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Analysis of Relaxation Functions Characterized by a Broad Monomodal Relaxation Time Distribution

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Abstract. — We demonstrate the advantage of using the so-called generalized exponential (GEX) function for the analysis of relaxation functions characterized by a monomodal broad relaxation time distribution. We give a number of characteristics of this function and compare it to two functions that are currently widely used for this type of analysis: the Kohlraush-Williams-Watt and the Havriliak-Negami functions. The main advantages of the GEX-function are that it can be used easily both in the time and the frequency domain, and that it has a relatively simple expression for the corresponding relaxation time distribution. Three important applications are discussed: the glass transition dynamics, and the relaxation of concentration fluctuations in dilute and concentrated solutions of broad distributions of selfsimilar particles. In the latter two cases the relation between the parameters of the GEX-function and the molecular characteristics of the solutions is made explicit.

Introduction

The relaxation function ($\varphi(t)$) of a wide variety of dynamical processes is characterized by a broad spectrum of relaxation times ($A(\tau)$):

$$\varphi(t) = \int_0^\infty A(\tau) \exp(-t/\tau) d\tau \quad (1)$$

Even if the relaxational process is non-exponential it can still often be described in terms of equation (1). In this case, of course, $A(\tau)$ has no physical meaning, but can still be useful for comparisons of experimental results obtained from different techniques or on different samples. In principle one could obtain the relaxation time distribution, $A(\tau)$, by taking the inverse Laplace transform (ILT) of $\varphi(t)$. However, experimentally $\varphi(t)$ is obtained as a discrete set of data points and the ILT is notoriously sensitive to noise in the data. A number of algorithms have been developed to overcome this problem [1]. They all aim at finding the spectrum that represents the best compromise between spurious detail and oversmoothing. The computer routines function generally well for relatively narrow relaxation time distributions, but very

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broad monomodal asymmetric distributions tend to be represented by several either discrete peaks or by one too symmetric peak. This effect is aggravated if the data contain non-random noise [2].

A different approach is to fit $\varphi(t)$ directly to an analytical function, which implies that we assume a specific shape of the relaxation function in question. Two such functions are the Kohlraush-Williams-Watt (KWW) and the Havriliak-Negami (HN) function which are frequently used to fit the relaxation function in the time and frequency (ω) domain, respectively. A detailed comparison of these functions is given by Alvarez *et al.* [3]. Alternatively one could use equation (1) and choose a suitable model for $A(\tau)$.

Here we will present an investigation of the so-called generalized exponential distribution (GEX) [4]:

$$A_g(\tau) = k\tau^{p-1} \exp[-(\tau/\tau_g)^s] \quad (2)$$

k is a normalisation constant such that $\int_0^\infty A(\tau) d\tau = 1$. This function allows a wide variety in shape and with a suitable choice of s and p we can recover a number of classical distributions such as the Schultz-Zimm and the Pearson distribution. In the past the GEX distribution has been used to analyse relaxation of concentration fluctuations in dilute polydisperse polymer solutions [5], relaxation of density fluctuations [6, 7] and structural relaxation in semi-dilute polymer solutions [8], but no connection was made between the model parameters (p , s , τ_g) and the physical properties of the system. The GEX distribution has also been used to describe the relaxation of the magnetization induced in a spin glass [9]. This problem is analogous to that of the relaxation of concentration fluctuations in polydisperse polymer solutions which we will discuss in Section 2.1.

In Section 1, we will give a number of general properties of the GEX distribution and its Laplace transform ($\varphi_g(t)$). We will compare $\varphi_g(t)$ with the KWW ($\varphi_w(t)$) and HN ($\varphi_h(\omega)$) functions. We will show that $\varphi_g(t)$ is more versatile than $\varphi_w(t)$ or $\varphi_h(\omega)$. In Section 2 we will discuss the application of GEX to the relaxation of concentration fluctuations in dilute and strongly interpenetrated polydisperse branched polymer solutions, and the relaxation of density fluctuations due to main chain segment relaxation the so-called α -relaxation. For the first two cases we will relate p and s to physical properties of the system. We will demonstrate the usefulness of this analysis for dynamic light scattering measurements on a broad distribution of β -lactoglobuline aggregates in aqueous solution.

1. Properties of the GEX Distribution and its Laplace Transform

1.1. GENERAL PROPERTIES OF GEX. — For broad distributions one generally uses a logarithmic scale for τ , so that we must consider $\tau A_g(t)$ in order to retain equal area representation. First, we note that:

$$\tau A_g(\tau, p, s) = \frac{1}{\tau} A_g(1/\tau, -p, -s) \quad (3)$$

Considering this symmetry, we will limit our study to cases $s > 0$, $p > 0$ and $s > 0$, $p \leq 0$. The others being directly deduced from the reciprocal space of relaxation rates ($1/\tau$).

For $p > 0$ and $s > 0$, the prefactor k is given by:

$$k = \frac{s}{\tau_g^p \Gamma(p/s)} \quad (4)$$

The maximum of $\tau A_g(\tau)$ is located at:

$$\tau_{\max} = \tau_g (p/s)^{1/s} \quad (5)$$

Table I. — *Expression for the normalisation constant k and the moments of the relaxation time distribution $A_g(\tau)$ for $s > 0$ and $p > 0$.*

	$s > 0$ and $p > 0$
	$k = \frac{s}{\tau_g^p \Gamma(p/s)}$
$n > -p$	$M_n = \tau_g^n \frac{\Gamma((p+n)/s)}{\Gamma(p/s)}$
$n = -p$	$M_{-p} = \tau_g^{-p} \frac{s \ln(\tau_g/\tau_0) - \kappa}{\Gamma(p/s)}$
$-(p+s) < n < -p$	$M_n = -s \tau_g^n \frac{(\tau_0/\tau_g)^{p+n} - \Gamma((p+n)/s + 1)}{(p+n)\Gamma(p/s)}$
$n = -(p+s)$	$M_{-(p+s)} = \tau_g^{-(p+s)} \frac{(\tau_0/\tau_g)^{-s} - s \ln(\tau_g/\tau_0) + \kappa}{\Gamma(p/s)}$
$n < -(p+s)$ etc...	etc...

The moment of order n is defined as:

$$M_n = \int_0^\infty \tau^n A_g(\tau) d\tau \quad (6)$$

For $n > -p$, M_n is given by:

$$M_n = \tau_g^n \frac{\Gamma((p+n)/s)}{\Gamma(p/s)} \quad (7)$$

For $n \leq -p$, the integral in equation (6) diverges for $\tau \rightarrow 0$. However, if we introduce a smallest relaxation time in the system, $\tau_0 \ll \tau_g$, M_n no longer diverges but depends on τ_0 . Table I shows expressions for M_n for a number of important cases.

For $p \leq 0$ and $s > 0$, τ_0 is needed even for the definition of the constant k (cf. Tabs. II-IV). The maximum of the distribution is of course at $\tau_{\max} = \tau_0$. The moments depend also on τ_0 and are given in Tables II-IV.

The average relaxation time $\bar{\tau}$ is equal to M_1 but can also be calculated directly as the area under $\varphi(t)$.

Table II. — Expression for the normalisation constant k and the moments of the relaxation time distribution $A_g(\tau)$ for $s > 0$ and $p = 0$.

	$s > 0$ and $p = 0$
	$k = \frac{s}{s \ln(\tau_g/\tau_0) - \kappa}$
$n > 0$	$M_n = \tau_g^n \frac{\Gamma(n/s)}{s \ln(\tau_g/\tau_0) - \kappa}$
$n = 0$	$M_0 = 1$
$-s < n < 0$	$M_n = -\frac{s}{n} \frac{\tau_0^n - \tau_g^n \Gamma(n/s + 1)}{s \ln(\tau_g/\tau_0) - \kappa}$
$n = -s$	$M_{-s} = \tau_g^{-s} \frac{(\tau_g/\tau_0)^s - s \ln(\tau_g/\tau_0) + \kappa}{s \ln(\tau_g/\tau_0) - \kappa}$
$n < -s$ etc...	etc...

1.2. ASYMPTOTIC BEHAVIOUR OF $\varphi_g(t)$. — In the limit of $t \ll \tau_g$ only short relaxation times influence $\varphi(t)$ and, depending on the value of p , $\varphi_g(t)$ has three different asymptotic behaviours. For $p > 1$, we obtain simply the result of the cumulants analysis (see below) :

$$\varphi_g(t) \approx \exp(-at/\tau_g) \quad t \ll \tau_g \quad p > 1 \quad (8)$$

where a is a positive constant.

For $p \leq 1$, the initial behaviour of $\varphi_g(t)$ depends on τ_0 , but in the limit $\tau_0 \ll t \ll \tau_g$ we have:

$$\varphi_g(t) \approx \exp(-b(t/\tau_g)^p) \quad \tau_0 \ll t \ll \tau_g \quad 0 < p < 1 \quad (9)$$

$$\varphi_g(t) \propto t^p \quad \tau_0 \ll t \ll \tau_g \quad p < 0 \quad (10)$$

where b is a positive constant.

In the limit of $t \gg \tau_g$ only long relaxation times influence $\varphi_g(t)$ and it can be shown that:

$$\varphi_g(t) \propto \exp\left(-c(t/\tau_g)^{s/(s+1)}\right) \quad t \gg \tau_g \quad (11)$$

where c is a positive constant.

Table III. — *Expression for the normalisation constant k and the moments of the relaxation time distribution $A_g(\tau)$ for $s > 0$ and $-s < p < 0$.*

	$s > 0$ and $-s < p < 0$
	$k = \frac{-p}{\tau_0^p - \tau_g^p \Gamma(p/s + 1)}$
$n > -p$	$M_n = \frac{-(p/s)\tau_g^{n+p}\Gamma((n+p)/s)}{\tau_0^p - \tau_g^p \Gamma(p/s + 1)}$
$n = -p$	$M_{-p} = -\frac{p}{s} \frac{s \ln(\tau_g/\tau_0) - \kappa}{\tau_0^p - \tau_g^p \Gamma(p/s + 1)}$
$-(p+s) < n < -p$	$M_n = \frac{p}{n+p} \frac{\tau_0^{n+p} - \tau_g^{n+p}\Gamma((n+p)/s + 1)}{\tau_0^p - \tau_g^p \Gamma(p/s + 1)}$
$n = -(p+s)$	$M_{-(p+s)} = -\frac{p\tau_g^{-s}(\tau_0/\tau_g)^{-s} - s \ln(\tau_g/\tau_0) = \kappa}{s} \frac{1}{\tau_0^p - \tau_g^p \Gamma(p/s + 1)}$
$n < -(p+s)$ etc...	etc...

1.3. COMPARISON WITH THE CUMULANTS ANALYSIS. — This data analysis procedure was introduced by Koppel [10] and is widely used to analyse dynamic light scattering results. It relates the behaviour of $\varphi(t)$, $t \rightarrow 0$, with the moments of the relaxation rate distribution function $G(\Gamma)$, where $\Gamma = 1/\tau$. The relation between $A(\tau)$ and $G(\Gamma)$ is given by:

$$G(\Gamma) = \frac{1}{\Gamma^2} A(1/\Gamma) \quad (12)$$

so that the moment of order n for $G(\Gamma)$ is simply the moment of order $-n$ for $A(\tau)$. $\varphi(t)$ can be written as:

$$\varphi(t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) d\Gamma \quad (13)$$

The essence of this method lies in expanding $\varphi(t)$ around the mean relaxation rate $\bar{\Gamma}$:

$$\exp(-\Gamma t) = \exp(-\bar{\Gamma} t) \left(1 - (\Gamma - \bar{\Gamma}) + \frac{(\Gamma - \bar{\Gamma})^2 t^2}{2!} - \frac{(\Gamma - \bar{\Gamma})^3 t^3}{3!} + \dots \right) \quad (14)$$

Table IV. — Expression for the normalisation constant k and the moments of the relaxation time distribution $A_g(\tau)$ for $s > 0$ and $p = -s$.

	$s > 0$ and $p = -s$
	$k = \frac{s\tau_g^s}{(\tau_g/\tau_0)^s - s \ln(\tau_g/\tau_0) + \kappa}$
$n > s$	$M_n = \tau_g^n \frac{\Gamma((n-s)/s)}{(\tau_g/\tau_0)^s - s \ln(\tau_g/\tau_0) + \kappa}$
$n = s$	$M_s = \tau_g^s \frac{s \ln(\tau_g/\tau_0) - \kappa}{(\tau_g/\tau_0)^s - s \ln(\tau_g/\tau_0) + \kappa}$
$0 < n < s$	$M_n = -\frac{s\tau_g^n}{n-s} \frac{(\tau_g/\tau_0)^{s-n} - \Gamma((n-s)/s + 1)}{(\tau_g/\tau_0)^s - s \ln(\tau_g/\tau_0) + \kappa}$
$n = 0$	$M_0 = 1$
$n < -(p+s)$ etc...	etc...

Substituting (14) in equation (13) we can express $\ln(\varphi(t))$ in terms of the normalized cumulants μ_i :

$$\ln(\varphi(t)) = -\mu_1 \bar{\Gamma} t + \frac{1}{2!} \mu_2 (\bar{\Gamma} t)^2 - \frac{1}{3!} \mu_3 (\bar{\Gamma} t)^3 + \dots \quad (15)$$

μ_1 is unity and $\bar{\Gamma}$ and μ_2 are given by:

$$\bar{\Gamma} = \int_0^\infty \Gamma G(\Gamma) d\Gamma = M_{-1} \quad (16)$$

$$\mu_2 = \frac{1}{\bar{\Gamma}^2} \int_0^\infty (\Gamma - \bar{\Gamma})^2 G(\Gamma) d\Gamma = \frac{M_{-2}}{(M_{-1})^2} - 1 \quad (17)$$

This method is only useful for weakly polydisperse distributions when $\mu_2, \mu_3, \dots$ are smaller than 1. Otherwise only a very reduced part of $\varphi(t)$ can be used in the analysis. This is a serious drawback especially when $\varphi(t)$ is sampled on a logarithmic time scale.

Even if one is only interested in $\bar{\Gamma}$ and μ_2 these values can be obtained from an analysis using the GEX function. For weakly polydisperse distributions $\bar{\Gamma}$ and μ_2 can be expressed in

terms of p , s and τ_g :

$$\bar{\Gamma} = \tau_g^{-1} \frac{\Gamma((p-1)/s)}{\Gamma(p/s)} \quad p > 1 \quad (18)$$

$$\mu_2 = \frac{\Gamma((p-2)/s) \Gamma(p/s)}{[\Gamma((p-1)/s)]^2} \quad p > 2 \quad (19)$$

For smaller values of p , $\bar{\Gamma}$ and μ_2 depend on the shortest relaxation time (τ_0) of the process (see tables).

1.4. COMPARISON WITH THE KWW EQUATION. — The KWW equation is given by:

$$\varphi_w(t) = \exp \left[- (t/\tau_w)^\beta \right] \quad (20)$$

with $0 < \beta < 1$. The average relaxation time is given by:

$$\bar{\tau} = \frac{\tau_w}{\beta} \Gamma \left(\frac{1}{\beta} \right) \quad (21)$$

There is no closed analytical expression for the relaxation time distribution associated with this function except in the special case $\beta = 0.5$ where $A_w(\tau)$ is a GEX distribution with $p = 0.5$, $s = 1$ and $\tau_g = 4\tau_w$. Lindsey and Patterson [11] have calculated numerically the distribution function for other values of β . For any value of β we can obtain an excellent approximation of $\varphi_w(t)$ using $\varphi_g(t)$ (see Fig. 1). The corresponding values of p and s are shown as a function of β in Figure 2. For $\beta < 0.6$, the corresponding value of p and $s/(s+1)$ are close to β as expected from the asymptotic behaviour of the GEX function given in equations (9) and (11). For larger values of β , $A_w(\tau)$ is more sharply peaked around its maximum than $A_g(\tau)$. However, if the distribution is narrow the detailed shape becomes less important for a correct description of $\varphi(t)$ and $\varphi_w(t)$ is well described by $\varphi_g(t)$ with $p > \beta$. When β approaches unity the values of p and s must diverge and are, therefore, ill defined. Using equations (7) and (21) we can easily relate τ_g to τ_w :

$$\tau_w = \tau_g \frac{\beta \Gamma((p+1)/s)}{\Gamma(1/\beta) \Gamma(p/s)} \quad (22)$$

We conclude from this comparison that any experimentally determined relaxation function that can be described by a KWW function can equally well be described by the GEX function. The advantage of using the GEX function is its larger degree of freedom and that we obtain a tractable expression for the corresponding relaxation time distribution. If one believes that the relaxation function is a stretched exponential in the time domain with $\beta < 0.6$, one could simply express p and s in terms of β ($p = \beta$ and $s = \beta/(1 - \beta)$) and use expressions (24) and (25) to fit data in the frequency domain, see below.

1.5. COMPARISON WITH THE HN EQUATION. — The HN equation is used to analyse the relaxation function in the frequency domain:

$$\varphi_h^*(\omega) = \frac{1}{[1 + (i\omega\tau_h)^\alpha]^\gamma} \quad (23)$$

with α and γ between 0 and 1. Experimentally one determines the real (φ') and imaginary (φ'') parts of φ^* , which, in analogy with equation (1), can be written as a superposition of

Fig.1.

Fig.2.

Fig. 1. — Comparison of KWW relaxation functions (symbols) with fits to the GEX function using equations (1) and (2) (solid lines). Equation (20) was used to calculate KWW functions with different values for β as indicated in the figure.

Fig. 2. — Values of p and s obtained from fits to KWW function as a function of β . For $\beta < 0.6$, $p \approx \beta$ and $s \approx \beta/(1-\beta)$ as indicated in the figure.

independent relaxation processes:

$$\varphi'(\omega) = \int_0^\infty \frac{1}{1 + \omega^2 \tau^2} A(\tau) d\tau \quad (24)$$

and

$$\varphi''(\omega) = \int_0^\infty \frac{\omega \tau}{1 + \omega^2 \tau^2} A(\tau) d\tau \quad (25)$$

The relaxation time distribution corresponding to the HN function is given by:

$$\tau A_h(\tau) = \frac{(\tau/\tau_h)^{\alpha\gamma} \sin(\gamma\theta)}{\pi \left[(\tau/\tau_h)^{2\alpha} + 2(\tau/\tau_h)^\alpha \cos(\alpha\pi) + 1 \right]^{\gamma/2}} \quad (26)$$

with

$$\theta = \arctan \left| \frac{\sin(\gamma\pi)}{(\tau/\tau_h)^\alpha + \cos(\alpha\pi)} \right| \quad (27)$$

The HN distribution is the same as the GEX distribution at $\tau \ll \tau_{\max}$ if we take $p = \alpha\gamma$. The important difference between these two distributions is that for $\tau \gg \tau_{\max}$ the HN distribution decreases as $\tau^{-\alpha}$, while the GEX distribution has a stretched exponential cut-off. As a consequence $\varphi_h''(\omega)$ has a power law dependence on ω for $\omega \ll \omega_{\max}$ and $\omega \gg \omega_{\max}$, while $\varphi_g''(\omega)$ only has a power law dependence for $\omega \gg \omega_{\max}$ ($\omega_{\max}$ is the peak position of $\varphi''(\omega)$). Alvarez *et al.* [3] have shown that for values of ω not too far from $\omega_{\max}$ the KWW function is equivalent to the HN function. Of course, for $\omega \ll \omega_{\max}$ the HN function is intrinsically

Fig. 3. — a) Semi logarithmic representation of the complex part of the relaxation function calculated using the HN equation (Eq. (23)) with $\alpha = 0.8$, $\gamma = 0.625$ and $\tau_h = 1$ (solid line) and using the GEX distribution in equation (25) with $p = 0.575$, $s = 1$ and $\tau_g = 1.55$ (symbols); b) Double logarithmic representation of the same data as in Figure 3a.

different from the KWW and GEX functions. The difference is illustrated in Figure 3 where we compare $\varphi_h''(\omega)$ with $\varphi_g''(\omega)$ calculated using equation (25) and the GEX distribution. We have taken p and s such that the two functions are very close around $\omega = \omega_{\max}$. The functions appear to be in good agreement when plotted on a semi-logarithmic scale, but a double logarithmic representation clearly reveals the different behaviour at $\omega \ll \omega_{\max}$ and $\omega \gg \omega_{\max}$. $\varphi_h''(\omega)$ and $\varphi_g''(\omega)$ can be made to superimpose for $\omega \gg \omega_{\max}$ if we take $p = \alpha\gamma$, but no choice of p or s gives an agreement at $\omega \ll \omega_{\max}$ (see Fig. 4). The difference is only important if we can determine $\varphi_h''(\omega)$ over a broad dynamical range e.g. the loss shear modulus using a rheometer, see below.

2. Applications

2.1. DYNAMIC LIGHT SCATTERING FROM DILUTE POLYDISPERSE POLYMER SOLUTIONS. — Dynamic light scattering experiments measure the normalised auto correlation function ($g_2(t)$) of the scattered intensity ($I(t)$) [12]:

$$g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I \rangle^2} \quad (28)$$

If the statistic of the scattered light is Gaussian, $g_2(t)$ can be related to the normalised autocorrelation function of the electric field ($g_1(t)$) by the Siegert relation :

$$g_2(t) = 1 + |g_1(t)|^2 \quad (29)$$

In polymer solutions $g_1(t)$ is equal to the normalized relaxation function of concentration fluctuations if we ignore the density fluctuations of the solvent. For very dilute solutions,

Fig. 4. — Double logarithmic representation of the complex part of the relaxation function calculated using the HN equation (Eq. (23)) with $\alpha = 0.8$, $\gamma = 0.625$ and $\tau_h = 1$ (solid line) and using the GEX distribution in equation (25) with $p = 0.5$, $s = 3$, $\tau_h = 2.5$ (symbols).

concentration fluctuations are related to the self-diffusion of the particles. For monodisperse solution, $g_1(t)$ is a single exponential decay:

$$g_1(t) = \exp(-t/\tau)$$

with

$$\tau = \frac{1}{q^2 D} \quad (30)$$

where D is the diffusion coefficient at zero concentration and q the scattering wave vector. Here we have assumed that particle are small compared to q^{-1} . D is related to the hydrodynamic radius of the particle (R_h) as:

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (31)$$

where k_B is the Boltzmann constant, T the absolute temperature and η the viscosity of the solvent.

For polydisperse solutions, $g_1(t)$ is a sum of exponential decays where the contribution of a particle with degree of polymerisation $DP = m$ is proportional to $m^2 N(m)$, with $N(m)$ the number distribution function of polymers, assuming again that all polymers are small compared to q^{-1} . The relaxation time associated with particles with $DP = m$ is:

$$\tau_m = \frac{1}{q^2 D_m} = \frac{6\pi\eta}{k_B T} R_{h_m} \quad (32)$$

We can now write $g_1(t)$ as:

$$g_1(t) \propto \int_1^\infty m^2 N(m) \exp(-t/\tau_m) dm \quad (33)$$

If we assume furthermore that $Rh_m \propto m^{1/d_f}$, where d_f is the mass fractal dimension of the particles then:

$$\tau_m = \tau_0 m^{1/d_f} \quad (34)$$

Using equation (34) in equation (33) we can write $g_1(t)$ as an integral over relaxation time:

$$g_1(t) \propto \int_{\tau_0}^{\infty} \frac{m^3 N(m)}{\tau_m} \exp(-t/\tau_m) d\tau_m \quad (35)$$

If we now identify $g_1(t)$ with $\varphi(t)$ in equation (1), we find:

$$\tau_m A(\tau_m) \propto m^3 N(m) \quad (36)$$

In many types of aggregation $N(m)$ can itself be described by a general exponential function [13]:

$$N(m) \propto m^{-\lambda} \exp(-(m/m^*)^\mu) \quad (37)$$

where λ is the polydispersity exponent and m^* a cut off mass for the distribution. Using equations (36) and (37), we find that $A(\tau)$ can be described by equation (2) with:

$$\begin{aligned} p &= d_f(3 - \lambda) \\ s &= d_f \mu \\ \tau_g &= \tau_{m^*} \end{aligned} \quad (38)$$

We will illustrate these results for three cases: swollen percolating clusters with $\lambda = 2.2$, $d_f = 2.0$ [14] and aggregates formed by reaction rate limited cluster aggregation (RLCA) with $\lambda = 1.5$, $d_f = 2.1$ or diffusion rate limited cluster aggregation (DLCA) with $\lambda = 0$, $d_f = 1.8$ [15]. In all cases μ is taken unity. In fact, for percolating clusters the real cut-off function does not have a stretched exponential form and the GEX distribution is only an approximation. Figure 5 shows simulated autocorrelation functions ($g_1(t)$) together with the resulting relaxation time distributions. It is clear that high precision data are needed to obtain accurate values of μ and λ . The situation is more favourable if μ is known. For instance in many kinetic aggregation processes $\mu = 1$ [16].

An example of this approach on real data is shown for a dilute solution of β -lactoglobuline aggregates. We know from static light scattering measurements that these aggregates have a fractal structure with $d_f = 2.05$ and a power law size distribution [5]. In Figure 6a $g_1(t)$ is shown which was measured at a scattering wave vector, q , so that $qR_{gz} < 1$, where R_{gz} is the z -average radius of gyration. The solid line is a non-linear least squares fit to equation (1) and $A(\tau)$ given by equation (2). The resulting values of p and s are $p = 4.1$ and $s = 2.1$, which means that λ and μ are close to 1. The corresponding relaxation time distribution is shown in Figure 6b.

2.2. DYNAMIC LIGHT SCATTERING FROM SOLUTIONS OF STRONGLY INTERPENETRATING BRANCHED POLYMERS. — The application of DLS to solutions of strongly overlapping polymers has been developed by Martin *et al.* [17] for the special case of percolating clusters. Here we will generalize this approach and demonstrate that the GEX function is very useful for the analysis of DLS experiments done on such systems.

If the concentration of the polymers is high enough, small polymers will interpenetrate larger polymers. Due to the branching, polymers of similar size will interpenetrate only weakly, contrary to the case of linear chains. The monomer-monomer correlation length (ξ_s) will be reduced from the overall polymer size to a value which decreases with increasing polymer

Fig. 5. — a) Normalized autocorrelation functions of aggregates formed by a percolation, RLCA and DLCA process; b) Relaxation time distributions corresponding to the autocorrelation functions shown in Figure 5a.

Fig. 6. — a) Normalized electric field autocorrelation function of a dilute solution of β -lactoglobuline aggregates. The solid line represents a non-linear fit to equations (1) and (2). The insert shows the residuals of the fit; b) Relaxation time distribution corresponding to the fit shown in Figure 6a.

concentration. As a consequence the intensity of the light scattered at $q \rightarrow 0$ by a single polymer with $R_g > \xi_s$ will be proportional to m instead of m^2 . In addition, the concentration fluctuations will relax mainly by cooperative diffusion which can be written as

$$D_c = \frac{k_B T}{6\pi\eta \xi_d} \quad (39)$$

Here ξ_d is the dynamic correlation length. ξ_d is determined by the screening of hydrodynamic interaction while ξ_s is determined by the screening of excluded volume interactions [18,19]. If the volume fraction of the strongly interpenetrating polymers is small, ξ_d is expected to be proportional to ξ_s and to have the same order of magnitude. However, not all concentration fluctuations can relax by cooperative diffusion due to the connectivity. One might expect that close to the branching points, the local density of monomers is higher. Concentration fluctuations due to connected monomers can only relax by self diffusion of the polymer or, if $R_g > q^{-1}$, by internal modes. The contribution of internal modes will, of course, only be present in the case of flexible polymers. We can treat the relaxation due to self diffusion in a way analogous to the case of very dilute solutions. For particles with $R_g > \xi_s$, $I(m) \propto mN(m)$ which implies that the part of the normalized auto correlation function due to the self diffusion becomes:

$$g_1(t)_{\text{self}} \propto \int_a^\infty mN(m) \exp(-t/\tau_m) dm \quad (40)$$

Here the lower bound of the integral is not the monomer but the polymer with size ξ_s and we neglect the contribution from smaller polymers. For strongly interpenetrated polymers the friction felt by the individual polymers is not simply determined by the solvent viscosity. However, for self similar systems it is still reasonable to assume that the friction coefficient scales with the size of the particles so that $\tau_m = \tau_a (m/a)^\nu$ with τ_a the relaxation time associated with particles of size ξ_s for which the self diffusion coefficient is close to the cooperative diffusion coefficient. Using the same reasoning as in the previous section, we find that equation (40) corresponds to a GEX function with $p = (2 - \lambda)/\nu$, $s = \mu/\nu$ and $\tau_g = \tau_m^*$ where τ_m^* is given by the self diffusion of the largest polymers. Interestingly, for λ larger than 2, as is the case for percolating clusters, p is negative and $\log(g_1(t)_{\text{self}})$ vs. $\log(t)$ is a straight line with slope $(2 - \lambda)/\mu$ for $\tau_a \ll t \ll \tau_m^*$. Martin derived the asymptotic behaviour of $g_1(t)_{\text{self}}$ at large and small values of t , see also Section 1, for the case of percolating clusters where $p = -0.2$. It is important to realize, however, that the asymptotic regime is not easily obtained when p is close to zero. Analysing $g_1(t)_{\text{self}}$ in terms of the GEX function will give better estimates of λ and μ . Here it is assumed that the elastic modulus is much smaller than the osmotic modulus which is a reasonable assumption in the case of good solvent systems. If the elastic modulus is not negligible which one might expect the relaxation of the elastic modulus to be reflected in the auto correlation function [20,21].

The measured autocorrelation function of solutions of strongly interpenetrated polymers will thus consist of two modes: a narrow relatively fast mode due to cooperative diffusion and a broader and slower mode due to the self diffusion. The relative amplitudes of the slower mode depends on the importance of the inhomogeneities in the solution. In the past the experimental correlograms obtained on percolating systems have been analysed by fitting $g_1(t)$ directly to a single exponential plus a power law decay for $t > \tau_a$ cut-off by a stretched exponential function for $t > \tau_{\text{max}}$ [17,22]. Instead one can analyse the data in terms of a narrow relaxation time distribution to represent the cooperative diffusion and a broad distribution described by the GEX function to represent the self diffusion of the polymers. The second method can be used independently of the value of λ and the fit parameters can easily be interpreted in terms of the theoretical model. Generally, the results of these two analysis methods are not the same. If

one wants to confront the data with the theory proposed by Martin *et al.* [17] one should use the GEX distribution.

2.3. APPLICATION TO THE α -RELAXATION. — The α -relaxation is characterized by a broad distribution of relaxation times [23, 24]. If the density fluctuations are measured in the frequency domain the relaxation function is often analysed in terms of the HN function. If they are measured in the time domain often the KWW function is used. We have seen above that if the relaxation function is well described by the KWW function it is also well described by the GEX function. The HN function, however, can only be well described by the GEX function if we don't consider frequencies much smaller than $\omega_{\max}$, but at any rate the HN function is not expected to describe the data at such frequencies. For a number of techniques like dielectric measurements the relaxation function can only be determined accurately around $\omega_{\max}$. In such a case using the GEX function in both the time and frequency domain is equivalent to using the KWW and the HN functions, respectively. The advantage of using the GEX function is that measurements in the time and frequency domain can be compared directly and that a simple analytical expression of the relaxation time distribution is obtained.

A number of techniques give accurate values of the relaxation function over a very large range so that they can meaningfully be represented on a double logarithmic scale, e.g. mechanical measurements of the shear modulus. In such measurements one is sensitive to long range relaxational processes such as normal modes or disentanglement due to reptation [25]. In this case it is not useful to analyse the data in terms of one single peaked relaxation time distribution.

An example of this approach is given in reference [7], where results of measurements of the α -relaxation of a polyurethane gel are reported. DLS measurements in the time domain are compared to mechanical measurements in the frequency domain. Both data sets were analyzed using the GEX distribution. A comparison is made with an analysis using the HN function for the mechanical measurements and the KWW function for the DLS measurements.

Conclusion

The GEX function provides a flexible and uniform way to analyse relaxation functions both in the time and frequency domain. The corresponding relaxation time distribution is expressed in a tractable way and we have given analytical expressions of the various moments of the distribution.

The relaxation of concentration fluctuations in dilute solutions of self similar particles is well described by a GEX function with parameters p and s directly related to the fractal dimension and the size distribution of the particles.

The relaxation of concentration fluctuations in solutions of highly interpenetrated self similar particles is also well described by a GEX function. In this case the parameters p and s are not only determined by the fractal dimension and size distribution of the particles, but also by the relation between the friction coefficient and the size of the particles.

Experimental relaxation functions that can be described by the KWW function or the HN function are equally well described by the GEX function except at $\omega \ll \omega_{\max}$ in the latter case.

Appendix

Moments and prefactor have been calculated using two well known definite integrals:

$$\Gamma(x) = \int_0^{\infty} t^{x-1} \exp(-t) dt \quad x > 0$$

$$\kappa = - \int_0^{\infty} \ln(t) \exp(-t) dt$$

where $\Gamma(x)$ is the gamma function and $\kappa = 0.5772$, the Euler constant. If the condition $x > 0$ is not satisfied, one integrates by part until x becomes positive.

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