Dynamics in Disordered Systems

H. Schiessel, P. Alemany*), and A. Blumen

Theoretical Polymer Physics, University of Freiburg, Germany
*) Instituto Balseiro, 8400 - Bariloche, Argentina

Abstract: In this work we focus on hierarchical relaxation in complex systems. Two means of describing relaxation are considered in detail: first we use a microscopic model based on continuous-time random walk (CTRW) ideas; this procedure is efficient in describing photoconductive behaviour and is used here also in the framework of polymer chain dynamics, by letting each bead move according to its own waiting-time distribution. Second, a more qualitative picture for relaxation emerges from constitutive expressions with fractional derivatives: we present two mechanical realisations for a basic fractional differential equation.

Introduction

The dynamics of disordered systems is often slowed down in a characteristic manner. In many cases experimental data show algebraic decay forms

$$\Phi(t) \propto \left(t/\tau\right)^{-\gamma} \tag{1}$$

with $0 < \gamma < 1$ over many decades in time. This behaviour is observed for example for the charge carrier transport in amorphous photoconductors [1] and for the dynamics of polymeric systems [2]. In photoconductive materials the motion of charge carriers through a sample becomes slower and slower with the passage of time, so that no diffusion constant in the usual sense exists. In fact, the diffusion coefficient often displays an algebraic dependence on time

$$D(t) \propto t^{\gamma-1} \quad (\gamma < 1, t \text{ large}) \tag{2}$$

which excludes the possibility of having a simple underlying process; Eq. (2) is a sign of a non-Markovian situation. Non-Markovian concepts have turned out to be very fruitful in the study of polymeric systems, as exemplified by DNA-diffusion through gels. Here the chains distort during the motion: typical are the formation of temporary entanglements with the matrix, which lead, say, to the appearance of U-shaped configurations [3, 4, 5]. As a result, the motion of the center-of-mass (CM) of the chain is not Markovian on the time-scales needed to leave such configurations, so that the configuration of the whole chain (and not only the CM-position) matters.

The theoretical understanding of the internal mechanisms leading to such characteristic behaviour is in many respects an outstanding problem. Here we focus on two theoretical approaches: continuous-time random walks (CTRW) and fractional calculus. In the first one, the disorder of the system is incorporated in the temporal behaviour of a waiting-time distribution $\psi(t)$, whereas the physical interpretation of the second one is not straightforward.

Recently, we have presented a model obeying generalised, fractional differential equations, which describe algebraic decay forms like Eq. (1) [6]. The characteristic feature of this model is a hierarchically constrained dynamics. Here we give another model, where the same relaxation behaviour results from parallel mechanisms.

Continuous-time random walks

Returning to Eq. (2), we note that it can be viewed as arising from a broad distribution of waiting times. Then the basic modelling problem is to account for such broad distributions. Technically, one introduces waiting-time distributions (WTD):

$$\psi(t) \propto 1/t^{1+\gamma} \quad . \tag{3}$$

For $0 < \gamma < 1$ the zeroth, but not the first moment $\langle t \rangle$ of the distribution $\psi(t)$ exists. In a simplified way one assumes the motion [1, 7] to take place on a regular lattice, say simple cubic. This leads to random walks in continuous time (CTRW). The major breakthrough here occurred with the realisation [1] that the basic CTRW framework (as formulated by Montroll and Weiss [7]), could readily incorporate complex $\psi(t)$-forms, such as the one given in Eq. (3).

On a technical note, we remark that the distribution given by Eq. (3) is not well-behaved at the origin. One may circumvent this problem by either adding a constant to the denumerator, see the form put forward by Schieber, Biller and Petruccione (SBP) [8]

$$\psi(t) = \frac{\gamma/\tau}{\left(1 + t/\tau\right)^{\gamma+1}} \quad , \tag{4}$$

or by using an analytical expression, such as the so-called Weierstrass function [9]

$$\psi(t) = \frac{1-a}{a} \sum_{n=1}^{\infty} a^n b^n \exp\left(-b^n t\right) . \tag{5}$$

In Eq. (5) and for longer times $\psi(t) \propto t^{-1-\gamma}$, with γ being given by $\gamma = \ln a / \ln b$.

The CTRW-model with a broad WTD offers an explanation for the appearance of anomalous diffusion, Eq. (2), and permits to compute the form of the photoconductive currents, such as measured through the time-of-flight (TOF) technique. In TOF-measurements charge carriers, generated by a short light pulse near the top surface of a thin film made of photoconductive material, drift through the sample under the influence of electric fields and give rise to transient photocurrents $I(t)$ in the external circuit. These photocurrents often show dispersive behaviour; $I(t)$ decreases monotonically, and one can in general distinguish two regimes: In the time regime before the so-called transit-time t_τ (the time which it takes the fastest carriers to pass through the sample) one has:

$$I(t) \propto t^{-1+\gamma} \tag{6a}$$

whereas for $t > t_\tau$ one observes:

$$I(t) \propto t^{-1-\gamma} . \tag{6b}$$

From Eqs. (6a) and (6b) one usually infers that the temporal aspect dominates the dynamics. Following Ref. [1] we have analysed in Ref. [9] the transient photocurrent in polysiloxane with pendant carbazole groups. There we found that the experimental and the theoretical curves, calculated with $\gamma \cong 0.58$, coincided over a range stretching over four decades in time.

The derivation of the results presented so far depends on the fact that a CTRW is linked to a renewal process in time and to a renewal process in space: after each step the motion of the particle starts anew under the same WTD and with

the same step-size probability distribution. What happens, however, when a whole polymer chain of N monomers moves, so that each monomer (viewed as a bead) follows its own dynamics under the WTD? Two difficulties emerge: first, due to the geometrical constraints, the beads, considered as random-walkers, are not free to move independently and thus the position of the CM is not given by a simple renewal process in space. Second, the fact that the CM moves according to the superposition ("pooling") of N renewal processes in time, does not necessarily lead to a renewal process for the stepping times of the CM: one remarkable exception are exponential WTDs corresponding to Poisson processes (and which in the CTRW-framework lead to simple diffusion) [10]. These two aspects of the problem are not independent and lead to a new situation in the theory of CTRW.

The problem is in fact of great interest: SBP have advanced a model for the motion of polymer chains in concentrated solutions, which they have analysed numerically [8]: In the SBP model the chain is frozen in space until a free volume (gap), which moves in the medium surrounding the polymer, reaches a bead of the chain. Such encounters are modelled at a mesoscopic level by assuming that the time between successive flips of the i-th bead ($i = 1,\ldots,N$) of the polymer chain follows WTDs of the form $\psi^{(i)}(t)$. For concentrated solutions or melts, the non-Poissonian occurrence of gaps next to the chain may be described using WTDs with long-time-tails, such as given by Eq. (3).

The motion of the chain involves thus a whole series of WTDs and is, from the point of view of stochastics, a "pooling" process. Now, as stressed above, the problem which arises in pooling arbitrary WTDs is that this "pooling" process is not necessarily a renewal process, i.e. it does *not* necessarily leads to a WTD, $\psi^{(\mathrm{CM})}(t)$, for the motion of the CM of the chain [10].

To proceed we use an approximate way to describe the mobility of the CM, and focus on the probability $\chi_n^{(\mathrm{CM})}(t)$ that the CM has performed n steps up to time t. In the SBP model each bead flips independently of the others, and thus $\chi_n^{(\mathrm{CM})}(t)$

can be written in terms of the individual $\chi_m^{(i)}(t)$, which give the probability that bead *i* has carried out exactly *m* flips up to time *t*.

One can now, using generating-functions techniques, find that:

$$\chi^{(\mathrm{CM})}(z,t) = \sum_{n=0}^{\infty} z^n \chi_n^{(\mathrm{CM})}(t) = \left[\quad {}^{-1}\left\{ \frac{1}{u} \frac{1-\bar{\psi}(u)}{1-z\bar{\psi}(u)} \right\} \right]^N . \tag{7}$$

Here we have, for simplicity, assumed that all $\psi^{(i)}(t)$ are the same, $\psi^{(i)}(t) = \psi(t)$. Furthermore $^{-1}$ is the inverse Laplace transform and the Laplace transform is defined by

$$\{f\} = \bar{f}(u) = \int_0^{\infty} e^{-ut} f(t)\, dt \ . \tag{8}$$

Decoupling the spatial and the temporal aspect, i.e. assuming that the mean squared displacement $\langle \boldsymbol{r}^2 \rangle$ of the CM obeys [11]

$$\langle \boldsymbol{r}^2(t) \rangle = \sum_{n=0}^{\infty} \langle \boldsymbol{r}_n^2 \rangle \chi_n^{(\mathrm{CM})}(t) \tag{9}$$

one finds, using the fact that $\langle \boldsymbol{r}_n^2 \rangle$ is proportional to *n* for large *n*, i.e. $\langle \boldsymbol{r}_n^2 \rangle \cong n S^2$ [12]

$$\langle \mathbf{r}^2(t) \rangle \cong NS^2 \ {}^{-1}\left\{ \frac{1}{u} \frac{\bar{\psi}(u)}{1-\bar{\psi}(u)} \right\} . \tag{10}$$

The decoupling approximation used in Eq. (9) is, however, very rough. Moreover, it is based on the assumption that the first step (starting at zero) can be treated on the same footing as the other steps (unrelaxed situation). For Poissonian $\psi(t)$ with $\gamma > 2$ Eq. (10) allows to obtain diffusive transport quickly. On the other hand, for long time-tailed $\psi(t)$ one finds at long times (unrelaxed condition)

$$\langle \boldsymbol{r}^2(t) \rangle \propto t^{\gamma} \ . \tag{11}$$

In the intermediate domain, for $1 < \gamma < 2$, one also obtains under the same assumptions at long times

$$\left\langle \mathbf{r}^2(t) \right\rangle \propto t/\bar{t} - O\left(t^{2-\gamma}\right) . \tag{12}$$

Although also in this case the final regime is diffusive, at intermediate times correction terms emerge. A more careful analysis of the situation (without the decoupling approximation and also including the relaxation) leads to a quite complex situation, which will be discussed elsewhere.

Fractional calculus

Fractional calculus is an extension of classical calculus. It evolves from the so-called Riemann-Liouville integral [13]

$$\frac{d^{\alpha} f(t)}{dt^{\alpha}} = \frac{1}{\Gamma(-\alpha)} \int_0^t \frac{f(\tau)}{(t-\tau)^{\alpha+1}} d\tau \tag{13}$$

with $\alpha < 0$, a convolution integral, which for $\alpha = -1, -2, -3, \ldots$ reproduces Cauchy's formula for repeated integration. To extend the domain of validity to positive α, one sets

$$\frac{d^{\alpha} f(t)}{dt^{\alpha}} = \frac{d^{n}}{dt^{n}} \left[\frac{d^{\alpha-n} f(t)}{dt^{\alpha-n}} \right] \tag{14}$$

where this definition is independent of the choice of the integer $n > \alpha$ (see Ref. [13] for details). For $\alpha = 1, 2, 3, \ldots$ d^{α}/dt^{α} represents the ordinary differential operator. Thus, Eqs. (13) and (14) allow to define the so-called *differintegration* of arbitrary order α.

A convenient means to express fractional calculus is provided by its behaviour under Laplace transformation; one has

$$\left\{ \frac{d^{\alpha} f(t)}{dt^{\alpha}} \right\} = u^{\alpha} \bar{f}(u) - \sum_{k=0}^{n-1} u^{k} \frac{d^{\alpha-1-k} f(0)}{dt^{\alpha-1-k}} \ , \tag{15}$$

where the integer n fulfils $n - 1 < \alpha \leq n$ [13]. For integer α one obtains the well-known transforms of integer-order derivatives and multiple integrals.

How can fractional calculus be applied to slow relaxation phenomena in disordered systems? Whereas no simple differential equations for the description of slow relaxation processes like Eq. (1) or (6) exist, fractional calculus provides a useful mathematical tool for their description. Two important so-called *extraordinary differential equations* [13] are

$$g(t) = \frac{d^{\alpha} f(t)}{dt^{\alpha}} \tag{16}$$

with $0 < \alpha < 1$ and

$$g(t) + \frac{d^{\gamma} g(t)}{dt^{\gamma}} = \frac{d f(t)}{dt} \tag{17}$$

with $0 < \gamma < 1$. For a Heaviside-type input $f(t) = f_0 \Theta(t)$ the solution of Eq. (16) is algebraic

$$g(t) = f_0 \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \Theta(t) \quad , \tag{18}$$

whereas Eq. (17) possesses a solution with the asymptotic behaviour

$$g(t) \propto \begin{cases} t^{-1+\gamma} & \text{for } t \to 0 \\ t^{-1-\gamma} & \text{for } t \to \infty \end{cases} \quad . \tag{19}$$

Now, we can apply these fractional expressions to anomalous diffusion of photoconductive currents. Denoting by $Q(t)$ the charge carriers generated in the system, a short light pulse at time $t = 0$ causes a Heaviside-type form of $Q(t)$, i.e.

$$Q(t) = Q_0 \Theta(t) \quad . \tag{20}$$

Using Eq. (18), it follows that the differential equation

$$I(t) = \tau_0^{\alpha} \kappa \frac{d^{\alpha} Q(t)}{dt^{\alpha}} \, , \tag{21}$$

where τ_0 and κ denote material dependent parameters, describes an algebraic relaxation of the photocurrent:

$$I(t) = Q_0 \kappa \frac{(t/\tau_0)^{-\alpha}}{\Gamma(1-\alpha)} \Theta(t) \quad . \tag{22}$$

The observed crossover behaviour (cf. Eqs. (6a) and (6b)), which is a consequence of the finite extension of the sample, can be described by the differential equation

$$I(t) + \tau_0^{\gamma} \frac{d^{\gamma} I(t)}{dt^{\gamma}} = \kappa \tau_0 \frac{dQ(t)}{dt} \tag{23}$$

with the transit-time $t_\tau \approx \tau_0$ (cf. Eqs. (17) and (19)).

A wide-spread application of fractional calculus is the formulation of rheological constitutive equations in polymeric materials [2, 6, 14, 15]. The extension consists in the replacement in the stress-strain-relationships of the first-order time derivatives (d/dt) by fractional derivatives (d^{γ}/dt^{γ}) of noninteger orders γ with $0 < \gamma < 1$. Thereby [16], it is possible to interpolate between simple rheological models such as a spring, for which Hooke's law holds

$$\sigma(t) = E\,\varepsilon(t) \tag{24}$$

(typical for solid-like behaviour), and a dashpot, whose stress and strain are related by Newton's law

$$\sigma(t) = \eta \frac{d\varepsilon(t)}{dt} \tag{25}$$

(typical for fluid-like behaviour). The extraordinary differential equation

$$\sigma(t) = \eta^{\gamma} E^{1-\gamma} \frac{d^{\gamma} \varepsilon(t)}{dt^{\gamma}} \tag{26}$$

with $0 < \gamma < 1$ interpolates between Eq. (24) ($\gamma = 0$) and Eq. (25) ($\gamma = 1$). After a strain jump $\varepsilon(t) = \varepsilon_0 \Theta(t)$, we recover an algebraic relaxation of the stress (cf. Eq. (18)):

$$\sigma(t) = \varepsilon_0 \eta^{\gamma} E^{1-\gamma} \frac{t^{-\gamma}}{\Gamma(1-\gamma)} \Theta(t) \ . \tag{27}$$

- Fig. 1 -

Fractional equations such as Eqs. (21), (23) and (26) seem to be rather formal because their physical realisation is not immediately obvious. To give a pictorial view of the situation we have developed in Ref. [6] a mechanical model which obeys the stress-strain-relationship of Eq. (26). In our model, shown in Fig. 1, we have a ladder-like arrangement of springs and dashpots. The analysis of Ref. [6] shows that $\bar{\varepsilon}(u)$ and $\bar{\sigma}(u)$ are related through

$$E_0 \frac{\bar{\varepsilon}(u)}{\bar{\sigma}(u)} = 1 + \frac{u^{-1}\frac{E_0}{\eta_0}}{1+} \frac{u^{-1}\frac{E_1}{\eta_0}}{1+} \frac{u^{-1}\frac{E_1}{\eta_1}}{1+} \frac{u^{-1}\frac{E_2}{\eta_1}}{1+} \cdots \frac{u^{-1}\frac{E_{n-1}}{\eta_{n-1}}}{1+} \frac{u^{-1}\frac{E_n}{\eta_{n-1}}}{1} \; . \tag{28}$$

Choosing the spring constants E_k and viscosities η_k in such a way that both $E_k \propto k^{1-2\gamma}$ and $\eta_k \propto k^{1-2\gamma}$ hold, it can be shown [6] that Eq. (28) obeys the simple form

$$E_0 \frac{\bar{\varepsilon}(u)}{\bar{\sigma}(u)} = \left(E_0/\eta_0\right)^{\gamma} u^{-\gamma} \; . \tag{29}$$

Using the boundary condition $\varepsilon(t \le 0) = \sigma(t \le 0) = 0$ one obtains directly from Eq. (15) that $\sigma(t)$ and $\varepsilon(t)$ fulfill the fractional differential equation (26).

A characteristic feature of the model presented in Ref. [6] is its hierarchically constrained dynamics in the sense of Palmer et al [17]. A strain jump causes a deformation of the first spring E_0. Then the deformation moves along the ladder overcoming the resistance of the dashpots.

- Fig. 2 -

Fig. 2 displays a possible technical realisation of the ladder model. It consists of concentric cylinders fixed on a bottom plate. Other cylinders, which are connected by springs, are placed in the spaces between them, which are filled with a damping fluid.

Our model may give the impression that Eq. (26) necessarily implies that the relaxation occurs in sequential fashion. This is not so, as we repeatly pointed out [11]; both parallel and sequential models lead to similar decay forms. In our

case it is also possible to construct mechanical models which relax via parallel mechanisms in such a manner, that their stress-strain relationship obeys Eq. (26). As an example, we consider a continuous model which was proposed by Wang [18] to describe the behaviour of rough electrode-electrolyte interfaces. Translating this discretized electrical model into its mechanical analogue we obtain the arrangement shown in Fig. 3. Its basic units are Maxwell elements consisting of a spring and a dashpot in series; these units are arranged in parallel. After a given strain jump each unit relaxes independently of the others in exponential fashion.

- Fig. 3 -

The model extends along the x-axis ($0 \le x < \infty$) and its viscosities and spring constants are $\eta(x)$ and $E(x)$ (in a continous formulation). One can verify readily, using Eqs. (24) and (25) in Laplace transformed form, that for an infinitesimal element $(x, x+dx)$ the relationship between stress and strain fulfils

$$\bar{\sigma}(u; x)\,dx = \bar{\varepsilon}(u)\frac{dx}{\dfrac{1}{E(x)} + \dfrac{1}{u\eta(x)}} \quad . \tag{30}$$

Therefore, we obtain for the whole arrangement

$$\bar{\sigma}(u) = \int_0^\infty \bar{\sigma}(u;x)\,dx = \bar{\varepsilon}(u)\int_0^\infty \frac{\eta(x)\,u}{1+\frac{\eta(x)}{E(x)}u}\,dx \quad . \tag{31}$$

By taking the distributions

$$E(x) = E_0\, x^{-\alpha},\ \eta(x) = \eta_0\, x^{\beta} \tag{32}$$

the integral in Eq. (31) can be solved exactly (see Ref. [18] for details) and one obtains

$$\bar{\sigma}(u) = \frac{\pi\eta_0\left(E_0^{-1}\eta_0\right)^{\gamma-1}}{(\alpha+\beta)\sin\left(\frac{\beta+1}{\alpha+\beta}\pi\right)}\, u^{\gamma}\,\bar{\varepsilon}(u)\ , \tag{33}$$

as long as $0 < \gamma = \frac{\alpha-1}{\alpha+\beta} < 1$. Therefore, we have another model obeying Eq. (26).

- Fig. 4 -

A technical realisation of this continuous model is shown in Fig. 4. The whole arrangement extends from $x = 0$ to infinity. The elongation ε is given by the height of the rigid plate above the ground. The elastic part of this model is represented by the grey layer below this plate. It consists of a homogeneous material with constant modulus of elasticity E, height l_0 in the relaxed state and a width $b(x)$ varying along x. Therefore, the distribution of $E(x)$ is given by

$$E(x)dx = E\frac{b(x)}{l}dx\ . \tag{34}$$

The elastic layer rests on a structure which is T-shaped perpendicular to the x-axis ; the T-shaped structure extends into a rigid block filled with a viscous liquid. A down- or upwards movement of the beam is accompanied by friction between its vertical part and the two immobile plates with constant distance a from the beam. Therefore, one obtains the following distribution of the shear viscosity:

$$\eta(x)dx = \eta\frac{d(x)}{a}dx\ , \tag{35}$$

where $d(x)$ denotes the varying width of the plates (see Fig. 4).

The independence of the Maxwell units (as can be seen in Fig. 3) is reflected in the request that the T-shaped structure has a vanishing shear modulus for shearings in the plane perpendicular to the x-axis. We have therefore drawn the T-shaped structure as a parallel arrangement of layers. Choosing the widths $b(x)$ and $d(x)$ as given in Eq. (32), the stress-strain-relationship of this arrangement obeys the fractional expression Eq. (26) with $\gamma = \frac{\alpha-1}{\alpha+\beta}$.

Conclusion

In this work we have concentrated on two means to mimic relaxation in disordered systems. A rich microscopic picture emerges when using the continuous-time random walk formalism. As a more qualitative picture we have discussed constitutive equations with fractional derivatives and have displayed mechanical models which obey them.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 60), by the Fonds der Chemischen Industrie and by a DAAD-grant to P.A. Extensive discussions with G. Huber, Dr. I. Sokolov and Dr. U. Zürcher are gratefully acknowledged.

(Figure legends)

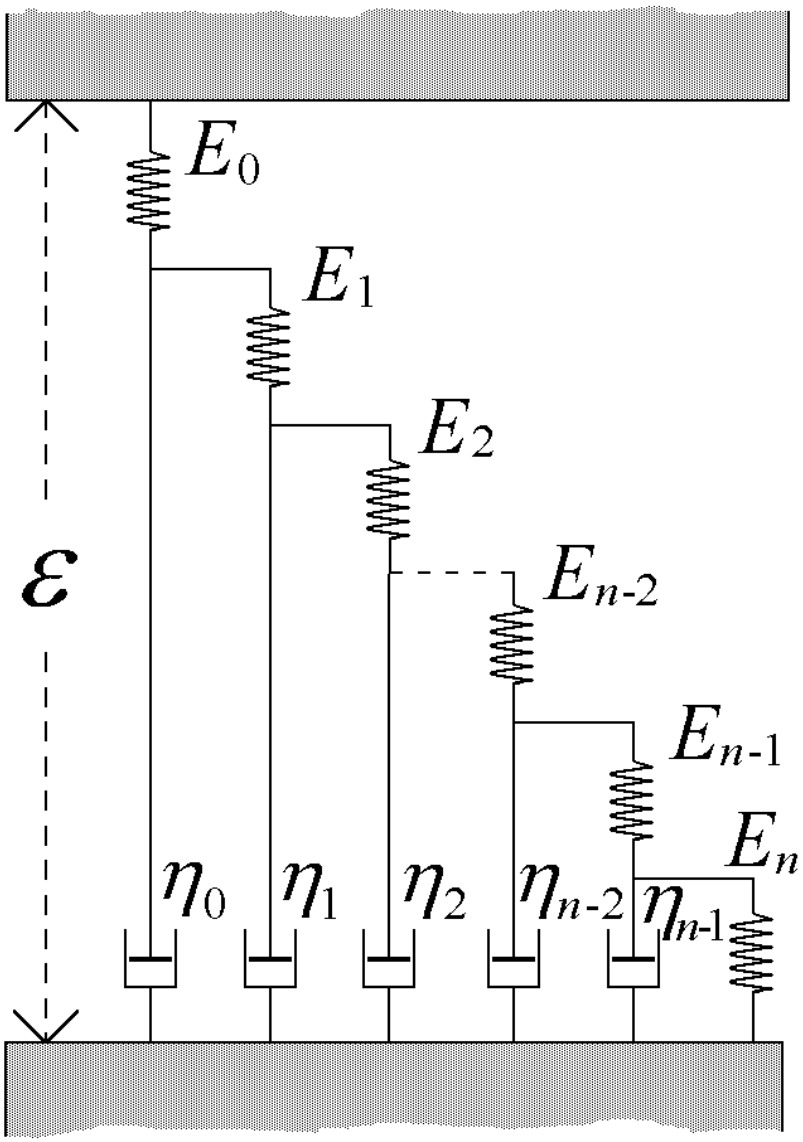

Fig. 1. Diagram of the finite mechanical arrangement used to model Eq. (26) (see text)

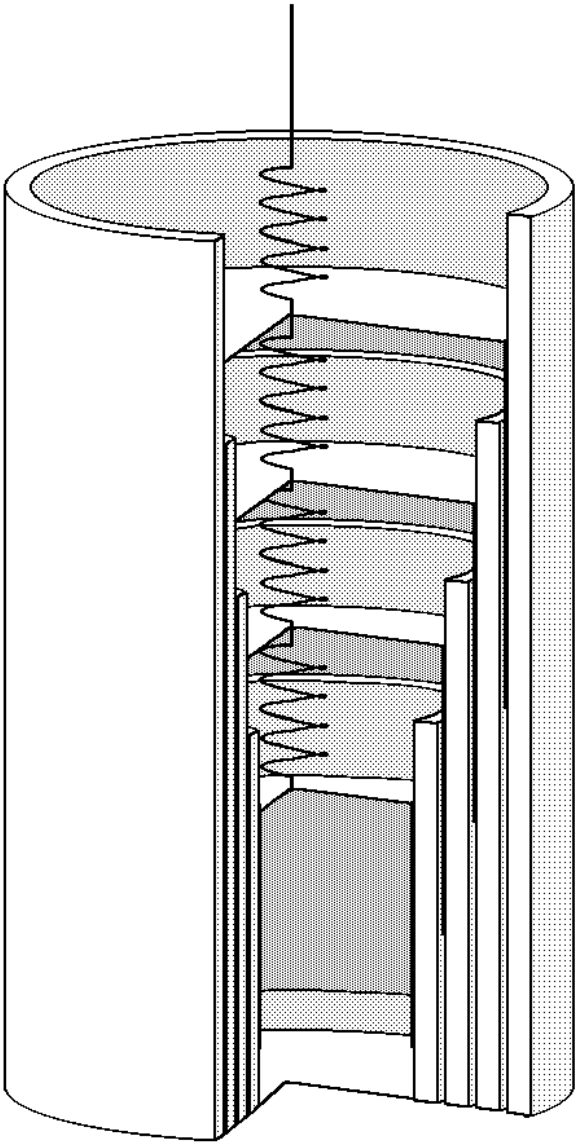

Fig. 2. Technical realisation of the hierarchy of Fig. 1 with $n = 3$

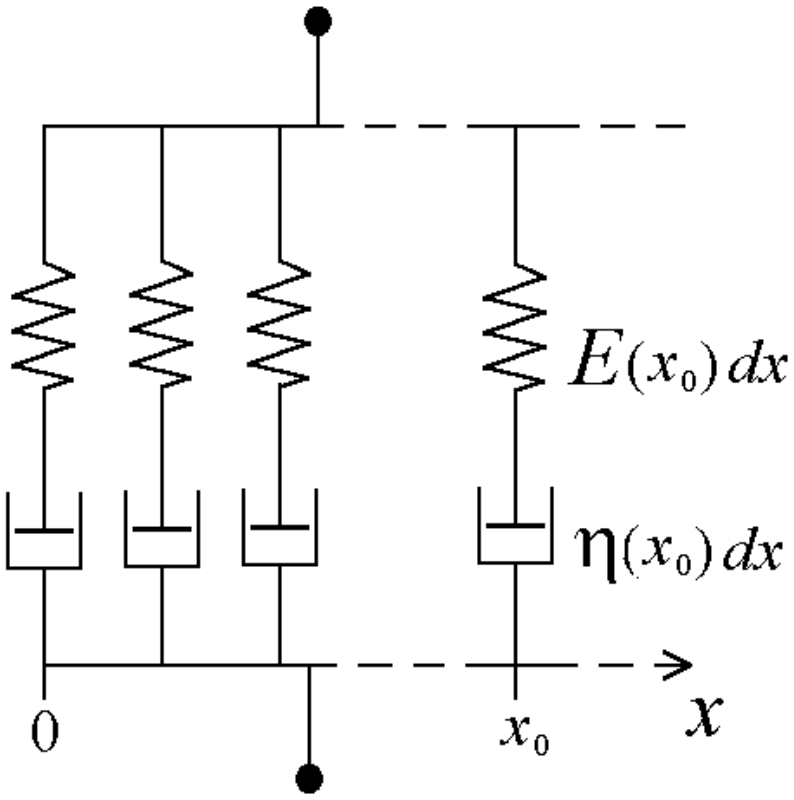

Fig. 3. Discretized version of the continuous mechanical model (see text)

Fig. 4. Technical realisation of the continuous model shown in Fig. 3

References

1. Scher H, Montroll EW (1975), Phys Rev B 12:2455
2. Friedrich C, Braun H (1992) Rheol Acta 31:309
3. Zimm BH (1988), Phys Rev Lett 61:2965
4. Zimm BH (1991), J Chem Phys 94:2187
5. Noolandi J, Slater GW, Lim HA, Viovy JL (1989), Science 243:1456
6. Schiessel H, Blumen A (1993) J Phys A 26:5057
7. Montroll EW, Weiss GH (1965) J Math Phys 6:167
8. Schieber JD, Biller P, Petruccione F (1991) J Chem Phys 94:1592
9. Blumen A, Schnörer H (1990) Angew Chem Intern Ed 29:113
10. Cox DR (1967) Renewal Theory, Methuen, London
11. Blumen A, Klafter J, Zumofen G (1988) In: Zschokke I (ed) Optical Spectroscopy of Glasses. Reidel, Dordrecht, pp 199-265
12. Verdier PH (1970) J Chem Phys 52:5512
13. Oldham KB, Spanier J (1974) The Fractional Calculus, Academic Press, New York London
14. Friedrich C (1991) Rheol Acta 30:151
15. Glöckle WG, Nonnenmacher TF (1991) Macromolecules 24:6426
16. Nonnenmacher TF (1991) In: Casas-Vázquez J, Jou D (eds) Lecture Notes in Physics No. 381. Springer, Berlin Heidelberg New York, pp.309-320
17. Palmer RG, Stein DL, Abrahams E, Anderson PW (1984) Phys Rev Lett 53:958
18. Wang JC, Solid State Ionics (1990) 39:277