.3, 6.4 and 6.5) with their shapes are relatively unchanged.
Ishida et al. [160] concluded from observed dielectric spectroscopy measurement done on different glassy polymers that both the width and the asymmetry of the experimental loss curves arise from the intrachain interaction and are thus characteristic of the long chain nature of the molecules [160].

A more useful analysis is the extraction of the glass transition temperature from the dielectric measurements. The location of the $\alpha$ peak in the $\varepsilon''$ dielectric spectrum, also present in the $\tan(\delta) = \varepsilon''(\omega)/\varepsilon'(\omega)$ response function, is an indicator of the mobility of the sample. As an indicator of the relaxation speed of the material, an accepted definition of the glassy state is when the $\alpha$-relaxation peak point to a time constant $\tau$ on the order of 100 seconds, or frequency of $\frac{1}{2\pi\tau} \approx 0.00159 \text{Hz}$. The location of the $\alpha$ peak versus
frequency is expected to match the form of the Vogel-Fulcher-Tammann (VFT) (Equation 6.4).

\[ f_{p\alpha} = f_{\alpha \infty} \exp\left(\frac{U}{T - T_0}\right) \quad 6.4 \]

Where \( f_{p\alpha} \) is the peak frequency at very high temperature, U is the activation energy, and \( T_0 \) is the Vogel temperature [161-163], which is the extrapolated temperature of infinite relaxation time.

Thus, we can fit the results to VFT form to extract the effective glass transition temperature \( T_g \) which we found approximately equal to 308.2K similar to what is reported in the literature (~308K) and \( T_0 = 259.65 \) K.

Figure 6.6 contains the measurement and data fitted to a VFT form. The intercept of the VFT fit with the accepted frequency of the glass transition relaxation time is used as a measure of the glass transition temperature.
Figure 6.6 VFT fit to the location of the $\alpha$-peak in the frequency spectrum in order to extract the effective glass transition temperature.

In order to discuss the dynamics of the $\alpha$ process in PVAc system, the observed complex dielectric constant $\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ in Figures 6.3 and 6.4 are fitted using the following developed model function of Havriliak-Negami (HN):

$$\varepsilon^*(\omega) = \varepsilon_\infty + A\omega^{-m}e^{-i\left(\frac{\pi}{2}\right)m} + \frac{\Delta\varepsilon}{\left[1+(i\omega\tau_0)^{\alpha_{HN}}\right]^{\beta_{HN}}}$$

6.5

Where $\omega = 2\pi f$ and $\varepsilon_\infty$ is the permittivity at very high frequency. The second term in the right hand (rhs) side is a contribution from space charge [164], and it may be attributed to
the pure dc ionic conductivity if $m=1$. In case of our system, the fitted value of $m$ was found to be between 0.41 and 0.89 depending on the temperature. The third term in the rhs comes from the $\alpha$ process and its form was empirically proposed by Havriliak-Negami [165], where $\Delta \varepsilon$ is the relaxation strength, $\tau_o$ is the characteristic time, $\alpha_{HN}$ and $\beta_{HN}$ are the shape parameters.

Figures 6.7, 6.8 and 6.9 illustrated the real, imaginary and loss factor of dielectric properties of PVAc at glassy transition temperature $T_g$ and above with the solid line demonstrated the fit by Havriliak Negami model function given in equation 6.5.

Figures 6.10 and 6.11 showed the temperature dependence of the conductivity parameters A and exponent $m$. Both parameters are increasing function of the temperature and of course is a contribution from space charge and at pure conductivity the exponent $m$ reach a value of 1 at high temperature.

Figure 6.7 $\varepsilon'$ dependence on frequency at various temperatures for PVAc with solid curves are calculated by equation 6.5.
Figure 6.8 $\varepsilon''$ dependence on frequency at various temperatures for PVAc with solid curves are calculated by equation 6.5.

Figure 6.9 Loss factor Tan($\delta$) dependence on frequency at various temperatures for PVAc with solid curves are calculated by equation 6.5.
Figure 6.10 The exponent parameter $m$ in the conductivity term of equation 6.5 vs. temperature.

Figure 6.11 The parameter $A$ in the conductivity term of equation 6.5 vs. temperature.
Figure 6.12 the temperature dependence of the shape parameters $\alpha_{HN}$, $\beta_{HN}$ of HN equation obtained by fitting the observed data at different temperature.

The fitting parameters $\alpha_{HN}$ and $\beta_{HN}$ of the HN equation are shown in Figure 6.12. It is found that in over all with increasing in temperature the parameter $\alpha_{HN}$ decreases and $\beta_{HN}$ slightly increases. The decrease in $\alpha_{HN}$ with increasing temperature implies the broadening of the distribution of the relaxation times. This is in good argument with the values found by Koji Fukao and al. in the bulk sample of PVAc at 333 K, $\alpha_{HN}=0.85$ and $\beta_{HN}=0.55$ [148].

The Debye theory of dielectric relaxation, as improved by Onsager, Fröhlich, and Kirkwood [166, 167], gives for the temperature dependence of $\Delta \varepsilon$ of N independent relaxing dipoles:
\[ \Delta \varepsilon = \varepsilon_{\text{stati}} - \varepsilon_{\infty} = F_{\text{onsager}} \frac{N \mu^2}{3kT} \]  
\[ F_{\text{onsager}} = \frac{1}{3} \frac{\varepsilon_{\text{stati}}(\varepsilon_{\infty} + 2)^2}{2\varepsilon_{\text{stati}} + \varepsilon_{\infty}} \]

Where \( \mu \) is the dipole moment of the moving unit, \( T \) is the temperature, \( k \) is the Boltzmann constant, \( F_{\text{onsager}} \approx 1 \), is the correction factor for internal field effects, and \( \varepsilon_{\infty} \) and \( \varepsilon_{\text{stati}} \) denote the permittivities at high and low frequencies with respect to the frequency of maximal loss \( f_p \) of the relaxation region under investigation from which a characteristic relaxation time can be obtained as:

\[ \tau = \frac{1}{2\pi f_p} \]

The Kirkwood correlation factor \( g \) was introduced to describe local, static correlation of dipoles [168-171].

For the \( \alpha \)-process, \( \Delta \varepsilon \) decreases with increasing temperature as shown in Figure 6.13. However several typical polymers studies showed that this decrease is much stronger than the temperature dependence predicted by Equation 6.6. From a practical point of view, therefore this equation 6.6 can be used only for a rough estimation of the dipole moment [150].
Figure 6.13 Temperature dependence of the relaxation strength $\Delta \varepsilon$.

Figure 6.14 illustrates the characteristic time relaxation $\tau_o$ dependence on temperature. It is a decreasing function of temperature. This plot exhibits a good agreement with the fit from VFT Equation 6.4. Also, we can determine the value of $T_g$ by extrapolating the plot to the temperature corresponding to relaxation time equal to 100 seconds ($T_g = 308.4 \pm 0.2$ K). However, because the temperature dependence of both $\tau_o$ and $\Delta \varepsilon$; there is a straight correlation between them and that can be understood in the framework of cooperativity which increases with decreasing temperature.
Figure 6.14 Temperature dependence of the characteristic time relaxation $\tau_0$.

The imaginary component of dielectric constant $\varepsilon''$ measured for several temperature, when normalized by peak value and peak frequency can collapse quite well into a single master curve as shown in figure 6.15.
Figure 6.15 Superposed loss curve of PVAc with the solid lines are theoretical curve calculated from Equation 6.5 (HN).

In Figure 6.16 the Argand diagram which represents the loss plotted against dielectric constant which is quite distinct for polymer glasses. The solid lines are fits of by Harviliak Negami equation 6.5. It shows an asymmetry in the loss factor. As an aside, the upturn in loss at low frequency is due to the conductance loss. That is, migration of charged impurities, as opposed to the dipolar reorientation associated with the loss peak, gives rise to an unbounded increase in loss as frequency decreases [150].
Figure 6.16 Argand complex plane plots of dielectric loss factor $\varepsilon''$ vs. dielectric constant $\varepsilon'$ for PVAc at different temperature, the solid lines are fits by HN equation 6.5.

6.3 Frequency-domain scaling of physical aging in PVAc

6.3.1 Typical thermal cycles

We use two different temperatures cycling to study the aging properties of PVAc dielectric response (Figure 6.17).
If the sample is heated to $T_{\text{max}}$ higher than $T_g$ then cooled down to $T_{\text{stop}}$ below $T_g$, the system exhibits an aging process. Otherwise, if $T_{\text{stop}}$ is greater than $T_g$, then no aging occurs and only the cooling behavior of the system toward equilibrium at $T_{\text{stop}}$ is observed.

### 6.3.2 Dependence on aging time of $\varepsilon''$ after quench

From the figure 6.18, we can clearly observe the decrease of the loss factor $\varepsilon''$ with increasing aging time and decreasing temperature. We notice that as the temperature $T_{\text{stop}}$ increases, the system reaches equilibrium very fast after quench during the time scale of the measurement. For better understanding this aging behavior, Figure 6.19 shows $\varepsilon'' (t_w, f = 1 \text{ Hz})$ after quenches to different $T_{\text{stop}}$ above and below $T_g$ with $t_w$ scaled by $\tau_o$ for each temperature. These values of the equilibrium relaxation times result from the Havriliak and Negami function fits in equation 6.5 of from setting $\tau_o = 1/2\pi f_{p\alpha}$, where we obtain $f_{p\alpha}$ from extrapolations of low temperature data through Equation 6.4. In glassy polymer systems the dielectric relaxation time, defined in this way, closely tracks with
temperature the structural relaxation times extracted from frequency-dependent specific heat, shear viscosity and dielectric measurements. As figure 6.19 illustrates, all measurable aging occurs at $t_w/\tau_o<2$, and beyond this point the susceptibility is independent of time for $T_{\text{stop}}<T_g$. As we can clearly see, the most significant portion of the aging, as measured by dielectric response, occurs within one $\tau_o$ of the quench.

Figure 6.18 Aging of $\varepsilon''$ at $f = 1$ Hz after quench at different stopping temperature
Figure 6.19 $\varepsilon''$ at $f = 1$ Hz after quench vs. $t_w/\tau_0$ at different stopping temperature.

6.3.3 Comparison with aging in spin glass

Analysis of aging in spin glasses provided insights into the microscopic physics of these systems, and one more stimulus for our study has been to compare the behavior we observe in glassy polymers with aging in spin glasses. A number of studies on spin glasses have monitored the aging-time dependence of the frequency-dependent magnetic susceptibility, $\chi(t_w, f)$, following temperature quenches. The time dependence of $\varepsilon''(t_w, f)$ at fixed frequency $f$, such as shown in figure 6.20, appears, at least superficially, very similar to that observed for $\chi''(t_w, f)$ at fixed frequencies [123, 172].
As an illustration of the similarity between the polymer solid and spin glass behaviors, the figure 6.20 shows $\varepsilon''$ for several frequencies at 300 K on Log ($t_w$) scale. The rate of decay, $d\chi''/d(\text{Log}(t_w))$, for a spin glass was reported to vary as $f^{-0.25}$ [172].

Fitting within the range $0.01\tau_o < t_w < \tau_o$, we find a similar frequency dependence for decay of $\varepsilon''$ as $f^{-0.275}$ which was illustrated in the Figure 6.21.

We have attempted to scale $\varepsilon''$ at different frequencies following a procedure suggested for $\chi''$. Susceptibility of spin glasses in which the difference in susceptibility from its equilibrium value is scaled against $f t_w$ (figure 6.22). This aging procedure shows a full aging as in spin glass similar to what is discussed by R. Orbach [31].

![Figure 6.20 Aging of $\varepsilon''$ at T=300 K after quench for different frequencies](image)
Figure 6.21 the rate of decay $d(\varepsilon'')/d\log(t_w)$, in the range of $0.01\tau_0 < t_w < \tau_0$ at $T=300\,$K.

Figure 6.22 Difference in the susceptibility from its equilibrium value scaled against $\log(ft_w)$ for $T=300\,$K.
Figure 6.23 Difference in the susceptibility from its equilibrium value scaled against $\log(\text{ft}_w)$ for different $T_{\text{stop}}$. 
Form the preceding plots we can clearly see that the scaling procedure proposed for spin glass works very well at 298 K, 300 K and 302 K but fails for 304 K and above (Figures 6.23).

At the temperature where \( 304 \, \text{K} \leq T \leq T_g \approx 308 \, \text{K} \), the system reaches equilibrium very fast in the observation time scale of order of the \( \alpha \)-relaxation time \( \tau_0 \). So, for that reason we should not expect the data at these temperatures to obey \( f_t \) scaling. On the other hand, for \( T > T_g \), the system is not aging at all; it is just cooling down to reach the equilibrium temperature.

![Graph](image)

**Figure 6.24** Log (\( \varepsilon'' - \varepsilon''\text{eq} \)) vs. \( t_w / \tau_0 \) at \( f = 1 \, \text{Hz} \) and different stopping temperature after quench.
For a better picture on the scaling procedure applied to our system, we plot Log($\varepsilon'' - \varepsilon''_{eq}$) after quench for $f = 1$ Hz and with $t_w$ scaled by relaxation time $\tau_o$ at each temperature stop. We noticed that the aging portion ($\varepsilon'' - \varepsilon''_{eq}$) at temperature $T < 304$ K had a complete and different slop shape from the parts for $T \geq 304$ K which can be approximately fitted to a logarithmic function. Also, the whole significant aging as mentioned above is occurring at observation times of order of one relaxation time $\tau_o$ and for low temperature $< 304$ K the system still involving in the aging process during our measurement time and did not reach the equilibrium yet, there $\alpha$-relaxation time is in the order of $10^6$ seconds which is much larger than the time scale of the experimental measurements.

We notice from literature that the successful $f t_w$ scaling of the transient response implies that, at sufficiently high frequency, the susceptibility reaches its equilibrium value arbitrarily rapidly. This scenario appears valid for spin glasses for which is $\chi'' (t_w, f)$ reaches equilibrium quickly at high frequency [172, 173]. However, in temperature stop after quench with $304$ K $\leq T \leq 308$ K, we did see that the transient response reached the equilibrium very fast at high frequencies, even though the scaling procedure was failed which we can also attributed this breakdown to the beginning of the $\alpha$-relaxation tails in the $\alpha$-peak.

From these observations we conclude that, in spite of the similarities highlighted by Figures 6.20 and 6.22, slight qualitative differences exist between aging in glassy polymers and in spin glasses and, in particular, that $f t_w$ scaling for transient portion of the susceptibility which breakdown in some temperatures below $T_g$. 
In this frequency domain study of aging in polymer glasses (PVAc), we have stressed comparisons with other techniques which monitor equilibration as well as with aging behavior in spin glasses. These comparisons have not only provided information about the non-equilibrium dynamics but have also touched the equilibrium properties of deeply glassy polymer systems. Also, our effort to make roughly detailed comparisons between aging in polymers and that in spin glasses has highlighted both the similarities between their behaviors as well as important differences.
CHAPTER 7

FDR MEASUREMENTS AND DIELECTRIC PROPERTIES OF PVAc

AFTER QUENCH

Both dipolar fluctuations and dielectric susceptibility were measured in polymer glass PVAc. Following a temperature quench, the experimental measurements revealed Fluctuation Dissipation Relation (FDR) violations with a complex dependence on aging time and measurement frequency. These measurements require immense concern to exterminate extrinsic noise. It is critical to evade or eliminate extrinsic spikes that have infected some of the other experiments, to be confident that the fluctuations are coming from the same degrees of freedom involved in glassy dynamics. In order to understand the origin of such large violations in our experiment, we have analyzed the noise signal during aging process. The result of this studies showed that the system conserved the Gaussian statistics in all times.

7.1 Temperature Heating and quenching cycle

Before the quenching process the system is almost in equilibrium state and at 300 K. The sample is heated by applying a voltage source to the heater underneath of it. The applied voltage value is approximately 6.3 Volt, for 9 seconds as shown in the figure 7.1.
This voltage source increases the sample temperature from 300 K to 328 K in 9s and the quench process starts when the heating voltage stops. The maximum quenching rate from 328 K to 300 K is 7K/sec right at the start of cooling process. A typical thermal history of a fast quench is shown in Figure 7.2. This corresponding temperature cycle is computed from matching the imaginary part of the dielectric susceptibility of the sample during the heating and quench process with its corresponding equilibrium values at different temperatures and for a fixed frequency of 13.307 Hz. The reproducibility of the capacitor impedance during this thermal cycle is always better than 2%.
We can clearly see that after turning the voltage source on, it takes the system less than 1 second to jump to 308 K, and 328 K is reached by the end of 9 seconds. The data analyzed in this work was from 0.3 second after the voltage source is stopped due to the amplifier transient oscillation at the beginning of the quench and the Figure 7.3 showed an example of the signal collected during the start of the cooling process demonstrating the transient behavior of the amplifier at these moments. The figure above shows that the system is still at high temperature immediately after the quench and it requires 7 to 8 seconds for the system to cool down to $T_g = 308$K which corresponds to glass transition temperature for PVAc. The system falls out of equilibrium at a temperature near $T_g$, which depends on the cooling rate and the aging process starts. However adjustment of
$T_g$ by one degree will shift the time axis by at most 0.33 second, without affecting our results.

![Figure 7.3 Amplifier transient oscillations immediately after the quench.](image)

7.2 Dielectric response function of PVAc

Before discussing the time evolution of dielectric properties and the thermal noise at $T_{\text{stop}}=300$ K, we show in Figure 7.4 the cooling cycle temperature dependence on waiting time after quench measured at different frequencies of 13.307, 3.32677, 1.6633 and 0.83169 Hz. We get this plot by matching the dielectric susceptibility imaginary part of the sample during the cooling process with its corresponding values at the equilibrium, so we can trace their fictive temperatures with time. We notice an existence of crossover
between plots of different frequencies around 308K where the system fall out of equilibrium at 7.5 seconds from the beginning of the quench. At 10 seconds the fictive temperature is 306 K but the temperature controller shows 303 K, which indicates good temperature stability around 303 K and reachable at fast quench of about 10 seconds.

Figure 7.4 cooling cycle temperature dependence on waiting time \( t_w \) for different frequencies.

We will present in this section, the dielectric measurements during aging process taken by both susceptibility methods of white noise (WN) and Lock-in Amplifier (LA). By the end, we will use only the white noise measurements in our analysis and
calculation which we are more confident about, especially in the earliest aging time of the system.

Figures 7.5 and 7.6 show the strong aging in the imaginary component of the dielectric susceptibility measured vs. waiting times for several fixed frequencies. Also, in figures 7.7 and 7.8 we show similar aging behavior for the real part of the dielectric susceptibility. This long time evolution is the signature of the aging in the PVAc.

Figure 7.5 $\epsilon''$ vs. aging time for different frequencies using WN technique, at $T_{\text{stop}} = 300$ K.
Figure 7.6 $C''$ vs. aging time for different frequencies from LA technique, at $T_{\text{stop}} = 300$ K.

Figure 7.7 $C'$ vs. aging time for different frequencies from WN technique, at $T_{\text{stop}} = 300$ K.
As we discussed early in this work, the dielectric susceptibility from white noise (WN) technique is more reliable for us than the Lock-in amplifier (LA) technique, because the latter is inaccurate and affected by the $2\omega$ signal which had influence on the low frequency measurements and especially at the early aging time when the signal is non stationary. As we can see in Figures 7.6 and 7.8, the peaks in the imaginary and real part of the capacitance measurement with LA method during early aging time and at low frequencies are not consistent with the white-noise measurements, Figures 7.5 and 7.7. So, in LA method, the $\alpha$-relaxation peak that is moving with time from high frequencies toward low frequencies in particular at the first 10 seconds when the system cools down from 328 K to 300 K, is plagued with $2\omega$ effect.
Figure 7.9 $C''$ vs. frequency for different aging times from WN technique, at $T_{\text{stop}} = 300 \, \text{K}$.

Figure 7.9 shows the frequency dependence of imaginary part of the capacitance $C''$ at different aging times from the WN dielectric measurements. We clearly see that the $\alpha$-relaxation peak is moving toward low frequencies and reaching a high amplitude at $t_w = 0.9\, \text{s}$ and after $t_w = 5.1\, \text{s}$ it has totally passed through to low frequencies out of measurement range.

Looking at the Figure 7.10 below, we see that the fractional change in the real part of the capacitance, $C'$, due to the $\alpha$-relaxation process is less than that of the imaginary part. And also the imaginary part of the susceptibility (Figure 7.9) shows a much larger fractional change ($\sim 10$) during aging than does the real part ($\sim 2.5$). So in order to study the glassy dynamics of this polymer (PVAc) during aging process, it is better to focus on the imaginary part of the susceptibility.
Figure 7.10 C’ vs. frequency for different aging times using WN technique, at $T_{\text{stop}} = 300$ K.

7.3 Noise time series signal in PVAc during aging process

The graphs below (Figure 7.11) show the current noise signal at different aging time after quench. We found that the signal is characterized by large low frequency events at the beginning of the quench which disappear at large aging time and which are responsible for the increasing of the noise in the low frequency spectrum (see next section). At equilibrium when FDR is not violated these large low frequency events are absent.
Figure 7.11 Current noise signals after quench at different aging times.
7.4 Choice of trusted times in the measurements after quench and SNR

Before we started showing the results of our measurements for power spectral analysis and their dependence on frequency and aging time, we need to stop for a while and demonstrate how far these starting times after quench are reliable in our finding. So, we can trust our results and be more confident about our analysis. We discussed before how we analyzed our signal prior to applying the FFT. First, we subtracted the drift from each single time series signal after quench as an average of the total signals. So, because the drift is not the same in all time series; there is a slight deviation in all of them from the averaged signal; the deduction is not 100% perfect and a fraction of this can remain in the resulting signal especially at the earliest times. This of course, can cause large effective temperatures at low frequencies data and harm our analysis.

Therefore, we come up with this last signal examination in order to get the trusted times in the measurements after quench where the signal to noise ratio (SNR) is an acceptable value and be sure that none of these damages caused by the residual drift affect our signals.

We computed the power spectrum of the averaged signal before any processing which will be the drift spectral density then we compare it to the averaged power spectrum of the signals. We see that the drift is not affecting the large frequencies as shown in the figure 7.12 for 13.307 Hz. But for low frequencies the amount of drift is significant as we are going down in the frequency range of our study as shown in the figure 7.13 for 0.2079 Hz. So, we compared the power spectral density of processed signal, which already had the drift, subtracted as an average of the total signals, with the residual
fraction of power spectral of the drift itself. We superposed both spectral density curves and we calculated the SNR (Figure 7.14), then we choose the times were \( \text{SNR} \geq 5 \) as adequate criteria for well trusted time after quench for power spectral density of different frequencies. The table 7.1 showed the reliable times after quench that we considered in the coming analysis.

Figure 7.12 Drift subtraction example vs. aging time for frequency of 13.307 Hz.
Figure 7.13 Drift subtraction example vs. aging time for frequency of 0.2079 Hz.

Figure 7.14 Signal to noise ratio vs. aging time $t_w$ after quench at frequency of 0.2079 Hz.
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</tr>
<tr>
<td>0.0259</td>
<td>23.501</td>
</tr>
</tbody>
</table>

Table 7.1 Trusted times after quench for different studied frequency.

7.5 Current noise spectral density

As explained in more detail in the technical methods chapter, the power spectrum of the system was obtained by Fourier transform of the time series signal after passing through many steps of signal cleaning process and also subtracting the background noise. The current noise spectra averaged ~120 quenches for waiting times of 500 seconds after the quench and the procedure was repeated 9 times, giving a total number of quenches of about 1080, and then averaged in order to reduce the statistical errors. And also, there is a last procedure that we did apply to the power spectral before averaging, which is we compare the value of each single batch of data at fixed time with order of 5 standard deviation of the total batches and if the value of spectral density is superior at our threshold, we replace it by the mean value. So, with this final cleaning technique, we get
rid off any left over spikes failing to spot in the early signal treatments. The mean result of this process is shown in the Figure 7.15. This shows the evolution of spectral density with aging time $t_w$ at corresponding frequencies. We clearly observe that the power spectrum amplitude decreases with increasing aging time.

Figure 7.15 Current noise power spectrums vs. aging time for different frequencies
Figure 7.16 Current noise power spectrums vs. frequency for different aging time.

Figure 7.16 represents the evolution of current noise power spectral $S_I(f, t_w)$ after quench. FDR is strongly violated for all frequencies at short aging times. $S_I$ changes by almost of two orders of magnitude between highest values at low frequency and early aging time and the equilibrium spectral. Then high frequencies relax toward the FDT, but there is a persistence of violation for low frequencies at large waiting time after quench. The strong increase of $S_I$ at low frequencies $< 1$ Hz soon after quench indicates strong violations FDR. This violation is clearly illustrated by the behavior of the effective temperature that we will discuss in the next section.
7.6 Effective temperature of PVAc after quench

We calculate the non-equilibrium effective temperature [40] via:

\[
T_{\text{eff}}(f, t_w) = \frac{S_I(f, t_w)}{4k_B \text{Re}(\frac{1}{Z(f, t_w)})} = \frac{S_I(f, t_w)}{4k_B \omega C''(f, t_w)}
\]  

7.1

Where \( k_B \) is Boltzmann constant, \( \omega = 2\pi f \) is the angular frequency, \( C'' \) is the capacity imaginary part.

Figure 7.17 Effective temperature vs. aging time \( t_w \) for different frequencies, using dielectric measurements from WN technique, at \( T_{\text{stop}} = 300 \) K.
We need to consider that the low frequencies $T_{\text{eff}}$ are very sensitive to the background subtraction even with careful signal processing; therefore there may be a small correction to be done for these frequencies.

Figure 7.17 shows a strong FDR violation for early aging time after quench and at low frequency; $T_{\text{eff}}$ climbs up to $10^3$ K at 0.0259 Hz. Whereas for long times and high frequencies, the FDR hold and the measured temperature is the $T_{\text{stop}}$=$T_0$= 300 K within the error bars. We can see that the violation persist at low frequencies for large times after quench.

This behavior of $T_{\text{eff}}$ as a function of waiting time after quench for different value of frequencies shows a power law dependence on $t_\omega$ for early time <50s and a kind of plateau at the intermediate large waiting time. The crossover from slow regime to the fast one obviously occurs at larger value of $t_\omega$. Similar behavior was theoretically discussed in structural glasses by Leticia F. Cugliandolo (Figure 7.18) [7].

![Figure 7.18 Sketch of the modification of FDR in frequency domain for glassy system in the mean field model with $\omega_1 > \omega_2 > \omega_3$ [7].](image)
In Figure 7.19, we plot $T_{\text{eff}}$ as a function of frequency at different $t_w$ after quench. We see visibly that just after quench $T_{\text{eff}}(f, t_w)$ is much larger than $T_0 = 300$ K in all frequency interval. High frequencies rapidly decay toward the FDT (Equilibrium state) prediction whereas at the smallest frequencies $T_{\text{eff}} \approx 10^3$ K. Furthermore, we notice that low frequencies decay more slowly than high frequencies and that the evolution of $T_{\text{eff}}(f, t_w)$ towards the equilibrium value is very slow.

In order to quantify the amount of this large FDR violation, we did a best fit of $T_{\text{eff}}(f, t_w)$ in Equation 7.1 where all other parameters are known. We started at large $t_w$ when the system is relaxed and $T_{\text{eff}} = T_{\text{stop}} = 300$ K for all frequencies. Inserting the values in Equation 7.1 and using $S(f, t_w)$ measured at the equilibrium, we find $T_{\text{eff}} \approx 303$ K, within
error bars for all frequencies. At short aging time $t_w$, we found that $T_{\text{eff}} \approx T_{\text{stop}}$ for frequencies larger than certain cutoff frequency $f_o(t_w)$ which is a function of $t_w$. In contrast, for $f < f_o(t_w)$, we found that $T_{\text{eff}}$ is proportional to $f^{-\gamma(t_w)}$, with $\gamma(t_w) \approx 5$. This frequency dependence of $T_{\text{eff}}(f, t_w)$ is quite well approximated by\cite{174, 175}:

$$T_{\text{eff}}(f, t_w) = T_{\text{stop}} \left[ 1 + \left( \frac{f}{f_o(t_w)} \right)^{-\gamma(t_w)} \right]^{\gamma(t_w)}$$  \hspace{1cm} 7.2

Where, $\gamma(t_w)$ and $f_o(t_w)$ are fitting parameters. We find that $\gamma(t_w) \approx 5$ for the data range that we had. So, the only free parameter in Equation 7.2 is $f_o(t_w)$.

In Figure 7.20, we plot the fitted $T_{\text{eff}}(f, t_w)$ as a function of frequency at different aging time using Equation 7.2. From the data Figure 7.21, the function $f_o(t_w)$ is a decreasing function of $t_w$, but the dependence is not simple as we can see in the graph. The continuous straight line is not a fit, but it represents $f_o(t_w)$ proportional to $1/t_w$ which seems a reasonable approximation for the data with $t_w < 30$ s. For $t_w > 30$ s we found the $f_o$ is almost a constant value of 0.02 Hz. Thus we can not follow the evolution of $T_{\text{eff}}$ anymore because the contribution of the experimental noise on $S_I$ is too important at large aging time and low frequencies.

From the figure 7.20 and equation 7.2, it is easy to see that $T_{\text{eff}}(f, t_w)$ can be superposed onto a master curve by plotting them as a function of $f/f_o(t_w)$ (Figure 7.22)\cite{174}.
Figure 7.20 Effective temperature vs. frequency $t_w$ for different aging times $t_w$, using dielectric measurements from WN technique, at $T_{stop} = 300$ K, with the dot dashed lines are the fit obtained using equation 7.2.

Figure 7.21 the cutoff frequency $f_0$ defined in Equation 8.2 plotted as function of $t_w$. 
Figure 7.22: The effective temperature plotted as a function of $f/f_0(t_w)$.

7.7 Scaling behavior during aging process

The effective temperature data do approximately scale well with $f t_w$ as might be expected from spin glasses [4] for early aging time $t_w \leq 50s$, see Figure 7.23. However, we were able to approximately scale the data against $f t_w^{0.1}$ for large aging time after quench $t_w > 50s$, as shown in Figure 7.24.
Figure 7.23 Scaling of the effective temperature with frequency and waiting time for early aging $t_w \leq 50s$.

Figure 7.24 Scaling of the effective temperature with frequency and waiting time for long aging $t_w \geq 50s$. 

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For dielectric susceptibilities, we found that the imaginary and real parts also follow a kind of scaling behavior with $f t_w$ as shown in the figure 8.25 and 8.26. The parts that did not follow the scaling law is for waiting time $t_w < 7.5$ seconds which is due to the $\alpha$-relaxation process during the cooling procedure of the system. The scaled parts showed when the system fall out of the equilibrium.

Figure 7.25 the Capacity imaginary part $C''$ scaling vs. frequency and waiting time from WN technique.
7.8 Spectral exponent $\alpha$ of current noise

The spectral exponent $\alpha$ of the current noise was calculated by:

$$\alpha = -\left( \frac{d \ln(S_f)}{d \ln(f)} \right)$$ \hspace{1cm} 7.3$$

The spectral exponent was computed over a decade in frequency [1.66-13.3Hz]. Figure 7.27 shows spectral exponent dependence on waiting time $t_0$, which clearly producing the same behavior observed in $C''$ dependence on aging time. When the
system cooled down from 328K to 300 K, the α exponent is a decreasing function with aging time at the first two seconds due the α-relaxation peak passing through from high frequencies to low frequencies. Then, for $t_w$ larger than 2 seconds, the α exponent is an increasing function of time with two different increasing slopes. First increase is from 2 s to 7.5 s which is due to the cooling process of the system and the second raise is from 7.5 s which is due to the out of equilibrium behavior of the system and it reaches the value of 0.93 at large times. This last behavior grows as a function of $t_w$ logarithmically that is $\alpha = 0.04436 \ln(t_w) + 0.60568$. This slow relaxation of the exponent $\alpha$ toward the equilibrium value ~ 1 is related to the aging phenomenon in the system.

Figure 7.27 Spectral exponent $\alpha$ vs. waiting time $t_w$ calculated from current noise (using equations 7.3) over a decade in frequency.
7.9 Statistical analysis of the noise

In order to understand such a behavior of the system during aging development, we have directly analyzed the current noise across the PVAc capacitance. This kind of analysis can be safely done in the data collected with our experimental apparatus because the amplifier noise is negligible with respect to the thermal noise of the PVAc sample even when the FDR is satisfied in the equilibrium. To compare with previous experiments showing non-Gaussian behavior [17, 46, 175, 176], we studied the probability density function (PDF) of the signal as a function of waiting time after quench $t_w$. To compute the PDF, the time series of the signal are divided in several time windows centered on desired $t_w$ and the width of this window is 10% of the corresponding time. Then, the PDF are computed in each of these windows and the results of several experiments are averaged. The PDF computed at different aging time $t_w$ are plotted in the figure 7.28.

![PDF of the current noise in PVAc during aging process, the solid lines are fit using equation 7.4.](image)

Figure 7.28 PDF of the current noise in PVAc during aging process, the solid lines are fit using equation 7.4.
We see that the amplitude of polarization fluctuation showed a Gaussian distribution which enlarged with increasing time and whose width reduced during aging process.  

In all aging times, the PDF conserved the Gaussian statistics and can be well fitted by the Gaussian distribution function in equation 7.4.

$$G_{X,\sigma}(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-X)^2}{2\sigma^2}}$$  \hspace{1cm} 7.4

With $X$ and $\sigma$ indicate the center and width of the distribution, $x$ in our case is the current noise $I \ (10^{-15} \text{ A})$.

Figure 7.29 Logarithmic representation of PDF vs. Current noise power for different aging time $t_w$. 

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Figure 7.29 is a good representation of the Gaussian statistic conservation during aging process in our system. The graph showed a logarithmic illustration of PDF plotted against Current noise power $I^2$, which is going to obviously show a linear dependence if the distribution follow a Gaussian statistic. Of course from the above results, we did see this linear relationship which is a good proof that the signal conserved the Gaussian characteristic through the aging course. The dashed lines in the graph are linear fit to the data.

![Graph showing PDF peak variations with aging time $t_w$.](image)

**Figure 7.30 PDF peak variations with aging time $t_w$.**

Figure 7.30 showed variations of PDF peak amplitude with aging time $t_w$. We see clearly that the graph can be divided in two parts. For $t_w < 8s$, the system is in the cooling process and it is not aging yet, its temperature still above $T_g = 308$ K. This part can be
fitted by a power law function as: $\text{PDF}_{\text{Peak}} = 0.063 t_w^{0.647}$ which is an increasing function of time. Instead, for $t_w > 8s$, the system temperature is below $T_g$ and it is in the aging stage. In this phase, the PDF Peak amplitude grows as a function of $t_w$ logarithmically, that is $\text{PDF}_{\text{Peak}} = 0.0011 \ln(t_w) + 0.0186$. This slow relaxation of the PDF Peak toward the equilibrium shows that this behavior is related to the aging phenomena.

Similar behavior of PDF Peak showed above, can be seen inversely in the PDF Width ($\sigma$) variations with aging times (Figure 7.31).

![Graph showing PDF Width variations with aging time](image)

**Figure 7.31 PDF Width $\sigma$ variations with aging time $t_w$.**

The PDF width $\sigma$ is a decreasing function with waiting time after quench. In the aging phase for $t_w > 8s$, it shrinks as a function of $t_w$ logarithmically, that is:
PDF$_{\sigma}$ = \(-0.833\ln(t_w) + 20.6854\). Also, this slow relaxation of the PDF width is associated with the aging process in the system.

The above statistical analysis is done on a cleaned signal from spikes > 5\(\sigma\) (\(\sigma\) is the standard deviation of the signal near equilibrium). The spikes removal method will be considered as a sufficient analysis because the probability that a measurement will lie outside 5\(\sigma\) width of the distribution is extremely small in the order of \(\approx 1 \times 10^{-3}\) %. In our time series signal the spikes above 5\(\sigma\) in height represent only approximately 2 \(\times 10^{-3}\) % of total the signal. By calculating approximately the total equilibrium noise integrated over all frequencies from dielectric susceptibility data; one can found a sum of order of \(\sim 5\sigma\). If only all of the dipoles in the sample involved were to reorient simultaneously in the same direction, we would get a single spike of 5 \(\sigma\) in its amplitude or perhaps a little higher due to an elevated effective temperature. Therefore, those spikes required global sample dipoles cooperation in order to produce a spike of 5\(\sigma\) in height. Indeed, they can not be from the same dipolar degree of freedom in the noise, they are coming form outside sources. In the global measurement, fluctuations could be smoothed by the volume average and therefore the PDF should be Gaussian which is in good agreement with the Central limit theorem (CLT) stating that the sum of a large number of independent and identically distributed random variables will be approximately normally distributed if the random variables have a finite variance. So, to get an idea how The PDF looks like at a typical case of spiky signal, we will analysis next our signal before spikes removed.
Figure 7.32 PDF of the current noise in PVAc during aging process for a spiky signal, the solid lines are just connecting the data.

Figure 7.32 shows PDF of signal with spikes in it (> 5σ). We clearly see that the PDF is not a Gaussian distribution and has a large and fat tails at both sides. Those tails are the consequence of existing spikes in the time series signal. So, for more illustration of non Gaussianity behavior in this case, we will plot the logarithmic representation of PDF which will be shown in the Figure 7.33. This figure is a clear evidence of non Gaussian statistic of the system in this case. The logarithmic representation of PDF didn’t follow a linear behavior with current noise power; it is really shows a large tails in all aging times.
Figure 7.33 Logarithmic representation of PDF vs. Current noise power for different aging time $t_w$ for a spiky noise signal.

For more comparison between two cases studied above and for showing the misleading behavior of existence of spikes $> 5\sigma$ in amplitude in the time series signal, we will use traditional methods based on the distribution of the signal in order to test the Gaussian and non Gaussian statistics. The simplest tests are based on the third and fourth order moments (Skewness and Kurtosis) of the distribution, both equal to zero for a perfect Gaussian distribution.

In probability theory and statistic, Kurtosis is a measure of the “peakedness” of the probability distribution of real-valued random variable. Higher kurtosis means more of the variance is due to infrequent extreme deviations, as opposed to frequent modestly-
sized deviation. In an intuitive sense, kurtosis measured how “spikiness” of a distribution 
or the size of the tails. The following is the definition of kurtosis:

$$kurtosis = \frac{\sum_{i=1}^{N}(x_i - X)^4}{(N-1)\sigma^4} - 3$$ \hspace{1cm} 7.5

Where $X$ is the mean, $\sigma$ is the standard deviation, and $N$ is the number of data points. This definition is used so that the standard normal distribution has a kurtosis of zero. In addition, positive kurtosis indicates a “peaked” distribution and negative kurtosis indicates a “flat” distribution.

In other side, the Skewness is a measure of the symmetry, or more precisely, the lack of symmetry. A distribution, or data set, is symmetric if it looks the same to the left and right of the center point. The formula for Skewness is:

$$Skewness = \frac{\sum_{i=1}^{N}(x_i - X)^3}{(N-1)\sigma^3}$$ \hspace{1cm} 7.6

Where also, $X$ is the mean, $\sigma$ is the standard deviation, and $N$ is the number of data points. The Skewness for a normal distribution is zero, and any symmetric data should have Skewness near zero. Negative values for Skewness indicate data are skewed left and positive values for Skewness indicate data that are skewed right. By skewed left, we mean that the left tail is long relative to the right tail. Similarly, by skewed right, we mean that the right tail is long relative to the left tail.
Figure 7.34 is shown that the Kurtosis for a cleaned time series signal from spikes $>5\sigma$ are very small in the whole range of aging time. Their values are nearly equal zero within the error bars ($\sim0.02\pm0.01$) which confirm the conservation of the Gaussian characteristics in this case. In the contrary, the Kurtosis of spiky signal showed a large positive value increasing with aging time which is clear evidence of non-gaussianity behavior. These values demonstrated how spikiness is the distribution and how large their tails at long aging times.
Figure 7.35 illustrates the variation of Skewness with aging time after quench for both cleaned and spiky signals. We clearly see that for a cleaned signal the Skewness is nearly fluctuates near zero within error bars which is a good indication of symmetrical behavior of the distribution. In the opposite side, the Skewness of spiky signal is a positive value (~0.04±0.02) which indicates that the data are skewed right which means the right tail is long relative to the left one. This is again a clear and illustrative test for measuring the non Gaussianity.
7.10 Noise simulation

In order to clarify what was discussed in the above section and to demonstrate the effect of spikes on the statistic behavior of the signal and also to confirm our experimental discovery, we did a noise signal simulation. We simulate a random noise with a normal distribution and has standard deviation $\sigma = 15$ (similar to the case of the sample near the equilibrium state). Without any spikes add, the distribution showed a Gaussian statistics then after adding different percentage of spikes to the original data the distribution illustrates the non Gaussian behavior as large tails in PDF representation with their height increase with increasing of spikes percentage (Figures 7.36). The spikes were added randomly with amplitude $\leq 20\sigma$.

![Figure 7.36 PDF calculated for a simulated normal noise signal for different percentage of added spikes, the solid lines are just connecting the data.](image)
The logarithmic representation of PDF for simulated noise signal (Figure 7.37) showed an obvious deviation from a linear dependence with the signal power $X^2$ with added spikes percentage which is in very good agreements with our experimental measurements.

![Figure 7.37 Logarithmic representation of PDF calculated for a simulated normal noise signal for different percentage of added spikes.](image)

This statistical study of the signal gives an information on the dynamics of the system during aging process and it is clearly showed the conservation of the Gaussian behavior in all times which is in contradiction with some experimental measurements.
done recently on Polymer glass (Polycarbonate) and Laponite complex fluid [17] that claim the existence of strong non Gaussian statistics in their system at the early time of aging. They related that violation to the existence of strong intermittency in the signal. They found that their signal is characterized by large intermittent event (Spikes) which produce large low frequency spectra. These experiments exhibited large delta-function-like noise spikes, which were often > 5 \( \sigma \) in height, where \( \sigma \) is the standard deviation of the background noise (near equilibrium) signal measured in two decade frequency window. The sample volumes were of order 10 cm\(^3\). We can calculate approximately the total equilibrium noise integrated over all frequencies from dielectric susceptibility data, would give \( \sim 5 \sigma \). If all of the dipoles involved were to reorient simultaneously, we would get a single spike of 5 \( \sigma \) in height or perhaps a little upper due to a higher effective temperature. Consequently, the detected spikes would involve the entire 10 cm\(^3\) sample to consistently fluctuate. For that reason, the spikes cannot be from the same dipolar degree of freedom as those which produce the rest of the noise signal, and are to be likely extrinsic, e.g. due to differential contractions and macroscopic strain release or to the power surge in the amplifier.
CHAPTER 8
DISCUSSION, CONCLUSIONS AND PERSPECTIVES

In this chapter, we will present a summary of the experiments conducted in this work, along with the most important and significant results, conclusions and perspectives. It is proposed that this section will provide the reader with a big picture of the findings from the experiments presented in the last chapters grouped together and wrapped up by their common conclusions.

8.1 Discussion

8.1.1 Experimental techniques & analysis

The aim of the experimental measurements done in this thesis is to study the aging phenomenon in glassy polymers polyvinyl acetate (PVAc) through the polarization noise and dielectric spectroscopy investigation in order to obtain and explain the aging dynamics and the fluctuation-dissipation-relation (FDR) during aging processes after the system quench to a final temperatures below and above the transition temperature $T_g$.

a) –Dielectric measurement techniques

The dielectric spectroscopy measurements are done in three different ways and each technique had its own advantages and disadvantages which will be useful in some context. The following are those three methods:
• **Novocontrol dielectric broadband technique:** this system has a very good reputation for highest quality and flexibility. It has a very high accuracy and precision for equilibrium measurements or slowly evolving responses. But it is less flexible when it comes to the measurement during rapidly changing conditions such as the very early aging regime. In that case the time resolution is very important to us for FDR computation in order to catch the earliest possible aging changes in the dielectric properties of the system. It takes 5.6 seconds in data collection time for high frequencies which is the lowest time for a single frequency measurement that can be done with the system. In contrast, for low frequency measurement the time required is much larger than 1/f, as an example, at 0.1 Hz the data collection time is about 85 seconds. We use this technique to study the frequency domain dielectric properties at equilibrium for different temperature and also to investigate the physical aging behavior of the system at longer times and compare their features with those of spin glass systems. In the last study, we are not concerned in collecting the data as fast as possible because we are satisfied with the system performance only for this type of investigation.

• **Lock-in amplifier measurement technique:** This is a mono-frequency measurement. In order to measure the dielectric properties of the sample, we collect the in-phase and out-of-phase current signal when a sinusoidal voltage was applied to the system. With this technique, we can collect the signal quite fast with a sampling rate of 18ms and averaging time of as little as 1/f, which is adequate in following the system changes in the aging phase. But this is still insufficient when the signal is changing rapidly for low frequencies such as
during and just after a fast quench. In this case the measured signal is obstructed by $2\omega$ signal which shows some wiggling shape in the data, because the response is no longer a single frequency sine wave.

- **White noise dielectric measurement technique:** This new method, which we have developed, measures simultaneously over a broad-band of frequency. It is straightforward in its principle but somewhat complicated in practice which required careful programming and statistical analysis. The white noise signal was sent through the sample and the input and output signals are collected in order to compute the in-phase and out-of-phase dielectric constants of the sample after many steps of statistical analysis as described in technical chapter. In order to reduce statistical errors, we repeat the measurement many times (~100 times) and we take the average of the runs. It does not have the early time artifacts of the lock-in technique, but its resolution is worse so considerable averaging is required. We adopt this technique in using its results in the FDR analysis which appear to be in good agreement with it.

b) – Noise measurement techniques

The current noise spectral density, $S_i$, is measured via an ultra-low noise current amplifier (Femto LCA-30-1T), in an electromagnetically shielded steel enclosure, mounted on a vibration isolation air table. The current noise is measured as a function of frequency, ($f =0.0259 \text{ Hz to } 13.307 \text{ Hz}$) and waiting time, $t_w = 0.0187 \text{ s to } 600 \text{ s}$ following the quench, and in equilibrium. The polarization noise was measured in macroscopic
samples of a polymer (PVAc) during aging in order to study FDR violations. These measurements require great care to eliminate extrinsic noise. It is very critical to avoid or eliminate extrinsic spikes, drifts, and FFT artifacts that have plagued some of the other experiments done in the field [14, 17, 86, 174, 175], to be certain that the fluctuations are coming from the microscopic degrees of freedom involved in glassy dynamics.

### 8.1.2 Dielectric spectroscopy measurement in equilibrium and aging phase

We measured the time dependence of frequency-dependent dielectric susceptibility of PVAc following quenches to below and above transition temperature $T_g$ during aging phase. We also investigate equilibrium phase at different temperature and frequencies in order to study the dynamical $\alpha$-relaxation process. Our measurements of the dielectric response in glassy polymer PVAc provide a direct analogy with the magnetic susceptibility aging studies in spin glasses which make us able examine if the theories proposed for spin glasses have relevance for glassy polymer systems.

**a) – Equilibrium phase**

For more understanding of the $\alpha$-relaxation process in PVAc, the dynamics are investigated in the frequency range of $10^{-3}\text{Hz}$ to $10^5\text{Hz}$, and in the temperature range of 296K to 339.5K. The most remarkable feature in the response is the peak due to $\alpha$ relaxation in the glassy sample. It is clearly demonstrated that the location of the $\alpha$-peak
in the frequency spectrum shifts with temperature, since the $\alpha$-peak is determined by the average relaxation time of molecules in the sample.

We observed that the magnitude of the dielectric $\alpha$ relaxation $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ decreases with increasing temperature, as found for most of other amorphous polymers at temperatures above $T_g$ [18, 159]. The first thing we noticed from the response functions in our measurements is the shift in the $\alpha$ peak toward high frequencies as the temperature increases with their shapes are relatively unchanged.

We extracted the effective glass transition temperature $T_g$ of PVAc from the dielectric measurements, using the Vogel-Fulcher-Tammann (VFT) function which we found approximately equal to 308.2 K similar to what is reported in literature[18].

For deep understanding of relaxation phenomena in glassy polymers, we fit our dielectric data using the model function of Harviliak-Negami (HN). We found that the shape parameters $\alpha_{HN}$ and $\beta_{HN}$ of the HN equation, in over all, with increasing in temperature the parameter $\alpha_{HN}$ decreases and $\beta_{HN}$ slightly increases. The decrease in $\alpha_{HN}$ with increasing temperature implies the broadening of the distribution of the relaxation times. This is in good argument with the values found by Koji Fukao and al. in the bulk sample of PVAc at 333 K, $\alpha_{HN} = 0.85$ and $\beta_{HN} = 0.55$ [148].

The characteristic time relaxation $\tau_\circ$ showed a complete dependence on temperature. It is a decreasing function of temperature. The data exhibits a good agreement with the fit from VFT Equation. However, because the temperature dependence of both $\tau_\circ$ and $\Delta\varepsilon$; there is a straight correlation between them and that can be understood in the framework of cooperativity which increases with decreasing temperature.
We found that the out phase dielectric constant $\varepsilon''$ measured for several temperature, when normalized by peak value and peak frequency can collapse quite well into a single master curve.

We can attribute that both the width and the asymmetry of the experimental loss curves arise from the intrachain interaction and are thus characteristic of the long chain nature of the molecules as concluded from the observation for many dielectric spectroscopy measurements done by Ishida, et. al. [160]

**b) – Aging phase**

We observe a decrease of the loss factor $\varepsilon''$ with increasing aging time and decreasing temperature. We notice that as the temperature $T_{\text{stop}}$ increases (final temperature stop after quench); the system reaches equilibrium very fast after quench during the time scale of the measurement. We detect that all measurable aging occurs at $t_w/\tau_o<2$ ($\tau_o$ is the relaxation time), and beyond this point the susceptibility is independent of time for $T_{\text{stop}}<T_g$. From the measured dielectric response, we can clearly see, the most significant portion of the aging occurs within one $\tau_o$ of the quench.

One most important motivation for our aging study has been to compare the behavior we observe in glassy polymers with aging in spin glasses in order to provide us with an insight into the microscopic physics of these systems [123, 172].

We illustrated the similarity between the polymers solid and spin glass behaviors. The rate of decay, $d\chi''/d(\text{Log}(t_w))$, for a spin glass was reported to vary as $t^{-0.25}$ [172], and by
fitting our data within the range $0.01 \tau_o < t_w < \tau_o$, we find a similar frequency dependence for decay of $\varepsilon''$ as $f^{-0.275}$.

We scaled $\varepsilon''$ at different frequencies following a procedure suggested for $\chi''$ Susceptibility of spin glasses in which the difference in susceptibility from its equilibrium value is scaled against $f t_w$. This aging procedure shows a full aging as in spin glass similar to what is discussed by R. Orbach [31]. We found that the scaling procedure proposed for spin glass works very well at 298 K, 300 K and 302 K but fails for 304 K and above. We can interpret the scaling failure in those temperatures by considering that for the temperature where $304 K \leq T \leq T_g \approx 308 K$, the system reaches equilibrium very fast in the observation time scale of order of the $\alpha$-relaxation time $\tau_o$. So, for that reason we should not expect the data at these temperatures to obey $f t_w$ scaling. On the other hand, the system is not aging at all for $T > T_g$; it is just cooling down to reach the equilibrium temperature.

When we plotted $\log (\varepsilon'' - \varepsilon''_{eq})$ after quench for $f = 1$ Hz and with $t_w$ scaled by relaxation time $\tau_o$ at different temperature stop. We noticed that the aging portion $(\varepsilon'' - \varepsilon''_{eq})$ at temperature $T < 304 K$ had a complete and different shape from the parts for $T \geq 304 K$ which can be approximately fitted to a logarithmic function. This can be understood as follows: for low temperature $< 304 K$ the system is still evolving in the aging process during our measurement time and wasn’t reaching the equilibrium values, while above 304 K the sample reaches equilibrium on our measurement time scale. Below 304K, the $\alpha$-relaxation time is on the order of $10^6$ seconds which is much larger than the time scale of our experimental measurements.
From spin glass theory, it was shown that the successful $f t_w$ scaling of the transient response implies that, at adequately high frequency, the susceptibility achieves its equilibrium value arbitrarily rapidly. This scenario appears valid for spin glasses for which is $\chi''(t_w, f)$ reaches equilibrium quickly at high frequency [172, 173]. However, in our temperature stop after quench with $304 \, \text{K} \leq T \leq 308 \, \text{K}$, we did see that the transient response reached equilibrium very fast at high frequencies, even though the scaling procedure was failed which we can also attributed this breakdown to the beginning of the $\alpha$-relaxation tails in the $\alpha$-peak.

We conclude from this study that, similarities do exist between the aging in glassy polymers and spin glasses, though as one approaches $T_g$ the $f t_w$ scaling for transient portion of the susceptibility breaks down.

### 8.1.3 Fluctuation-dissipation-relation measurements

We have studied the fluctuation-dissipation-relation during the aging phase of the system using electrical measurements. We clearly observed that the power spectrum amplitude decreases with increasing aging time $t_w$ at fixed frequency. In the current noise power spectral $S_I(f, t_w)$ after quench; FDR is moderately violated for all frequencies at short aging times. $S_I$ changes by almost of two orders of magnitude between highest values at low frequency of early aging time and the equilibrium spectrum. Then high frequencies relax very quickly toward the FDR prediction, but there is a longer persistence of violations at low frequencies. The strong increase of $S_I$ at low frequencies $< 1 \, \text{Hz}$ soon after quench corresponds with moderate violations of FDR.
The observed effective temperature $T_{\text{eff}}$ reaches $10^3$ K at frequency $f = 0.0259$ Hz (it is of order of $T_{\text{eff}} \approx 3.25 \ T_g$) at early aging time. However, for long times and high frequencies, the FDR holds and the measured temperature is in the proximity of $T_{\text{stop}} = 300$ K within the statistical error bars. We can also see that the violation persist at low frequencies for longer times after quench.

The effective temperature data do approximately scale well with $ft_w$ as might be expected from spin glasses[4] for early aging time $t_w \leq 50$s.

The spectral exponent was computed over a decade in frequency [1.66-13.3Hz]. It is found to show a dependence on aging time $t_w$. This behavior in the aging regime grows as a function of $t_w$ logarithmically that is $\alpha = 0.04436 \ \text{Ln}(t_w) + 0.60568$. This slow relaxation of the exponent $\alpha$ toward the equilibrium value $\sim 1$ is associated to the aging phenomenon in the system

8.1.4 Noise Statistical analysis

We observe that the time series signal is characterized by large low frequency events at the beginning of the quench which almost totally disappear at large aging time and which are responsible for the increasing of the noise in the low frequency spectrum. At equilibrium when FDR is satisfied these large low frequency events are absent.

The amplitude of polarization fluctuation showed a Gaussian distribution which enlarged with increasing time and whose width reduced during aging process. In all aging times, the probability density function (PDF) conserved the Gaussian statistics and can be well fitted by the Gaussian distribution function
In the aging regime, the PDF Peak amplitude grows as a function of $t_w$ logarithmically, that is $\text{PDF}_{\text{Peak}} = 0.0011 \ln(t_w) + 0.0186$. This slow relaxation of the PDF Peak toward the equilibrium shows that this behavior is related to the aging phenomena and it is similar to what is seen in the spectral exponent behavior.

We showed in both experimental and simulation data that the PDF of signal left with spikes in it ($>5\sigma$) was not a Gaussian distribution and has a large and fat tails at both sides. Those tails are the consequence of existing spikes in the time series signal. The calculated kurtosis and skewness of a cleaned signal from spikes are much smaller than spiky signal which give us a clear separation between a Gaussian and non-Gaussian behavior of the system.

### 8.2 Conclusions

As a summary of results, in the frequency domain study of aging in polymer glasses (PVAc), we have investigated the comparisons with aging behavior in spin glasses. These comparisons have not only provided us with information about the out of-equilibrium dynamics but have also touched the equilibrium properties of glassy polymer systems. Also, our effort to make roughly detailed comparisons between aging in polymers and that in spin glasses has highlighted both the similarities between their behaviors as well as important differences.

We found in the measured dielectric response function in the aging regime that the most significant portion of the aging occurs within one $\tau_o$ relaxation time of the quench. Also the out phase dielectric constant scales as $f t_w$ following the procedure
proposed for spin glasses for T<304 K and fails above this temperature. We attribute this failure to the fact that the system reaches the equilibrium value very fast in the observation time scale of order of the $\alpha$-relaxation time $\tau_0$ and also to the influence of the appearance of the $\alpha$-relaxation tails of the $\alpha$-peak in those temperature stop.

In the study of fluctuation dissipation relation, we have reported here experimental observation of moderate FDR violations in PVAc, which we have analyzed in terms of the effective temperature. As predicted by the theory the amplitude and the persistence time of this violation are decreasing function of frequency and time. The violation is observed even at $\omega t >> 1$ and it may last for more than 100s for $f > 0.415$ Hz. Modest effective temperature found ($T_{\text{eff}} \approx 10^3 \text{ K} \approx 3.25 T_g$) at low frequencies and short aging time similar to what was measured in spin glasses ($T_{\text{eff}}/T_g \approx 2.2$ to 7) depending on the cooling rate and final temperature stop [5]. This is in striking contrast to the very large and long lived violations ($10^6 \text{K}$) found in other polymer experiments, suggesting that those results may be due to extrinsic noise spikes. These results agree with the experiment of ref. [17, 44, 175] but it is different from what is theoretically predicted and computed in simulation. The $f \tau_0$ scaling observed at the only earliest $t_0<50$s. In the other hand, the data do scale with weaker dependence on $t_0$ for large aging time after quench $t_w >50$s. In addition, we also see violations at higher frequencies at short times during the actual temperature quench, which is a new feature that has not yet been studied theoretically.

Elimination of extraneous noise spikes, which are unlikely part of glassy dynamics, due to differential thermal contractions and macroscopic strain release are very important for accurately determining the effective temperature. Specifically, the present
results succeed in quantifying the smaller and longer-lived violation, which are not found in the simpler models.

The statistical study of the time series signal gives an information on the dynamics of the system during aging process and it is clearly showed the conservation of the Gaussian behavior in all times witch is in contradiction with some experimental measurements done recently on polymer glass (Polycarbonate) and Laponite complex fluid [17] that claim the existence of strong non Gaussian statistics in their system at the early time of aging. They related the violations to the existence of strong intermittency in the signal which are much larger than 5σ (σ is the standard deviation of the signal near the equilibrium state).

These results of FDR measurements give new insight into the interpretation of the aging dynamics. Indeed, aging has been always characterized only by the measurements of the response function. We have shown here that the association of this measurement to that of the thermal fluctuations may show new and unattended aspects of aging behavior. The successful aging models should take account of these experimental results in order to explain the mechanism of aging dynamics in different glassy materials.

8.3 Perspectives

We would like to end these results by mentioning some of the directions for future development in this area. A few and important questions remain opens in this field.

The first concerns the quench rate. Indeed, is it the quench rate which is the speed in which T_{g} is crossed that determines the dynamics or the time in which T_{stop} is
approached? This question has been already studied in the framework of the response functions it will be very important to analyze it in terms of noise fluctuations.

The second important open question is the different dynamics of the thermal noise measured on different observables. In fact even from a theoretical point of view the effective temperature of different observables is the same in certain models [177] and different in others [47]. This is certainly useful information that can give new approach to the problem of the mechanism of aging dynamics in different kind of materials.

The third interesting question is to investigate the existence of memory effect on the thermal noise fluctuation. These types of study are done in the context of the response function of the system [79-81]. I will be very motivating to probe this effect in thermal noise measurements.

The fourth exiting open question is to see if the application of an electrical field polarizing the polymer molecules had an effect on the relaxation dynamic of the system in equilibrium and aging regime in the context of thermal noise studies.

All these problems are challenging and very interesting. Many more could be added to this short list. We can expect to see progress in this very active area of research in the near future with an extension of studies in different type of materials and other various measurement techniques. A continuous exchange of ideas among theory, simulation and experiments is highly desirable and certainly required to improve our present understanding in this field.
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