

# Time scales in the reinforcement of elastomers

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## Abstract

Reinforcement of nano composite materials requires the consideration of various length and time scales. In this paper it is shown, how dynamical properties of the rubber phase localized on the filler particles will contribute in a special way to the reinforcement and the viscoelastic properties of the elastomers. The contribution from the disorder surface determines mainly the viscoelastic behavior in some of the frequency regimes.

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## 1. Introduction

Most of the chemical aspects of the reinforcement of composite materials are far from being simple [1]. A typical and well known example is reinforced elastomers, which find their application in the car tire industry. These materials allow indeed a physical formulation of most of the problems and offer at least for some questions suggestions for solutions. The main reason for the complication is the relevance of many length and time scales, which is one of the issue which will be developed during this paper.

The basic achievement of filling relatively soft networks, i.e. cross-linked polymer chains, is to reach a significant reinforcement of the mechanical properties. For that purpose, active fillers like carbon black (cb) or silica are of special practical interest as they lead to a strong modification of the elastic properties of the rubber than a mere addition of hard randomly dispersed particles. The additional reinforcement essentially is caused by the complex structure of the active fillers (see e.g. [2] and references therein).

The main intention of the present work is to gain further insight into this relationship between disordered filler surface and the reinforcement of elastomers. Most fillers show universal structural features on different length scales,

see Fig. 1: carbon black consists of spherical particles with a rough and energetically disordered surface [3,4], forming rigid aggregates in the 100 nm range with a fractal structure. Agglomeration of the aggregates on a larger scale leads to the formation of filler clusters and even a filler network at high enough cb concentrations.

These universal features are reflected in the corresponding universal properties of filled systems. It has been shown for example, that the geometry and activity of the filler surface plays a major role for the polymer–filler interaction: the physical and chemical binding of polymers to the filler surfaces depends on the amount of surface disorder. On intermediate and large length scales the contribution of aggregate and agglomerate structure is expected to be dominant, respectively. Interesting phenomena like the enhanced hydrodynamic reinforcement and the Payne effect can be attributed to the fractal nature of the filler and cluster structure. From these considerations it is clear that the classical approaches to rubber elasticity are not sufficient to describe the physics of such systems. Instead, different theoretical methods have to be employed to deal with the various interactions and, consequently, reinforcing mechanisms on different length scales. Within this respect, we have to indicate physically relevant length scales as well. Considerable reinforcement can only be achieved if the relevant scales which concern the filler particles coincide with those of the polymer matrix, see Fig. 2.

Fig. 2 visualizes the interplay between the length scales by comparison of the relevant sizes. The scales of interactions coincide on the relevant length scales between the monomer size, important for adsorption and chemical

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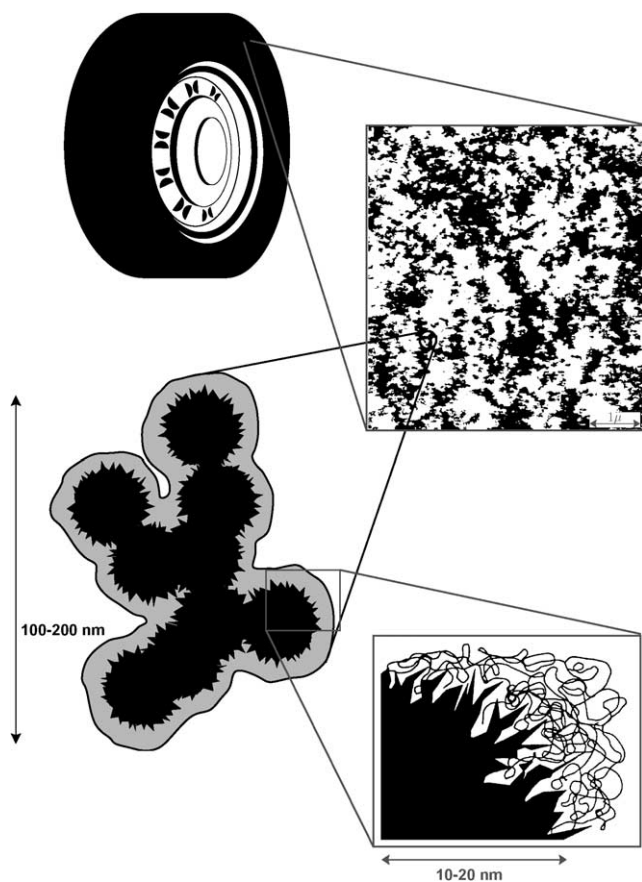


Fig. 1. Structural disorder in carbon black filled elastomers on different length scales.

sticking. The structures on larger scales, such as agglomerates and aggregates do have similar scales with typical polymer radii. Thus we may expect scale dependent contributions to the modulus based on the interactions between rubber matrix chains and filler particles.

Earlier studies indicate that the enhancement of the elastic modulus cannot be understood by one simple theory, since several types of interactions and many different length scales are involved [2,5]. In carbon black and silica filled elastomers, the contribution to reinforcement on small scales can be attributed to the complex structure of the branched filler aggregates as well as to a strong surface polymer interaction, leading to the bound rubber. The filler particles are 'coated' with polymer chains [2]. On larger scales the hydrodynamic aspect of the reinforcement dominates. Hydrodynamic reinforcement plays a major role not only in carbon black filled elastomers, but also in composite systems with soft inclusions. At macroscopic length scales the filler networking at large filler volume fractions plays the dominant role. The simplest approach was presented by Smallwood [6], where it was shown that filler particles in a rubber matrix yield  $G = G_0(1 + 2.5\phi)$ , where  $\phi$  is the volume fraction of the filler components and the elastic modulus of the rubber matrix [7].

However, these classical theories and most of their

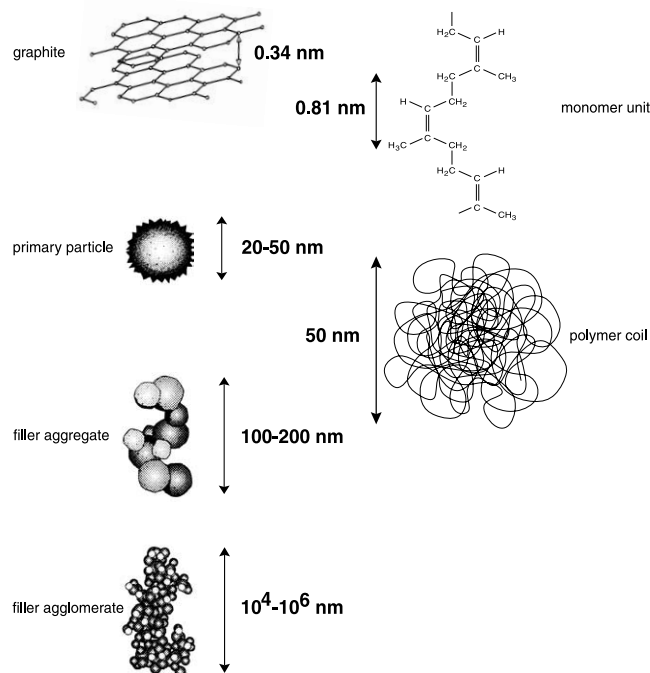


Fig. 2. Comparison of the length scales for the different structural elements. The filler particles, here carbon black have basically carbon surfaces. These interact directly with the monomers on their length scales. However, the aggregates and agglomerates have similar dimensions as the polymer coils, i.e. they can directly interact with each other.

extensions ignore the important role of the filler polymer interactions. Its strong appearance and important contribution can be viewed from the aggregation of the filler particles to large clusters and their associated huge surfaces. The heterogeneities of these surfaces yield a peculiar dynamic behavior of the polymer chains close to them. Often the literatures classify the dynamic phase as bound rubber. In the present paper, we will emphasize the local polymer–filler interaction and discuss their consequences in more detail. In the present paper, we concentrate, therefore, on the contribution to reinforcement from the filler polymer interactions. It turns out, that the heterogeneous surface provides a basis for strong correlations on dynamic scales, which are relevant for the viscoelastic properties of the macroscopic systems in specific frequency regimes.

## 2. Polymer localization on heterogeneous surfaces

To begin with we start from some naive scaling considerations concerning the statistics of chains close to heterogeneous surfaces. Although the behavior of polymers on heterogeneous surfaces is a general problem in theoretical physics it provides deep insight in the problem of reinforcement and contributions. It is well accepted that the filler particles form large clusters which may percolate at large filler concentration the ideal case to provide a most

significant reinforcement effect on large macroscopic scales [5,8–10]. In consequence these clusters form large surfaces inside the elastomer and allows for a significant polymer–filler contacts as in Fig. 3.

However, the filler particles do not have homogeneous surfaces, but they are strongly disordered. Their disorder can basically distinguished by two extreme cases. The first is that they are spatially disordered, i.e. rough in a classical sense. Indeed several studies [11–13] suggest a strongly heterogeneous surface. Gerspacher provided several data which suggest even fractal surface properties for several carbon blacks [11,12].

Secondly, the surfaces may be characterized by a strong energetic disorder. That means that the surface is strongly heterogeneous with respect to their interaction with the environment (Fig. 4). In an earlier paper, we have already investigated the static matters from a general point of view [14], and we refer the reader to this reference.

The main idea is to model the polymer–filler–surface interaction in a sufficiently simple but still appropriate way. It turns out that it is most useful to model the filler surface by a random potential, which covers to some extent the two aspects already mentioned, i.e. spatially rough surfaces and energetically heterogeneous surface. Therefore, we use as a random potential  $V(\mathbf{R}(n))$  whose properties must be specified.

The theoretical description of a chain in a random potential starts with a Hamiltonian for the polymer which interacts with the random surface as

$$\beta\mathcal{H} = \frac{3}{2b^2} \int_0^N dn \left( \frac{\partial \mathbf{R}(n)}{\partial n} \right)^2 + \int_0^N dn V(\mathbf{R}(n)). \quad (1)$$

Here, the first term is nothing but the Gaussian connectivity of the chain, which leads to the Gaussian distribution if the potential is set to be zero. The parameter  $n$  counts the monomers along the contour and  $N$  is the chain length. For simplicity we assume that the potential has a completely random structure, i.e.

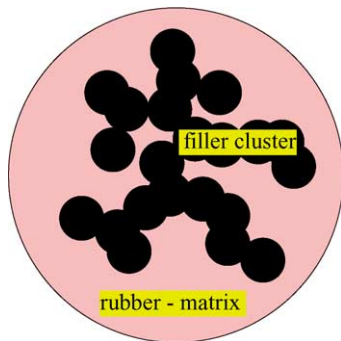


Fig. 3. A cluster of filler particles embedded in the rubber matrix. The cluster itself contributes to the so-called hydrodynamic reinforcement, which is mainly given by the volume effects and the cluster structure.

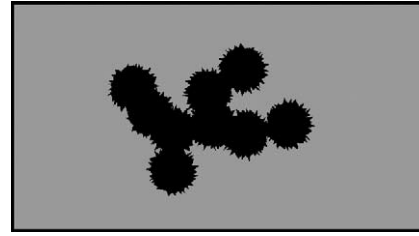


Fig. 4. Aggregate with spatially or energetically rough surface. The irregularities at the boundaries visualize both types of disorder.

$$\langle V(\mathbf{R}(n)) \rangle = 0 \quad (2)$$

$$\langle V(\mathbf{R}(n))V(\mathbf{R}(n')) \rangle = \Delta \delta(\mathbf{R}(n) - \mathbf{R}(n'))$$

En plus, this simplification makes calculations feasible from a technical point of view. An illustration of the surface is depicted in Fig. 5.

At first sight the use of such an uncorrelated random potentials might appear not appropriate to model the surface of filler particles, but it turn out that it satisfies already many conditions which yield the main physical properties in statics and as well in dynamics. Most of the surface properties are described in the parameter  $\Delta$ , which defines typical volume (of ‘hole’ in surface).

However, it is not a major problem to generalize all what follows to potentials with different (fractal properties) as it is shown in Fig. 6.

Then the additional fractal correlations show up in a surface fractal dimension  $d_s$  and the correlation of the potential is changed to be

$$\langle V(\mathbf{R}(n))V(\mathbf{R}(n')) \rangle = \frac{\Delta b^{-d_s}}{|\mathbf{R}(n) - \mathbf{R}(n')|^{3-d_s}} \quad (3)$$

with its well known limits:  $d_s \rightarrow 0$  for the totally random case as discussed above,  $d_s = 2$  for completely flat surface, and finally the most interesting case  $2 < d_s < 3$  for Brownian surfaces. For the present discussion we will stay, however, with the simplest case, i.e. uncorrelated surfaces.

The main theoretical results after tedious calculations can be summarized in terms of the free energy

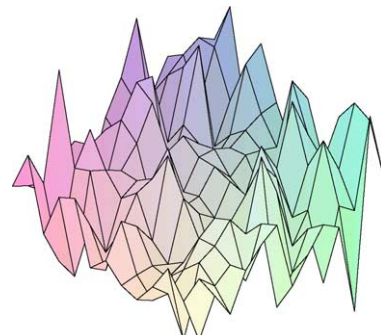


Fig. 5. Theoretical model for the filler surface.

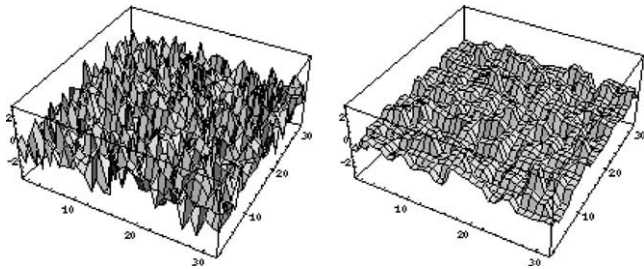


Fig. 6. Brownian surfaces with different surface fractal properties. The fractal dimension on the left picture is close to  $d_s = 2$ .

$$\frac{\mathcal{F}}{k_B T} \simeq \frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} - \Delta^{1/2} \frac{N}{R^{3/2}} \quad (4)$$

The first two terms represent the nature of the Gaussian chain in extension and confinement. The negative sign of the effective disorder potential has its origin by the effective attraction from the disorder. In earlier publications we have already shown that any disorder induces an effective attraction [5,14]. The special form of the potential corresponds to a typical energy barrier produced by the disorder. This attractive nature is of special significance, since it conforms earlier statements and confines the chain. In order to find a significant chain confinement the disorder  $\Delta$  must become larger than the entropy term. This yields the condition that the critical surface roughness is  $\Delta_c \simeq b^3 N^{-1/4}$ . Only for values for  $\Delta$  larger than this critical value the filler particle is substantially active to attract the chains. If this is the case the chains become ‘localized’. Indeed upon minimization of the free energy we find for the chain size

$$R \simeq b \left( \frac{b^3}{\Delta} \right) \quad (5)$$

which means that the size of the Gaussian chain is entirely determined by the disorder. Physically this shows that the chain becomes attracted by the surface and localized in an appropriate hole of the typical size as cartooned in Fig. 7.

It is important to realize that the chain conformations are totally determined by the disorder, thus that upon the localization process the chain adopts the disorder size. So far the argument applies for single chains. In filled rubbers the chains are not free but bound into a network. However, it can be shown that similar arguments apply. The only

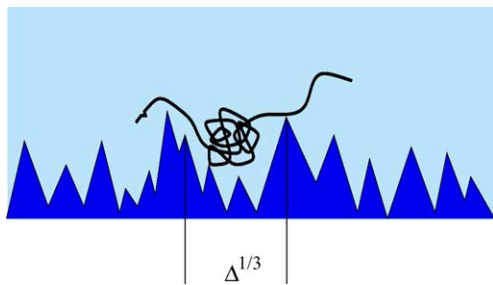


Fig. 7. Localization of a chain in a typical spatial or energetic hole of size  $\Delta$ . The Gaussian chain adopts the size specified by the disordered structure.

change, which has to be made, concerns the disorder strength. It can be shown by a simple calculation that the localization criterion modifies in the case of networks to

$$\frac{\Delta}{b^3} > N_{\text{mesh}} \quad \Rightarrow \quad \Delta > \xi^3 \quad (6)$$

dense networks

where  $N_{\text{mesh}}$  is the meshsize of the network and  $\xi$  the corresponding correlation length, i.e. the mean distance between to crosslinks (see Fig. 8).

More detailed calculations show that for a given (sufficiently large) filler activity  $\Delta$  parts of the network localize in a similar way compared to the free chain. The localization expressed by the strong conformational chain may let us conclude that the strongly bound chains close to the surface form the occluded rubber in certain particle reinforced elastomers.

### 3. Dynamics of localizing chains

So far we have discussed static picture only. It is most challenging to study the dynamics of such localized chains and discuss their contribution to the viscoelastic properties of the reinforced elastomers. These considerations are of special importance since it will state nature of polymer dynamics in the localized phase. Moreover, it will describe the dynamic behavior of occluded ‘rubber phase’ and the chain change in the local dynamics of the chains, which will contribute to the shear modulus  $G(\omega)$  in a natural way.

We have studied the dynamics of polymers confined in a random potential by the use of Langevin dynamics. This is the natural way to find modifications of the motion of the center of mass and the change of the Rouse modes. In the following we will only summarize the results and refer the reader for the details of the extended mathematical paper [15].

The first observation is that the center of mass (CM) diffusion ‘freezes’, and we observe a behavior for the diffusion constant of the chain

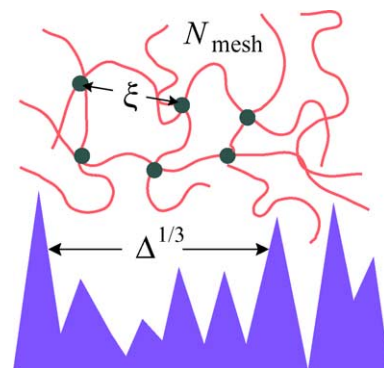


Fig. 8. Localization of network chains in a typical spatial or energetic hole of size  $\Delta$ . The localization takes place on scales larger than the meshsize  $\xi$ , if the they are able to fit in, i.e. for large enough disorder.



$$D_{CM} = D_0(1 - \Delta/\Delta_c) \quad (7)$$

where  $D_0$  denotes the bare diffusion constant without disorder. Therefore, we may conclude that the chains are dynamically localized as well. Once the filler activity exceeds a certain value  $\Delta_c$  the chains become frozen in the disorder, i.e. they do not diffuse anymore and are bound by the surface. This result suggests already a naive estimate of the shift of the glass transition temperature of the chains localized at the active surface to  $\Delta T_g \propto (\Delta/b^3)^2$ . Although this appears, speculative several experiments suggests measurable shift of the glass transition temperature, which is at least in accord with the model presented here.

The more important problem is related with the internal modes of the chain. If the chains freeze in the disordered surfaces, some of the internal modes have to freeze also. It is not sufficient that the CM motion ceases, also several Rouse modes must freeze out such that the chain can localize. To do so we use the simplest approximation and study Rouse chains in the random potential. Usually the chain dynamics is described by Rouse modes, which decompose the chain motion into different modes, which are characterized by a typical relaxation time

$$\tau_q \propto \frac{\zeta N^2 b^2}{k_B T} \frac{1}{q^2} \quad (8)$$

Here  $\zeta$  is the friction coefficient and  $q$  are the Rouse modes. Large values of  $q$  correspond to small distances in the chain, i.e. local motions inside the chain. Small numbers of  $q$  describe large scale motions. The center of mass motion can be viewed as the limit  $q \rightarrow 0$ . Usually in free polymer chains all motions relax to zero, i.e. their correlation function can be described as

$$\text{correlations} \propto \exp(-t/\tau_q)$$

In localized Rouse chains these statements no longer hold. To begin with we may try the most naive scaling, by introducing the equation of motion for the Rouse modes in terms of a Langevin equation. The most simple estimates ignore the coupling between different modes which is naturally introduced by the disorder or the random potential. Although we neglect an essential part of the physics, the following scaling argument is useful, because it introduces some limits, which are relevant for applications.

The Hamiltonian Eq. (1) can be represented in terms of classical Rouse modes [16]. The first term, i.e. the gaussian connectivity is diagonal in the modes. The disorder term cannot be represented simply in modes, therefore, it is left here as a mean field like acting term. The Hamiltonian reads then simply

$$\beta H = \frac{d}{2b^2} \sum_q q^2 |\mathbf{R}_q|^2 - \sqrt{\Delta} \frac{N}{R^{d/2}}, \quad (9)$$

and the corresponding Rouse equation is then given by [16]

$$\zeta_0 \frac{\partial \mathbf{R}_q}{\partial t} = - \frac{\delta H}{\delta \mathbf{R}_q} + \mathbf{f}_q(t). \quad (10)$$

Here  $\zeta_0$  is the monomer friction coefficient and  $\mathbf{f}_q(t)$  a random force with white noise character. In general these types of stochastic differential equations are hard to solve, especially for problems involving disorder. The simplest approximation is then to try a mode decoupling and making use of an appropriate approximation for the disorder term. To see some of the important issues we may use the Hamiltonian directly and estimate the last term by its mean value, as it has been done already earlier in a similar Ginzburg argument, i.e.  $\sqrt{\Delta \frac{N}{R^{d/2}}} \sim \sqrt{\Delta} N^{(1-nd/2)}$ . Then, when we ask for localized chains, there should be according to the static considerations above no chain length dependence involved, i.e. the radius of gyration scales as  $R \sim N^0$ . In terms of the mode dependence this can be expressed by.

$$\langle |\mathbf{R}_q|^2 \rangle \sim \frac{1}{q}. \quad (11)$$

Then we may distinguish between the large and small scale modes via

$$q_c^2 < \left( \frac{\Delta}{b^d} \right) N^{(2-nd)} \quad (12)$$

which suggests that large scale motions frozen for a certain disorder strength and a certain chain length. For three dimensional gaussian chains the mode separation comes at  $q_c^2 \simeq (\Delta/b^3)N^{1/2}$ . This result suggests that, all modes which satisfy the inequality are frozen. Especially this means that large-scale motions freeze out at a certain disorder. The criterion for the freezing is also determined by the radius of gyration  $R_g = bN^{1/2}$  and chain density  $\rho = N/R^3$ . This means, that only the appropriate chain density with its  $N$  Rouse modes fit into the hole of volume  $\Delta$  the chain localizes its modes which satisfy the inequality (12). Then modes  $q < q_c$  localized modes are fitted inside, and only local motion possible.

These considerations are naturally too simple. However, more sophisticated theories show, that the disorder induced freezing of the chains implies a non-exponential decay [15]. Moreover certain correlations do no longer relax to zero and follow a non-exponential decay law and relax only to a finite value larger than zero, i.e.

$$\text{correlations} \propto \exp(-(t/\tau_q)^\beta) + f(q) \quad (13)$$

The appearance of the non-ergodicity parameter  $f(q)$ , which is mode dependent, monitors then the localization process. If the solution of the Langevin equation shows  $f(q) = 0$ , no localization and mode freezing takes place. Only for finite values for  $f(q)$  we can expect freezing effects. Indeed detailed calculations show that whenever the non-ergodicity parameter is zero, all relaxations should be exponential, i.e.  $\beta = 1$ . We expect, therefore, a non-zero value for  $f(q)$  from a certain value of the filler activity or disorder parameter  $\Delta$ .

To be more precise, the mathematical (and numerical) analysis requires the solution of the Langevin equation directly. The dynamics of the chain and all the relevant correlation functions is determined by the following Langevin equation

$$\zeta_0 \frac{\partial}{\partial t} R_j(s, t) - \frac{3k_B T}{b^2} \frac{\partial^2 R_j(s, t)}{\partial s^2} + \frac{\delta}{\delta R_j(s, t)} H_{\text{int}}\{\mathbf{R}(s, t)\} + \frac{\delta}{\delta R_j(s, t)} V\{\mathbf{R}(s, t)\} = f_j(s, t) \quad (14)$$

where  $j$  labels Cartesian components and  $\zeta_0$  is a bare friction. Due to the non-linearity of the problem the solution cannot be carried out analytically but only numerically. It can be shown in detail, that the problem can be mapped on a mode–mode coupling equation, which shows that upon increasing disorder strength  $\Delta$  relaxations are no longer exponentially, but decay much slower.

Omitting all details (see [15]) we just provide the essential results, which are important for the conclusions on the elastic contribution on the modulus. The general numerical analysis of the (non-linear) equations yield the result in Fig. 9.

The figure shows more or less what has been described so far. For small disorder parameter  $\Delta < \Delta_c$  nothing interesting happens. The non-ergodicity parameter  $f(q)$  is zero for all modes. Therefore, small disorder does not affect the chain dynamics dramatically. For larger disorder strength the modes become frozen, monitored by a finite value of  $f(q)$ . The way the modes are affected depends on the mode number itself. The figure suggests that the local motions (large mode number) are less influenced by disorder as large scale motions. The thick line in the  $(\Delta, q)$ -plane corresponds to the inequality (12) for three dimension. However, a more detailed look on the mode coupling, i.e. the behavior beyond the condition Eq. (12) shows that all modes freeze at the

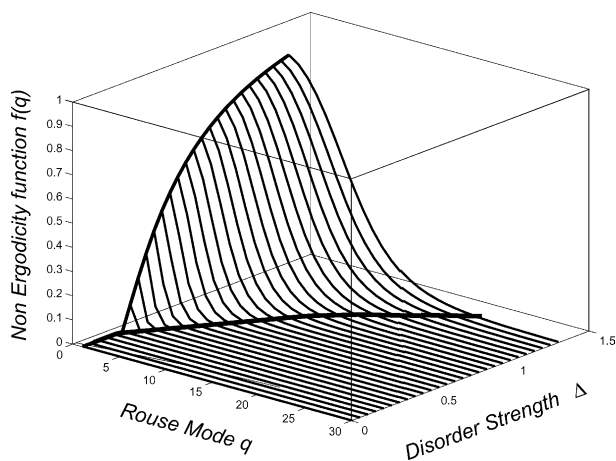


Fig. 9. The localization of the modes for varying disorder. The non-ergodicity parameter  $f(q)$  is calculated it shows the selective freezing of the Rouse modes numbered by  $q$ .

same disorder parameter, but the slope of their freezing depends on the mode number.

Therefore, the results shown in Fig. 9 corresponds to a finite resolution of the time scale in real experiments. The use of the mode coupling, however, shows that the modes indeed freeze at the same disorder  $\Delta_c$ , but the slope how they freeze depends strongly on the mode index, see Fig. 10. Thus the modes will be selected according to their slope, which is proportional to the mode index itself.

The slow dynamics is responsible for an unusual decay of correlations in the mode relaxation of the chain. Therefore, it is tempting to consider their non-exponential relaxation and their contribution to the shear modulus.

#### 4. Viscoelastic contributions to the modulus

Obviously the dynamics of the localized chains contribute to the elastic and viscoelastic properties of the elastomer. The present theory allows scaling predictions of the frequency and time dependence on the modulus.

We calculate, therefore, the contribution of the localized chains to the modulus in the limiting time scales  $\tau_1 < t < \tau_1 N^2$ . As stated above the theory suggests non-trivial stretched exponential in the form

$$G(t) \propto \sum_q \exp\left\{-\left(\frac{b^3}{\Delta}\right) \Omega(q) \left(\frac{t}{\tau_1}\right)^\beta\right\} \quad (15)$$

where the value of  $\beta = 3/4$  is independent of the disorder. The quantity  $\Omega$  is by

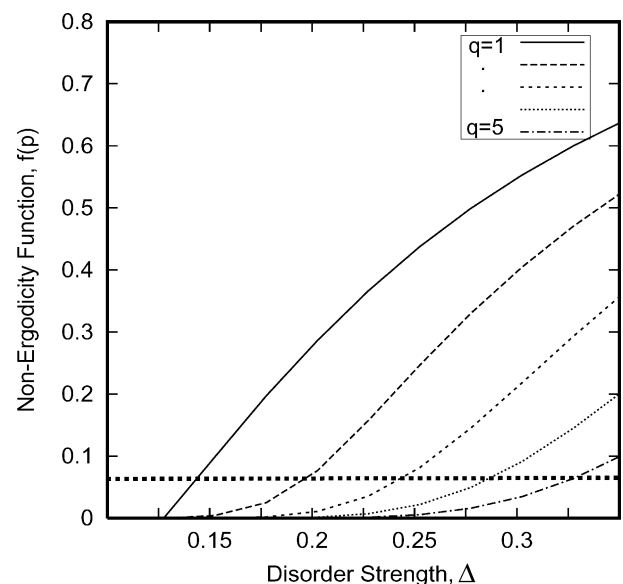


Fig. 10. Freezing of modes according the mode coupling model. The non-ergodicity parameter  $f(q)$  is zero at the same disorder, but their slope close to  $\Delta_c$  is proportional to  $q$ . Thus large modes, i.e. local motion still appears mobile for a finite resolution, shown by the horizontal line, which separates from the non-coupled (above) from the mode coupled regime.

$$Q \propto \tau_1 q^2 \quad (16)$$

In the following, we present a scaling estimate of the modulus. The results for the storage modulus can be summarized as follows

$$G'(t) \propto \left(\frac{\Delta}{b^3}\right)^{1/2} \left(\frac{t}{\tau_1}\right)^{-3/8} \quad (17)$$

which transforms into the frequency dependence:

$$G'(\omega) \propto \tau_1 \left(\frac{\Delta}{b^3}\right)^{1/2} (\omega\tau_1)^{3/8} \quad (18)$$

Therefore, the time or frequency dependence of the modulus becomes strongly influenced by the disordered surface. The scaling exponent, however, does (in this model) not depend explicitly on the disorder parameter itself, but is merely defined by the general scaling well known from disordered systems.

## 5. Concluding remarks

We studied in the strong localization regime (very high filler activity), the dynamics of the localized (occluded rubber) phase is changed completely. For a certain strength of the filler activity the chain dynamics appears glassy. Only local motions are possible. We discussed several consequences of this model with respect to the glass transition properties and the viscoelastic behavior. We expect, however, further detailed predictions under the incorporation of more detailed surface models. Nevertheless the

main features are already set up by the simple surface model proposed in this research. In the near future we plan to apply these predictions to experimental data in more detail.

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