

Relaxation phenomena in disordered systems

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Abstract

In this article we discuss how the assumptions of self-similarity imposed on the distribution of independently relaxing modes, as well as on their amplitude and characteristic times, manifest in the global relaxation phenomena. We also review recent applications of such approach to the description of relaxation phenomena in microemulsions and molecular glasses.

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1. Introduction

Relaxation phenomena in disordered systems are characterized by some common pattern, notwithstanding the large differences among the systems themselves [1]. Common characteristics of the relaxation are the presence of a slow dynamics, i.e., of decay processes which extend over several orders of magnitude, the presence of power-law regions at intermediate times and of a stretched exponential decay at late times. In this article we discuss how such patterns can be derived by the simple assumption of self-similarity, imposed on the distribution of independently relaxing modes, as well as on their amplitude and characteristic times [2]. We perform a careful study of the relaxation in such systems, not only in the power-law regime, but also at early and late times, i.e., in the region in which scaling starts and ceases to exist. Indeed, self-similarity is never observed over an infinite range of values. The finite size and/or time of the smallest units introduces a lower cutoff in the distribution of modes. A more interesting cutoff is usually acting at large times, limiting the range over which self-similarity is observed. Very often, the upper cutoff depends on external fields (like temperature, pressure, etc.) and controls the approach to a *critical* point, where the self-similarity extends over all the range of values.

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The conceptual framework of such approach is offered by percolation theory [3]. In such a theory, the presence of disorder manifests itself in the presence of a poly-disperse set of clusters, characterized by a scale-invariant cluster size distribution. The scale-invariant disorder of the system may impose scale-invariant relaxation phenomena in dynamical processes taking place on the clusters. In percolation theory, the lower cutoff is related to the smallest geometrical unit, the monomer, while the upper cutoff is controlled by the distance from the *percolation* point. At percolation the upper cutoff becomes infinite.

The underlying assumption of a self-similar set of independently relaxing units may appear, at a first glance, as an oversimplification. Indeed models based on serial (as opposed to parallel) decay processes [4], i.e., on hierarchical organization in time, have been proposed to interpret relaxation in complex systems. Such sophisticated models predict a functional form for the decay of correlation which is not different from the one obtained by postulating independently relaxing units. For the sake of simplicity, we retain in this discussion the assumption of independence in the relaxation of each mode. Moreover, systems composed of interacting units may be converted, under the appropriate transformation, into a system composed of non-interacting eigenmodes. The assumption of independence is thus equivalent to the assumption of the existence of such (a priori unknown) transformation.

The correlation function resulting from the assumptions outlined above is given by a sum of exponential relaxation processes weighted by a power-law distribution of relaxation times. The three exponents controlling the self-similarity of the distribution of modes of the relaxation amplitudes and times combine into two new exponents controlling the distribution of relaxation times and the shape of its upper cutoff. According to the values of these two exponents, we find different functional forms for the decay of the correlation function and for the scaling of its moments.

Section 2 discusses the basic ingredients of the independent-modes approach and the functional forms characterizing the time behavior of the correlation function. Section 3 compares the predictions of the theory in a few disordered systems we have recently worked on, including microemulsion systems close to critical and percolation points and molecular glasses.

2. Relaxation times distribution

We write the time correlation function of the fluctuations $C(t)$ as the sum of contributions of various decay times, enumerated by the continuous variable k , relaxing independently and in parallel. These modes are characterized by a Debye-type relaxation with an amplitude $A(k)$ and a characteristic time $\tau(k)$. The modes are distributed according to the density function $N(k)$:

$$C(t) = \frac{1}{N} \int_1^{\infty} dk N(k) A(k) \exp \left[-\frac{t}{\tau(k)} \right]. \quad (1)$$

The relaxation amplitude is assumed to be a power-law $A(k) = k^{\alpha+\sigma}$, while the distribution $N(k)$ is a power-law limited by an exponential cutoff

$$N(k) = N_1 k^{-\sigma} \exp\left[-\frac{k-1}{k_c}\right]. \quad (2)$$

The k th relaxation time is also assumed to be a power-law in k characterized by the exponent γ , $\tau(k) = \tau_1 k^\gamma$, where τ_1 is the shortest time. The exponent γ will be equivalently expressed in terms of another exponent β as $\gamma = (1 - \beta)/\beta$. N is given by the normalization of the correlation function $C(t=0) = 1$. In summary,

$$C(t) = \frac{1}{k_c^{1+\alpha} \Gamma\left(1 + \alpha, \frac{1}{k_c}\right)} \int_1^\infty dk k^\alpha \exp\left[-\frac{k}{k_c} - \frac{t}{\tau_1} k^{-\gamma}\right], \quad (3)$$

where $\Gamma(a, x)$ is the incomplete gamma function. Note that when $\gamma = 0$, or $\beta = 1$, the correlation function reduces to the simple exponential $\exp[-t/\tau_1]$.

In terms of the variable $\tau(k)$, the relaxation time, $C(t)$ is given by

$$C(t) = \int_{\tau_1}^\infty \frac{d\tau}{\tau} g(\tau) \exp\left[-\frac{t}{\tau}\right], \quad (4)$$

$g(\tau)/\tau$ is the distribution of times

$$g(\tau) = \frac{1}{\gamma \Gamma\left(1 + \alpha, \left(\frac{\tau_c}{\tau_1}\right)^{-1/\gamma}\right)} \times \left(\frac{\tau}{\tau_c}\right)^{(1+\alpha)/\gamma} \exp\left[-\left(\frac{\tau}{\tau_c}\right)^{1/\gamma}\right], \quad (5)$$

where $\tau_c = \tau_1 k_c^\gamma$ is the cutoff relaxation time. Note that the relaxation times distribution function $g(\tau)$ is characterized by a power-law limited by a stretched exponential cutoff time. A similar distribution function is used in the Cole–Davidson expression for the $C(t)$, which introduces a cutoff through the upper limit of integration but has no lower relaxation time limit [5].

2.1. Properties of $C(t)$

The behavior of $C(t)$ for small times is given by a linear decay, followed by a power law and finally by a stretched exponential. This behavior defines two timescales τ_1 and τ_c , corresponding to the shortest and the longest relaxation times available to the system. The average decay time can be easily calculated and is dominated by τ_1 or τ_c according to the values we give to the indices, the behavior of which we examine in detail in the various time regions.

We start by evaluating $C(t)$ for short times $t \ll \tau_1$. For $1 + \alpha < 0$, $C(t)$ is a function of τ_1 only

$$C(t) \approx 1 + \frac{1 + \alpha}{\gamma - 1 - \alpha} \times \frac{t}{\tau_1}. \quad (6)$$

In the opposite case, $1 + \alpha > 0$ we obtain for $0 < \gamma < 1 + \alpha$, a function of τ_c only

$$C(t) \approx 1 - \frac{\Gamma(1 + \alpha + \gamma)}{\Gamma(1 + \alpha)} \times \frac{t}{\tau_c}, \quad (7)$$

while for $0 < 1 + \alpha < \gamma$ we get

$$C(t) \approx 1 - \frac{1}{(\gamma - 1 - \alpha)\Gamma(1 + \alpha)} \times \left(\frac{\tau_1}{\tau_c}\right)^{(1+\alpha)/\gamma} \times \frac{t}{\tau_1}. \quad (8)$$

In the intermediate time regime, $\tau_1 \ll t \ll \tau_c$ the self-similarity of $g(\tau)$ manifests in a power-law dependence in $C(t)$ in two different ways according to the sign of $1 + \alpha$. For $1 + \alpha > 0$, $1 - C(t)$ behaves as a power law

$$C(t) \approx 1 - \frac{\gamma}{(1 + \alpha)(\gamma - 1 - \alpha)} \times \frac{\Gamma(2 - (1 + \alpha)/\gamma)}{\Gamma(1 + \alpha)} \times \left(\frac{t}{\tau_c}\right)^{(1+\alpha)/\gamma}. \quad (9)$$

For $1 + \alpha < 0$, we get the true power law

$$C(t) \approx -\frac{1 + \alpha}{\gamma} \left[\Gamma\left(-\frac{1 + \alpha}{\gamma}\right) - \Gamma\left(-\frac{1 + \alpha}{\gamma}, \frac{t}{\tau_1}\right) \right] \left(\frac{t}{\tau_1}\right)^{(1+\alpha)/\gamma}. \quad (10)$$

For $t \gg \tau_c$, $C(t)$ is a stretched exponential decay times a power

$$C(t) \approx \frac{\sqrt{2\pi}/(\gamma + 1)}{\Gamma\left(\alpha + 1, \left(\frac{\tau_c}{\tau_1}\right)^{-1/\gamma}\right)} \left(\frac{\gamma t}{\tau_c}\right)^{(\alpha+0.5)/(\gamma+1)} \exp\left[-\left(\frac{t}{\beta(1 - \beta)^{1/\beta-1}\tau_c}\right)^\beta\right], \quad (11)$$

where the universal exponent β has been defined before. Note that one obtains a pure stretched exponential only when $\alpha = -0.5$ [2].

3. Applications in disordered systems

3.1. Dielectric relaxation in microemulsion systems at percolation

In [6], the idea discussed in the previous sections have been applied to dielectric relaxation in microemulsion systems. A mixture of water-in-oil microemulsion droplets has been modeled as a polydisperse set of clusters, containing k droplets each, distributed according to random percolation, i.e., with a scaling expression [3]

$$N(k) = \frac{k^{-\tau} e^{-k/k_c}}{k_c^{2-\tau} \Gamma(2 - \tau, k_c^{-1})}, \quad (12)$$

characterized by a power-law behavior with index τ and a cutoff cluster size k_c which diverges as the system approaches the percolation threshold. The scattering amplitude and correlation time, in the simple case of a conducting microemulsion in a non-conducting medium, have been evaluated on the basis of the following argument [6].

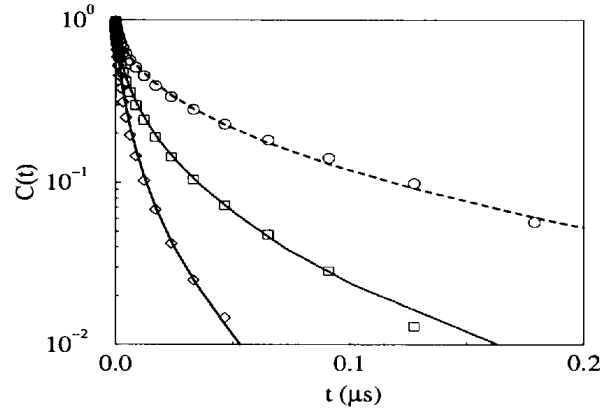


Fig. 1. Points are the $C(t)$ for water–AOT–decane microemulsion for different values of ϕ (0.24 (\diamond), 0.28 (\square) and 0.32 (\circ)), $T = 25^\circ\text{C}$ and $X = [\text{H}_2\text{O}]/[\text{AOT}] = 40.8$, calculated by Laplace transform of the measured conductivity and permittivity [7]. The full lines are given by Eq. (3) with $(1 + \alpha)/\gamma = 0.41$ and $\beta = 0.4$.

A_k is related to the product of the mean square charge fluctuations, proportional to the cluster size k , and the radius of gyration squared R_k^2 , where $R_k \sim k^{1/D}$ and D is the fractal dimension of the cluster. Consequently, A_k will scale as kR_k^2 . The decorrelation time is proportional to the time it takes a charge carrier to visit all sites of the cluster. If the clusters were compact objects τ_k would be proportional to R_k^2 since the charge carriers perform diffusive motion in the clusters. Since the motion is instead on a fractal aggregate, it is governed by anomalous diffusion and τ_k will be related to the radius of gyration through a power which takes into account the anomaly, i.e., the ratio D/\tilde{d}

$$\tau_k \sim (R_k^2)^{D/\tilde{d}}, \quad (13)$$

where \tilde{d} is the spectral exponent.

In [6], the amplitude and relaxation times for the more complex case of conducting droplets in a moderately conducting medium are given. Using $\tau = 2.2$, $D = 2.5$, $\tilde{d} = 1.36$, one obtains $(1 + \alpha)/\gamma = 0.41$ and $\beta = 0.4$. The results are shown in Fig. 1, where we report the comparison of the measured conductivity and the dielectric constant of the microemulsion with the Laplace transform of the time derivative of $C(t)$, with a rather good agreement. The details of the comparison are given in [6,7].

3.2. Glassy relaxation of density correlations in the mode-coupling theory

In the last 10 years, significant efforts have been devoted to the study of the slow dynamics in glass forming supercooled liquids. In such systems, correlations in space decay in a multi-step process. An initial decorrelation, controlled by the microscopic dynamics only at early stages, towards a non-zero plateau value (the so called non-ergodicity factor, f_{EA}). In the liquid state this decay is followed by a much slower relaxation controlled by collective dynamics, often described as cage restructuring process, which restores ergodicity in the system. The behavior of the correlation function

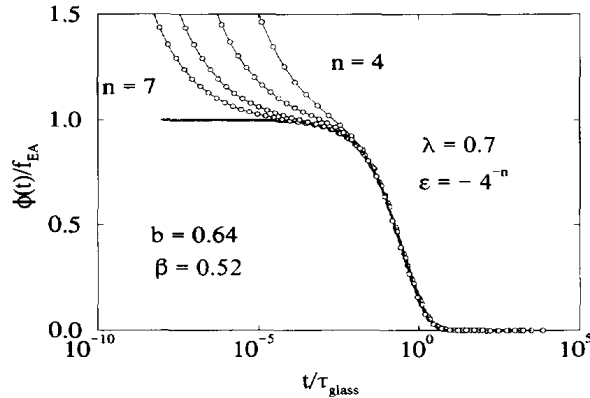


Fig. 2. Decay of the correlator $\phi(t)$ for the F_{12} model. Points are numerical solutions of the model, plotted in the scaled variable t/τ_{glass} . The full curve is the fit to the scaled data according to Eq. (3).

close to the plateau (β -region) and at late times (α -region) is very often the same in completely different systems, speaking for an underlying universality in the dynamics. Two empirical laws have been proposed to describe the late β -region and the α -region, the von-Schwindler law ($C(t) - f_{EA} \sim (t/\tau_{glass})^b$) and the stretched exponential form ($C(t) \sim e^{-(t/\tau_{glass})^\beta}$), where τ_{glass} is the characteristic time which diverges at the MCT glass transition point. The MCT exponent b depends on the glass transition point only. All these observations have been rationalized by the mode-coupling theory (MCT) for the glass transition [8], the first successful theory for supercooled liquids. MCT predicts indeed the existence of β and α regions, as well as the power-law and stretched exponential decays. It predicts also the existence of scaling at different temperatures and pressures for the late β and α regions. Interestingly enough, all these features are also found in Eq. (3) when $(1 + \alpha)/\gamma > 0$.

The essential ingredients of MCT are a non-linear coupling of the correlators in the retarded memory function controlling the evolution of the correlators themselves. For simple forms of the memory function, the evolution of the correlators can be calculated numerically. Fig. 2 shows the decay of $C(t)$ for the so-called F_{12} model [8]. Different curves are calculated for different distances from the glass transition point, measured by the value of ϵ . Curves have been plotted as a function of t/τ_{glass} to highlight the scaling behavior in the α regime. For the chosen glass transition point, MCT predicts $b = 0.64$ and $\beta = 0.52$.

Motivated by the similarity in the behavior of $C(t)$ as predicted by MCT and of $C(t)$ calculated as sum of independently relaxing modes, we have compared the two curves in Fig. 2. We have used $\gamma = 0.92$ and $1 + \alpha = 0.59$, in agreement with the MCT exponent of the von-Schwindler law. In this region of $1 + \alpha$ the relevant parameter is τ_c and all curves can be scaled in t/τ_c , corresponding to the MCT time-temperature superposition principle [8]. Thus, τ_c plays the role of τ_{glass} .

Of course, while MCT is able to describe also the approach to the plateau as well as to predict the value of the exponent in the power-law regime and the scaling

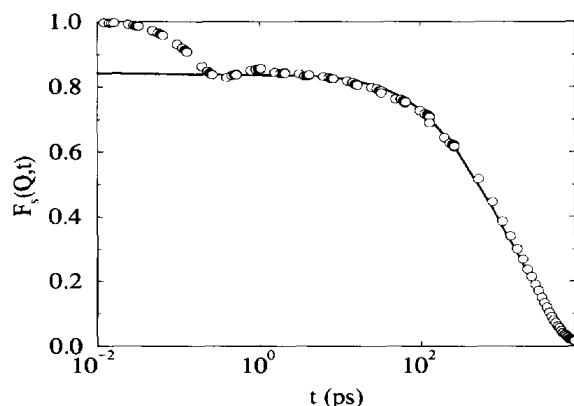


Fig. 3. $F_s(Q, t)$ at $T = 210$ and $Q = 1.8 \text{ \AA}^{-1}$, corresponding to the position of the maximum in the static structure factor from [10]. The full line is a fit with Eq. (3) for times larger than 3 ps, i.e., after the plateau.

behavior of τ_{glass} from the chosen model, in our case we arbitrarily chose γ and α . This notwithstanding, the agreement is surprisingly good, suggesting that cage-restructuring dynamics close to the glass transition is the result of a self-similar distribution of relaxation times. This may offer an explanation on why alternative approaches [9] to the description of the dynamics close to the glass transition, based on an a priori assumption of distribution of relaxation times, succeed in describing the behavior of supercooled liquids.

3.3. Slow dynamics in water

The single-particle dynamics in deeply supercooled water have been recently studied via molecular dynamics [10]. It has been shown that at low temperatures the decay of the intermediate incoherent scattering function, $F_s(Q, t)$, is characterized by a two-step process, with a characteristic separation time coinciding with the onset of the cage effect. For lengths comparable to the cage size the slow decay is well described by a stretched exponential decay. Fig. 3 shows that the slow decay of $F_s(Q, t)$ can be well described by a distribution of relaxation times, with $1 + \alpha = 0.22$ and $\gamma = 0.43$, suggesting that a self-similar distribution of relaxation times can be an alternative description to the slow dynamics in molecular systems.

3.4. The droplet model of critical phenomena

We turn next to the discussion of some aspects of the droplet dynamics near the critical point. Scattering data close to the critical point have been interpreted in terms of independent clusters [11] of fractal dimension $D = 2.5$. Authors of [11] have used Eq. (12) (with $\tau = 2.2$) as cluster size distribution

$$S_k(Q) = ke^{-(QRg_k)^2/3} \quad (14)$$

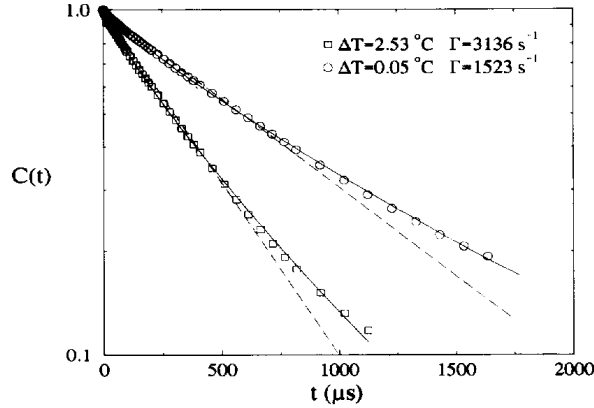


Fig. 4. Measured correlation functions showing deviations from the exponential behavior. The dashed lines represent the fit to an exponential, full lines are a fit with Eq. (3) (from [11]).

(where $Rg_k \sim k^{1/D}$ is the radius of gyration of a cluster of size k) as relaxation amplitude and

$$\tau_k = D_k Q^2 = Q^2 D_1 k^{-1/D} \quad (15)$$

as relaxation time. Here, D_k is the diffusion coefficient of the k -cluster and D_1 is the renormalised diffusion coefficient of a single droplet. In the hydrodynamic regime, the structure factor $S_k(Q) \approx k$. Such a choice fixes the value of the exponents to the values $1 + \alpha = -0.2$ and $\gamma = 0.4$. Fig. 4 shows the measured correlation function and the fit according to the present model.

On the basis of these relaxations one obtains not only a successful description of the decay of correlations close to the critical point but also a correct description of the static scattering. Indeed, when k_c becomes large, the resulting static scattering reduces to the well-known Ornstein–Zernike relation [11].

4. Conclusions

We have presented a detailed study of the behavior of the decay of correlation in disordered systems characterized by a power-law distribution of independently relaxing modes.

The independently relaxing modes approach has been often used to describe the decay of correlation in complex systems [5]. The well-known empirical Cole–Davidson description of relaxation is indeed based on a power-law distribution of relaxation times. In this paper, we build upon such previous works and extend it to include the consequences introduced by the presence of an upper (τ_c) and lower (τ_l) cutoff on the time distribution.

We have studied how the value of the exponent controlling $g(\tau)$ enters in the functional form describing the decay. Interestingly enough, we find that, in the region of

time such that $\tau_1 < t < \tau_c$, the self-similarity in $g(\tau)$ determines a power-law behavior in $C(t)$ or in $1 - C(t)$, according to the sign of $1 + \alpha$. Moreover, in the same time window, $C(t)$ does not or it does depend on τ_c . The long-time behavior is always described by a power-law times a stretched exponential behavior.

We have shown how the independent modes picture is able to describe the decorrelation process in microemulsions. We have investigated the electrical conductivity close to the percolation line and the dynamical light scattering close to the critical point. In these two examples, the value of the exponents α and γ can be obtained theoretically. In the first example, $1 - C(t) \sim t^{(1+\alpha)/\gamma}$, while in the second, $C(t) \sim t^{(1+\alpha)/\gamma}$. In the end, we have also shown that a self similar $g(\tau)$ is a very good representation of the decay in supercooled liquids and theoretical glasses.

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