Disorder-Induced Enhancement of Polymer Adsorption—A Model for the Rubber–Polymer Interaction in Filled Rubbers

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ABSTRACT: Various models for adsorption of polymers and disordered surfaces are presented. Such models range from certain weak random surfaces to fractal surfaces possessing self-similar properties. Common to all models is that adsorption properties are enhanced compared to the adsorption on flat surfaces. The reaction for this enhancement is that the configurational entropy in the disordered case is less restricted compared to the flat case where the chains become significantly non-Gaussian for large adsorption energies.

1. Introduction

The motivation for this study has very practical reasons. Reinforcement of rubbers by filler particles is basically not entirely understood.[1] Although there are many empirical relations which describe the interaction between the filler particles and the polymer matrix, no microscopic model has been presented for a detailed description of this phenomenon. This is a relatively complicated task, and thus simple models which are useful at the present stage to model the principal problems can be given.[2–4]

The filler particles moulded in the rubber matrix are most commonly made from carbon black (cb) or silica fillers. The choice of these filler materials has many different reasons. Firstly they are relatively easy to produce, and secondly the mechanical reinforcement of the rubber material is significantly large. It is the reinforcement which is the basic property of the particle use of such materials that are widely used in car tire treads.

Hydrodynamic theories (see, for example, refs 5 and 6) predict reinforcement and lead to the celebrated Einstein–Smallwood–Guth–Gold formula for the static modulus of a cb-filled rubber.

$$G = G_0(1 + a\phi + b\phi^2 + ...) \qquad (1.1)$$

where G_0 is the modulus for an unfilled sample, i.e., $G_0 \sim MkT$ (M being the number of rubber–rubber cross-links), and ϕ the volume fraction of the filler particles. a and b are numbers which depend on the geometry of the filler particles, e.g., the Einstein coefficient $a = 2.5$ for spherical fillers. In rubber technology, the second-order Guth–Gold term, $b = 14.1$, is usually used, although several other computations found considerable lower values.[6] Equation 1.1 is restricted to low values for the filler volume fraction ϕ and is based on the assumption of an incompressible elastic continuum and "perfect" sticking between medium and inclusion. In practice the volume fraction of the filler particles is relatively large, i.e., so large that the filler particles themselves form a network within the rubber. Practically this mans that ϕ is of order $\phi \propto O(0.25)$. However, it is empirically known that the actual network modulus is in most cases higher than that predicted by the pure hydrodynamic interaction model.[2–4] This result is mainly attributed to additional couplings between the filler and the polymer matrix as has been investigated by the authors in ref 7. In order to achieve significant reinforcement of the material, ϕ has to be so large that the filler particles form themselves a **percolating** network leading to additional energetic contributions to the modulus. Hence the particles are not separated from each other but form a strongly temporarily interacting solid-like structure within the rubber sample. This is often called (in the case of cb) "carbon black networking".

In such phenomenological formulae for filler reinforcement as given in eq 1.1 and in their corresponding theories, all detailed interactions between the polymer matrix and the filler particles are not taken into account. Recently an equation of the form of eq 1.1 has been derived on a molecular statistical model.[7] In this model, it was assumed that the filler particles with a finite diameter act as extended multifunctional cross-links in addition to the rubber–rubber pointlike cross-links. This model has several drawbacks, however. The first one is the assumption that the filler particles are regular spherical particles with a certain fluctuation in diameter. The second weak point is the assumption that the polymer chain sticks with infinite strong interaction as the particles. From various measurements and practical experience, it is often shown that the pure hydrodynamic reinforcement is not enough to explain the strong binding of the polymer to the surface of the filler particles. Indeed the technical term "bound rubber" has been introduced to visualize the strong binding of the polymer on the surface. The explanation of this strong binding is an outstanding problem. This technological important problem is examined from a different view point in the present paper where the physical consequences of the irregularity of the suspended particles is emphasized.

The technical use of rubbers as highly elastic but significantly strong material in many applications, e.g., car tires, relies strongly on the presence of very strong polymer–filler particle interaction. It is indeed the aim

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to produce rubbers with a certain amount of bound rubber in the material. It is essential for high-frequency damping and frictional properties such as wet skid behavior and rolling resistance.

The models described in the paper suggest a new possibility to this practical problem. In this paper we do not aim at the solution of detailed practical and industrial questions but introduce a new physical view on such material used in practice. In theoretical physics, the problem of polymers in the presence of (quenched) disorder has been discussed recently.[8] This is a tempting problem on its own, and a detailed solution has not been given yet. Nevertheless one common result seems to establish itself, i.e., the polymer under certain circumstances is able to take unusual configurations, which deviate strongly from their shape in good or bad solvent or in melts. Such configurations are called localized configurations, and in many cases it has been shown that the size of the polymer is independent of its molecular weight, i.e., $R \propto$ constant.[9-12] The constant depends on the nature of the disorder and is not universal in many cases. In most publications quoted above, the disorder is treated as quenched *per sé*. Several authors suggest that this is not necessary,[10,13] since in the thermodynamic limit the polymer can sample the entire disorder; hence the partition function is self-averaging, and the annealed and quenched disorders lead to identical results. This statement seems to be true as long the polymer is not kept fixed in a certain environment. If it is fixed at some point, the quenched disorder formalism has to be employed, which uses in most cases "replicas". If the polymer is not bound at an arbitrary point, i.e., can move freely through the disordered environment, it is enough to use the annealed average to find the configurational properties of the polymer.

We use similar ideas in this paper. In fact the surface of the filler particles is very rough and disordered over the large length scales. X-ray scattering measurements by Gerspacher et al.[14] have shown that the surface of cb particles is fractal with a surface fractal exponent of $D_s = 2.4$. This means that the surface of the particles is not smooth at all but shows many irregularities. The carbon black particles themselves are able to stick together and form themselves clusters of significant size and roughly a fractal dimension of $d_f = 2.5$, corresponding roughly to (diffusion-limited) aggregates. Therefore the filler clusters form together with the fractalitiy of the primary particle a huge internal surface in the material. This surface interacts strongly with the polymers around. These heterogeneous surfaces of the filler particles together with the fact that the volume fraction is very large and forms the filler network give rise to a very strong reinforcement. The basic result of this paper is that several mechanisms are proposed which lead to a significant binding of the polymer molecule to such heterogeneous surfaces. That means in practice that not only is the reinforcement a result of the presence of the filler particles, i.e., the hydrodynamic reinforcement, but a significant part of the bound rubber is a consequence of the additional localization of the polymers at the percolating filler clusters.

The main goal of this paper is to investigate a variety of examples for the localization of free and bound polymers near heterogeneous surfaces that will lead naturally to the phenomena of "bound rubber". It is shown that disordered surfaces enlarge the probability of adsorption. The models in this paper are simple but will lead to this effect. Often the annealed cases will be studied in this paper. For such cases the polymer is assumed not to be bound from the beginning to the surface, but a disorder-induced bound potential will be the result.

The paper will be organized as follows. In the second paragraph a short reminder of the adsorption potential for polymers on flat surfaces will be given. The third paragraph discusses the case of weak disorder. Although this is a very simple and almost unphysical case, it will result in a long range enhancement of the adsorption potential. In the following paragraph, more relevant cases will be discussed. The final section is a pure localization model in which it is assumed that the polymer is bound with one arbitrary point at the surface. A quenched disorder calculation is presented which enables the quantification of the localization effect in terms of relevant length scales.

2. Polymers on Flat Surfaces—A Reminder

First we review the case of polymers at flat surfaces. In this brief section, well-known results will be recovered, but it is useful for extensions of the model. It is shown below how the common surface Hamiltonian for polymers can be calculated. We present these results to extend them to rough surfaces. In the following, the Edwards–Wiener model for flexible Gaussian polymers is used. The Edwards–Hamiltonian for an excluded volume polymer is given by[15]

$$\beta H(\{\mathbf{R}(s)\}) = \frac{3}{2\ell^2}\int_0^{\mathrm{N}}\left(\frac{\partial\mathbf{R}}{\partial s}\right)^2 \mathrm{d}s + v\int_0^{\mathrm{N}}\mathrm{d}s\int_0^{\mathrm{N}}\mathrm{d}s'\delta(\mathbf{R}(s) - \mathbf{R}(s')) \quad (2.1)$$

where $\mathbf{R}(s)$ is the chain vector at contour length $(s\ell)$, N the chain length, ℓ the Kuhn length, and $v \propto \mathrm{O}(\ell^3)$ the excluded volume parameter. The description of the surface interactions can be given in the following naive way. The flat surface can be defined by two (unit) vectors, $\hat{\mathbf{n}}_x$ and $\hat{\mathbf{n}}_y$, and $\hat{\mathbf{n}}_z$ is perpendicular to the flat surface. The surface itself is then given by the set

$$S(x) = \{x | x = \hat{\mathbf{n}}_x x + \hat{\mathbf{n}}_y y, x, y \in \mathcal{R}\} \quad (2.2)$$

where $\mathcal{R}$ is the set of real numbers. The short range interaction term for the polymer with the surface can be written as the gain of energy for the polymer when a segment is located close to the surface, i.e.,

$$W(\{\mathbf{R}(s)\}) = -w\int_0^N \mathrm{d}s\int_{-\infty}^{+\infty}\mathrm{d}x\int_{-\infty}^{+\infty}\mathrm{d}y\,\delta(\mathbf{R}(s) - \hat{\mathbf{n}}_x x - \hat{\mathbf{n}}_y y) \quad (2.3)$$

In this equation it is assumed that the polymer gains the energy $-W$ when a segment is touching the surface. The second assumption is that the surface is infinitely extended in space.

For flat surfaces, eq 2.3 can be simplified further by the usual δ-function representation by an integral over momentum space and carrying out the x- and y-integrals. This yields immediately

$$W(\{\mathbf{R}(s)\}) = -w\int_0^N \mathrm{d}s\sum_{\mathbf{k}} \mathrm{e}^{i\mathbf{k}\mathrm{R}(s)}\delta(\mathbf{k}\cdot\hat{\mathbf{n}}_x)\varrho(\mathbf{k}\cdot\hat{\mathbf{n}}_y) = w\int_0^N \mathrm{d}s\sum_{k_z}\mathrm{e}^{ik_zR_z(s)} = -w\int_0^N \mathrm{d}s\,\delta(R_z(s)) \quad (2.4)$$

This is the exactly usual surface potential utilized very often[16] for renormalization group computations for

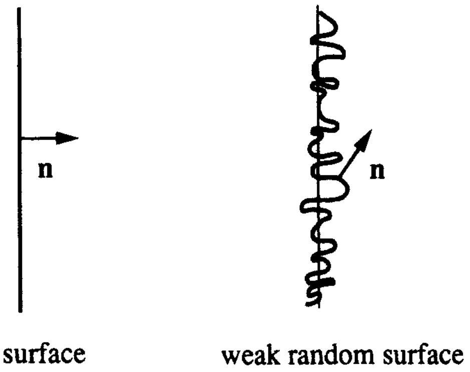

Figure 1. Weak random surface in comparison to a flat surface. Weak means that the surface is still comparably smooth and a basis line can be defined.

polymer near surfaces. The Hamiltonian for a polymer near a flat surface can therefore be written as

$$\beta H = \frac{3}{2\ell^2}\int_0^N \mathrm{d}s\left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 + v\int_0^N\int_0^N \mathrm{d}s\mathrm{d}s'\delta(\mathbf{R}(s)-\mathbf{R}(s')) - w\int_0^N \mathrm{d}s\ \delta\ (R_z(s)) \quad (2.5)$$

So far nothing new has been derived, but below it will become obvious how this calculation can be generalized to random surfaces. In the following we will distinguish between weak random surfaces and strong random surfaces. This is basically not necessary but instructive.

3. Weak Random Surfaces

In the flat surface model, it was assumed that the vectors which generate the surface are unit vectors. For random surfaces this is not the case. A simple view of this statement is given in Figure 1. A simple generalization for weak random surfaces can be introduced, when the vectors $\hat{\mathbf{n}}_x$ and $\hat{\mathbf{n}}_y$ are no longer unit vectors pointing in the same direction with the same unit length but becomes randomly distributed. A simple choice of the distribution of the vectors that generates a suitable irregular surface is a Gaussian distribution of the form

$$P(\hat{\mathbf{n}}_x,\hat{\mathbf{n}}_y) = N\exp\left\{-\frac{\hat{\mathbf{n}}_x^2+\hat{\mathbf{n}}_y^2}{2\Delta^2}\right\} \quad (3.1)$$

The surface described by

$$S = \{x|x = \hat{\mathbf{n}}_x x + \hat{\mathbf{n}}_y y\} \quad (3.2)$$

where $\hat{\mathbf{n}}_x$ and $\hat{\mathbf{n}}_y$ are random vectors, can be considered as a weakly random surface since the x- and y-variables are only running along a mean line of the surface (see Figure 1). Moreover the surface is considered to be quenched, the two-point correlation function of the polymer has to be calculated subject to such constraints, and the replica method[8] has to be employed. There are basically two important cases. The first one is to assume that the polymer is not bound at any point to the surface at the beginning. In this case the use of the replica method is irrelevant and the use of the annealed average is sufficient. This holds as long as the polymer can move along the surface and sample the entire disorder, so that the partition function is self-averaging. If the polymer is adsorbed at any point on the surface from the beginning, the annealed average is not sufficient, since the polymer does not sample the entire disorder. Here the polymer feels the local disorder at the range of its own radius of gyration. The important point to realize is that the polymer can stick at any point on the surface, so that at the end the free energy or any Green function under consideration has to be averaged. This corresponds to the case of quenched disorder. In the case of weak disorder, this distinction is irrelevent to the approximation considered in the following. Thus the Green function, $G(\mathbf{r},\mathbf{r}'\ N)$, can be written as

$$G(\mathbf{r},0,N,[\mathbf{n}_x,\mathbf{n}_y]) = \int_{0=\mathbf{R}(0)}^{\mathbf{r}=\mathbf{R}(N)} D\boldsymbol{R}(s)\exp\{-\beta H(\{\mathbf{R}(s)\})\} \quad (3.3)$$

where $\beta H(\{\mathbf{R}(s)\})$ is given by

$$\beta H(\{\mathbf{R}(s)\}) = \frac{3}{2\ell^2}\int_0^N \left(\frac{\partial\,\mathbf{R}}{\partial\, s}\right)^2 \mathrm{d}s + v\int_0^N\int_0^N \mathrm{d}s\mathrm{d}s'\delta(\mathbf{R}(s)-\mathbf{R}(s)) - w\int_0^N \mathrm{d}s\int_{-\infty}^{+\infty}\mathrm{d}x\int_{-\infty}^{+\infty}\mathrm{d}y\delta(\mathbf{R}(s)-\mathbf{n}_x x+\mathbf{n}_y y) \quad (3.4)$$

The Green function in eq 3.3 has to be averaged over the distribution function (eq 3.1). We assume for a moment that the chain is bound at an arbitrary segment on the surface. The replica method has then to be employed since the disorder disappears in the numerator and the denominator in eq 3.2. Note that

$$G(\mathbf{r},\mathbf{0},N,[\mathbf{n}_x,\mathbf{n}_y]) = \frac{\int D\mathbf{R}\ \delta\left(r-\int_0^N \frac{\partial\,\mathbf{R}}{\partial\, s}\mathrm{d}s\right)\mathrm{e}^{-\beta H}}{\int D\boldsymbol{R}\ \mathrm{e}^{-\beta H}} \quad (3.5)$$

The replicated Hamiltonian subject to eq 3.5 is then given by

$$\beta H(\{\mathbf{R}_a(s)\},[\mathbf{n}_x,\mathbf{n}_y]) = \frac{3}{2\ell^2}\sum_{a=0}^{n}\int_0^N\left(\frac{\partial\,\mathbf{R}_a(s)}{\partial\, s}\right)^2\mathrm{d}s + v\sum_{a=1}^{n}\int_0^N\int_0^N \mathrm{d}s\ \mathrm{d}s'\ \delta(\mathbf{R}_a(s)-\mathbf{R}_a(s')) - w\sum_{a=1}^{n}\int_0^N\mathrm{d}s\int_{-\infty}^{+\infty}\mathrm{d}x\int_{-\infty}^{+\infty}\mathrm{d}y\ \delta(\mathbf{R}_a(s)-\mathbf{n}_x x-\mathbf{n}_y y) \quad (3.6)$$

The averaging procedure is generally not simple here. The disorder average is taken by a second moment approximation

$$\langle \mathrm{e}^{W}\rangle = \mathrm{e}^{\langle W\rangle + {}^1\!/_2(\langle W^2\rangle - \langle W\rangle^2)+\ldots} \quad (3.7)$$

where W is the disorder term, i.e., last term in eq 3.6.

We restrict ourselves to the first terms only, which correspond to lowest order only. Indeed, we have

$$\langle W\rangle = \frac{w}{2\Delta}\sum_{a=1}^{n}\int_0^N \mathrm{d}s\sum_{\mathbf{k}}\mathrm{e}^{i\mathbf{k}\mathbf{R}(s)}\frac{1}{\mathbf{k}^2} = \frac{w}{2\Delta}\sum_{a=1}^{n}\int_0^N\frac{1}{|\mathbf{R}_a(s)|} \quad (3.8)$$

The second term which appears from the averaging procedure can be calculated analogously and is found to be

$$w^2 \sum_{a,b=1}^{n} \int_0^N \mathrm{d}s \int_0^N \mathrm{d}s' \sum_{\mathbf{q},\mathbf{k}} \mathrm{e}^{i\mathbf{k}\mathbf{R}_a(s)+i\mathbf{q}\mathbf{R}_b(s')} + \langle \mathrm{e}^{i(\mathbf{k}+\mathbf{q})(\mathbf{n}_x x+\mathbf{n}_y y)} - \langle W^2\rangle\rangle \quad (3.9)$$

Performing the average and the **k** and **q** integrals yields

$$\langle W^2\rangle - \langle W\rangle^2 = \frac{w^2}{2\Delta^2} \sum_{a,b=1}^{n} \int_0^N \mathrm{d}s \int \mathrm{d}s' \frac{1}{|\mathbf{R}_a(s)|} \left\{ \delta(\mathbf{R}_a(s) - \mathbf{R}_b(s')) - \frac{1}{2\Delta^2} \frac{1}{|\mathbf{R}_b(s')|} \right\} \quad (3.10)$$

This is an interesting result. The lowest order term provides already a long range attractive potential and no replica mixing. Higher order terms contain replica mixing **and** retain the long range character. Since the first term is the strongest, we may write for the effective Hamiltonian

$$\beta H(\{\mathbf{R}(s)\}) = \frac{3}{2\ell^2} \int_0^N \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 \mathrm{d}s + v \int_0^N \int_0^N \mathrm{d}s\, \mathrm{d}s'\, \delta(\mathbf{R}(s) - \mathbf{R}(s')) - \frac{w}{2\Delta^2} \int_0^N \mathrm{d}s \frac{1}{|\mathbf{R}(s)|} \quad (3.11)$$

The last term is an attractive disorder-induced long range potential, which can be interpreted in a such way that localizes the chain at a random surface. This is the first sign that the presence of a weak disorder already attracts the chain to the irregular surface. Indeed this can be physically understood in the following way. Assume a chain to be absorbing at a flat surface. In this case the chain gains most energy when all segments are adsorbed on the surface. On the other hand, the entropy penalty in this case is very large, and not all segments will be adsorbed. The chain will form a more or less flat layer at the surface and will form tails and trains, as is well known.[16] In the case of random surfaces, the entropy penalty is much lower although many chain segments are able to adsorb (see Figure 2). Therefore the energy gain is very large and the entropy penalty is very low, since the chain does not have to change its natural shape too much. This intuitive picture has to be investigated in more detail, as will be done in the following. To find an estimate of the chain size in the presence of this weak disorder, let us translate the effective Hamiltonian to a Flory type free energy. For convenience we use this argument for general spatial dimensions. The d-dimensional scaling free energy that corresponds to the Hamiltonian (eq 3.11) is

$$\beta F = \frac{R^2}{N} + v\frac{N^2}{R^d} - \frac{W}{\Delta^2}\frac{N}{R^{d-2}} + v^2\frac{N^3}{R^{2d}} \quad (3.12)$$

A stabilizing three-body interaction has been added. In the regime

$$vN^{2-d/2} - \frac{W}{\Delta^2} N^{1-\mathrm{d}-2/2} < o \quad (3.13)$$

the repulsive excluded volume interaction and the attractive disorder potential are balancing each other. When the effect of the attraction is larger than the excluded volume repulsion, the chain collapses or localizes. The size can be estimated by using the stabilizing three-body term. As a consequence, the polymer is localized at the surface. Its size is estimated from the Flory free energy and leads to

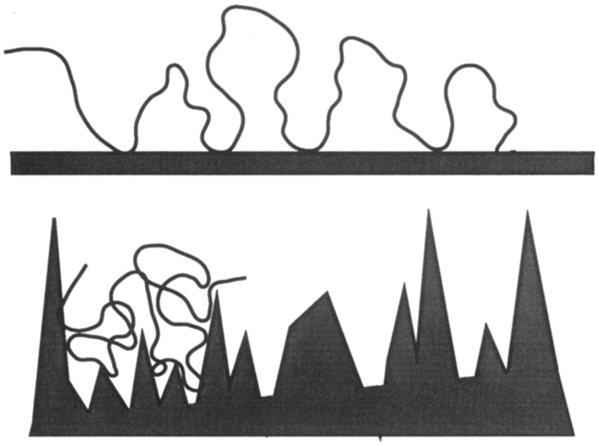

Figure 2. At a significantly random surface, the chain does not have to stretch out to gain energy in contrast to a flat surface. It gains energy by adsorption without paying entropy penalty by simultaneous stretching as in the case of flat surfaces.

$$R \sim \left(\frac{v^2\Delta^2}{W}\right)^{1/\mathrm{d}+2} N^{2/d+2} \quad (3.14)$$

by comparing all interaction terms. It is interesting to note that the coil is **not** collapsed, i.e., $R \propto N^{1/d}$, since its fractal dimension, d_f, is given by

$$d_\mathrm{f} = \frac{d+2}{2} < d \quad (3.15)$$

and is in all dimensions $d > 2$ less than the space dimension itself. Note that only $d_\mathrm{f} < d$ makes physical sense.

4. Edwards–Chen Type Models

So far, the weak disorder surface model provides a crude model that contains already the adsorption enhancement for polymers on rough surfaces. The model has of course several drawbacks. Fluctuations and higher order terms have been neglected completely. In principle, extensions of this model are possible. The weak random surface model can be extended in more ways, which we will not explore in detail. The most obvious possibility is the introduction of a "bare surface" with random and large fluctuations around it. The surface interaction term reads in this case

$$W = -w \int_0^N \mathrm{d}s \int_{-\infty}^{+\infty} \mathrm{d}x \int_{-\infty}^{+\infty} \mathrm{d}y \int_{-\infty}^{+\infty} \mathrm{d}z\, \delta(\mathbf{R}(s) - \mathbf{n}_x x - \mathbf{n}_y y - \mathbf{n}(z)) \quad (4.1)$$

where the vectors $\mathbf{n}_x$ and $\mathbf{n}_y$ span up the basic surface as before and $\mathbf{n}(z)$ is a random vector in the z-direction. Such a model corresponds to a more general class which has been investigated recently by Edwards and Chen.[17] A further generalization can be achieved by the introduction of an interaction term

$$W(\mathbf{R}(s)) = -w \int_0^N \mathrm{d}s \int \mathrm{d}^D x\, \delta\left(\mathbf{R}(s) - \mathbf{h}(\underline{x})\right) \quad (4.2)$$

where $\mathbf{h}(\underline{x})$ describes a random surface, S, with some dimension, D. Here we have introduced a special notation. Bold face characters describe vectors corresponding to the chain or other Euclidean vectors, whereas underscored symbols describe internal vectors belonging to the surface. A structureless surface with a correlation function

$$\langle \mathbf{h}(\underline{x})\, \mathbf{h}(\underline{x}')\rangle = \Delta^2 \delta(\underline{x} - \underline{x}') \tag{4.3}$$

leads immediately to a significant increase of the adsorption. The lowest order term is

$$W \cong -\frac{w}{2\Delta} \int_0^N \exp\left\{-\frac{\mathbf{R}^2(s)}{2\Delta^2}\right\} \mathrm{d}s \tag{4.4}$$

which reduces for $\Delta \to 0$ to the short range potential. The scaling results for such models have been discussed by Cates and Ball.[10] The size of the chain is independent of the chain length, i.e.,

$$R \sim \left(\frac{w}{\Delta}\right)^{\frac{2}{4-\mathrm{d}}} \tag{4.5}$$

This result has now been derived by various methods, including field theoretic calculations,[11,12] and will not be commented upon further in this paper.

5. Fractal and Self-Affine Surfaces with Arbitrary Dimension

For the problem of rubber reinforcement, other models are more significant. The surface-formed carbon black filler particles have a certain surface roughness exponent, ζ, which can be defined as

$$\langle (\mathbf{h}(\underline{x}) - \mathbf{h}(\underline{x}'))^2\rangle = |\underline{x} - \underline{x}'|^{2\zeta} \tag{5.1}$$

$\underline{x}$ is a $D(=2)$-dimensional internal vector on the surface. D describes the connectivity of the surface. The location of the surface in the embedding Euclidian space is described by a d-dimensional vector, $\mathbf{h}(\underline{x})$. The probability distribution for the function $\mathbf{h}(\underline{x})$ can be given as

$$P(\{\mathbf{h}(\underline{x})\}) = N \exp\{-\sum_{\underline{Q}} |\mathbf{h}_{\underline{Q}}|^2\, |\underline{Q}|^{2\zeta+D}\} \tag{5.2}$$

$\underline{Q}$ is a "wave vector" conjugate to the transverse coordinate $\underline{x}$.

For the purpose in this paper, it is more convenient to introduce a vector, $\mathbf{h}(\underline{x})$, in embedding space which describes the fractal nature of the surface. An equivalent distribution function to eq 5.2 is given by

$$P(\{\mathbf{h}(\underline{x})\}) = N \exp\{-\sum_{\underline{Q}} |\mathbf{h}_{\underline{Q}}|^2\, |\underline{Q}|^{\alpha}\} \tag{5.3}$$

where α is an exponent which specifies the fractal properties of the surfaces. Of course α can take the value given in eq 5.2.

The disorder average of the corresponding Hamiltonian including the surface term, i.e.,

$$\langle \exp\{-\sum_{a=0}^{n} \int_0^N \mathrm{d}s \int \mathrm{d}^D x\, \delta(\mathbf{R}_\alpha(s) - \mathbf{h}(\underline{x}))\}\rangle \tag{5.4}$$

can be done in a similar way as it was already carried out in section 2, and we can be brief here. A second moment approximation is employed as above to find the leading term which is given by

$$\exp\{-\sum_{a=1}^{n} \int_0^N \mathrm{d}s \int \mathrm{d}^D x \sum_k \mathrm{e}^{i\mathbf{k}\mathbf{R}_\alpha(s)} \mathrm{e}^{-k^2 x^{\alpha-\mathrm{D}}}\} \tag{5.5}$$

Performing the remaining x-integration yields the effective Hamiltonian

$$\beta H_{\mathrm{eff}} = \frac{3}{2\ell^2} \int_0^N \mathrm{d}s \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 + v \int_0^N \int_0^N \mathrm{d}s\, \mathrm{d}s' \delta(\mathbf{R}(s) - \mathbf{R}(s')) - w \int_0^N \mathrm{d}s \int \mathrm{d}^d k\, \mathrm{e}^{i\mathbf{k}\mathbf{R}(s)} \frac{1}{k^{\frac{2D}{\alpha-D}}} \tag{5.6}$$

In Euclidian space, the last term in eq 5.6 is equivalent to an effective disorder-induced adsorption potential,

$$W(R) \cong -w \frac{1}{R^{d-\frac{2\mathrm{D}}{\alpha-\mathrm{D}}}} \tag{5.7}$$

which has a clear dependence on the surface dimension D.

The general conclusion for all these considerations is that all models that are used lead to an effective pronunciation of the adsorption of the chain. Again, eq 5.6 can be translated to a Flory free energy from which the size of a the chain can be estimated. The localization exponent $R \sim N^\nu$ in this case is given by $\nu = 2/(d + 2D/(\alpha - D))$. The latter result is a simple generalization of what has been derived earlier.

6. Localization Models

The model described in this section leads also to an adsorption enhancement by rough surface. The main difference to the considerations above is that we now assume that the polymer is already fixed by chemosorption or other processes on the surface. Another generalization put forward in this section is that not only a single polymer is considered but a melt of polymers. The first generalization is a significant influence of the quenched disorder in contrast to the cases discussed in the previous sections of the paper. On the other hand, the melt case is simpler since excluded volume interactions are screened.[15] Therefoe we will neglect them completely. This is not necessary, but leads to simpler algebra. The methods used for this problem are in close analogy by those put forward by Edwards and Muthukumar.[9] The basic method used here is the variational principle in its simplest form. Indeed the same Hamiltonian as before is used. One possible extension of the introduction term recapitulated in eq 2.4 for surfaces with surface fractal dimensions $D_s > 2$ is

$$W(\{\mathbf{R}(s)\}) = -w \int_0^N \delta(\mathbf{R}_z(s) - h(x,y))\mathrm{d}s \tag{6.1}$$

where $h(x,y)$ is the surface height function. In contrast to the previous sections, a two-valued function $h(x,y)$ is used as a two-variable function (see Figure 3).

As a technical remark, we note that the introduction of a unit vector, $\mathbf{u}$, normal to the x–y surface enables to us represent the z-component of the chain variable $\mathbf{R}_z(s)$ as vector

$$\mathbf{R}_z(s) = (\mathbf{R}(s)\cdot\mathbf{u})\cdot\mathbf{u} \tag{6.2}$$

$\mathbf{R}_z(s)$ measures therefore the relevant perpendicular coordinate of $\mathbf{R}_z(s)$ perpendicular to the mean x–y plane.

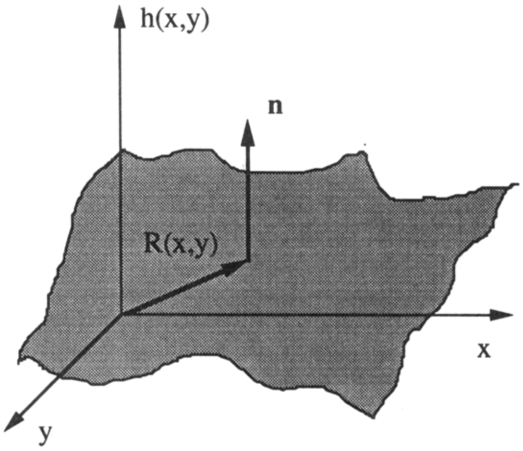

Figure 3. Definition of the variables and the coordinate system used in section 6.

The aim of this section is to calculate the range of localization in terms of a localization length composed to its own size, i.e., its radius of gyration. To do this, we write in analogy to Edwards and Muthukumar[9] the end to end distance as functional of a replica field theory

$$[\langle \boldsymbol{R}^2\rangle]_h = \lim_{n\to 0}\lim_{\lambda\to 0}\frac{\partial}{\partial n}\frac{\partial}{\partial\lambda}[Z^n]_h \tag{6.3}$$

where Z^n is the generating functional

$$Z^n = \int\prod_a D\mathbf{R}_a(s)\exp\Bigg\{-{}_n\sum_{a=1}\lambda\left[\int_0^N \mathrm{d}s_a\left(\frac{\partial\mathbf{R}_a}{\partial s_a}\right)\right]^2 - \frac{3}{2\ell^2}\sum_{a=1}^{n}\int_0^N \mathrm{d}s\left(\frac{\partial\mathbf{R}_a}{\partial s_\alpha}\right)^2 - -w\sum_{a=1}^{n}\int_0^N \mathrm{d}s_a\int \mathrm{d}x\,\mathrm{d}y\,\delta\,(\mathbf{R}_z^a(s)-\mathbf{h}(x,y))\Bigg\} \tag{6.4}$$

In eqs 6.3 and 6.4, the ⟨ ⟩ average is the usual thermal average over the chain configuration whereas $[\;]_h$ is the average over the disordered surface $\mathbf{h}(x,y)$. To proceed with the Hamiltonian in eq 6.4, a variational principle is employed which is analogous to that developed in rubber theory[18,19] and ref 9. The usual trial Hamiltonian is given by

$$H_0 = \frac{3}{2\ell^2}\sum_{a=1}^{n}\int_0^N \mathrm{d}s_a\left(\frac{\partial\mathbf{R}_a}{\partial s_a}\right)^2 + Q \tag{6.5a}$$

where the trial potential Q is chosen to be quadratic, i.e.,

$$Q = \frac{q^2}{6}\sum_{a=1}^{n}\int_0^N \mathrm{d}s_a\,\mathbf{R}_a^2(s) \tag{6.5b}$$

where the strength q is the localization parameter. According to the rules of the variational principle, the free energy is given by

$$\exp(-F(n)) = \int\prod_{a=0}^{n} D\mathbf{R}_a(s)\exp\{-H_0 + Q - W\} \tag{6.6}$$

where W is the disorder potential

$$W = w\sum_{a=0}^{n}\int_0^N \mathrm{d}s\int \mathrm{d}x\int \mathrm{d}y\,\delta\,(\mathbf{R}_\perp^a(s)-\mathbf{h}(x,y)) \tag{6.7}$$

Following Edwards and Muthukumar[9] and straightforward algebra, we find the localization parameter from the usual variational equation, $\frac{\partial F}{\partial q} = 0$,

$$1 = \frac{w}{(2\pi)^{3/2}}\frac{\ell}{q^2\sigma^2}\frac{1}{\sigma^3\left(1+\frac{1}{2}\frac{\ell}{q\sigma^2}\right)^{3/2}} \tag{6.8}$$

This equation defined the optimum for the localization parameter. It is important to realize that no degree of polymerization appears in eq 6.8. The physical reason for this is that the polymer is localized at the nonpolymeric surface, unlike in networks where the polymer chain is localized by other network chains. σ is usually defined as variance of the function $\mathbf{h}(x,y)$, i.e., in the simplest case

$$\langle \mathbf{h}(x,y)\,\mathbf{h}(x',y')\rangle = \sigma^2\delta\,(x-x')\delta(y-y')$$

However, σ^2 can be related to the spectral density of the surface. Now we turn to the discussion of important limiting cases of the result in eq 6.8.

(A) The Limit of Strong Localization , $\ell \ll q\sigma^2$. In this case we find

$$q \cong \sqrt{w}\frac{1}{\ell^2}\left(\frac{\ell}{\sigma}\right)^{5/2} \tag{6.9}$$

It is useful to introduce the ratio $\Lambda = 1/q\ell \equiv \mathbf{r}_{\mathrm{loc}}/\ell$ fo later discussions. For this ration, we find

$$\Lambda \sim \frac{1}{\sqrt{w}}\left(\frac{\sigma}{\ell}\right)^{5/2} \tag{6.10}$$

This result agrees with the physical intuition, since the range of localization, r_{loc}, is inversely proportional to w, the strength of the surface potential.

$$r_{\mathrm{loc}} \sim w^{-1/2} \tag{6.11}$$

This means that with vanishing surface interaction $w \to 0$, $r_{\mathrm{loc}} \to \infty$ the chains are not localized at all, whereas if $w \to \infty$ or $r_{\mathrm{loc}} \to 0$, the chains are bound to the surface. The nontrivial power law for the σ dependence

$$r_{\mathrm{loc}} \sim \sigma^{5/2} \tag{6.12}$$

is a direct consequence of the strong localization limit, $\ell \ll q\sigma^2$.

(B) Weak Localization Limit, $\ell \gg q^2$. In this opposite case we find

$$\Lambda \sim \frac{1}{w^2}\left(\frac{\sigma}{\ell}\right)^4 \tag{6.13}$$

A similar discussion as above applies, but different power laws are found. These will be discussed below, in the context of a "realistic" model for polymers near fractal carbon black particles. In the following we compare these predictions with the case of polymers near carbon black filler particles.

(C) A "Realistic" Example. At this point we would like to come back to the initial aim of the paper, that is, to describe the disorder formation of bound rubber. Three length scales are of importance. The first and second ones are related to the rough surface that is formed by the carbon black particles and clusters. It is the cluster size itself and a lower cutoff of the roughness. The third relevant scale is the size of the polymer, which is in the case of networks the mesh size, i.e., the chemical distance between two cross-links (if no entanglements are present). Surfaces of carbon black particles are rough and even fractal down to the molecular size range. X-ray scattering measurements on carbon black particles have been performed by Gerspacher and co-workers.[14] In this case the particle surface is fractal in the range of the polymer chain dimension ($\sim 10^0 \ldots 10^2$ nm). That means the roughness and the size if the polymers in the network are comparable. In recent years many studies of the fractal nature of surfaces have appeared in the literature.[20] We discuss the fractal nature of the cb surface in the context of the set of these observations and the collected results. Therefore we have to make a few remarks on the fractal properties of rough surfaces.

The variance

$$\sigma^2 = \langle h^2(x) \rangle \tag{6.14}$$

is a measure of surface roughness, where the height h is measured as a function of the distance x along some direction; $\langle\,\rangle$ is the average over the set of repeated observations of surface topography, $\langle h(x) \rangle = 0$. Consider the correlation function

$$\varphi(\Delta x) = \langle h(x + \Delta x) h(x) \rangle \tag{6.15}$$

For stationary surfaces the correlation function may be expressed in terms of the power spectral density, $S(f)$, by a Fourier transform

$$\varphi(\Delta x) = \frac{1}{2} \int_{-\infty}^{+\infty} S(f) e^{2\pi i f \Delta x} \, df \tag{6.16}$$

f is the spatial "frequency", i.e., a wave number for the surface roughness which is related to the wavelength, λ, of the modulations of the surface by $f = 1/\lambda$. Physical systems have a finite extension, L_0, and therefore a minimum spatial frequency, $f_{\min} = 1/L_0$. Thus eq 6.16 has to be modified in the following sense

$$\varphi(\Delta x) = \int_{f_{\min}}^{+\infty} S(f)\, e^{2\pi i f \Delta x} df \tag{6.17}$$

For carbon black we make the following reasonable assumptions: the finite extension corresponding to the lower cutoff of the spatial wave number f is of the order of $L_0 \sim 10^2$ nm that corresponds to the particle size itself. The lower wave number cutoff is assumed to be of the order of the Kuhn segment of the polymer, $\ell = 1$ nm. This assumption is reasonable since experiments have confirmed the fractal character of the cb particles in the range of the order of 1−100 nm. We recall again that the surface fractal properties of cb should not be confused with the fractal properties of the aggregate/agglomerate morphology. These define fractal properties at scales larger than 10^2 nm and are different from the usual cb grades. Indeed the lower cutoff is not very much important, and the latter assumption corresponds roughly to the value where ℓ collects one to three monomers. Thus we find the ratio $L_0/\ell \sim 10^2$ of order to the mesh size in the technically relevant network.

We note that these assumptions are consistent with very recent scanning tunnelling microscopy (STM) investigations on carbon black.[21] At low magnification, nearly spherical particles constituting the carbon black aggregates were imaged. Their size has been reported, about 10 nm, depending on the carbon black type. The particle size distribution in an aggregate (of the order of 100 nm) seemed to be narrow, and joints between particles appeared to be very sharp. At larger magnification, approximately circular ordered zones of about 2 nm diameter were observed on the cb surface. At atomic resolution, these ordered zones of the size of the lower cutoff length, ℓ, present an arrangement in a rectangular network of the order of 0.10 nm, corresponding to the end "scales" of the graphite layers. The STM observations can be made consistent with the scattering determination of the fractal surface dimension of the cb particles if it is assumed that the surface is constituted by a stochastic overlapping of many graphite layers. This leads to a disordered arrangement of the large number of edges of the "scales" that favor (entropically) the deposition of rubber chains at the surfaces. These results support the assumption that $\Lambda_0 = L_0/\ell \sim 10^2$; the precise value of this constant ratio depends on the type of cb.

Berry and Hannay[22] comment that statistically isotropic surfaces which have no scale and whose height is well defined but nondifferentiable may have spectra of the fractal form

$$S(f) = K/f^{\beta} = K f^{-2H-1} \tag{6.18}$$

where the prefactor K is called the "topethesy". The dimension H[20] is the fractal codimension and is given in terms of the surface fractal dimension, D_s, by

$$D_s = 3 - H \tag{6.19}$$

which yields $\beta = 7 - 2D$ for the power spectra in eq 6.18. The variance is then estimated by

$$\sigma^2 = \varphi(0) = \frac{1}{2} \int_{-\infty}^{+\infty} S(f) df = K \int_{f_{\min = 1/L_0}}^{+\infty} f^{-\beta} \, df \tag{6.20}$$

In the special case of $\beta = 1$, the variance behaves logarthmically, i.e.,

$$\sigma^2 = K^{(1)} \ln(L_0/\ell) \tag{6.21a}$$

The latter case corresponds to very irregular surfaces, i.e., $D_s = 3$. This surface fractal dimension is very large, and realistic filler particles are better described by $D_s = 2.3-2.5$. In such cases the logarithmic law is not relevant. For those intermediate fractal dimensions, the variance is of the form

$$\sigma^2 = K^{(\beta)} \frac{1}{\beta - 1} L_0^{\beta - 1} \text{ for } 1 < \beta \leq 3 \tag{6.21b}$$

This result enables us to consider the scaling of the localization length, i.e., the inverse of the variational parameter q as a function of the surface fractal dimension. By simple algebra, it is shown that in the case of the strong localization limit $1/q$ is given by

$$r_{\mathrm{loc}} = q^{-1} \propto \Lambda_0^{5/2(3 - D_s)} \tag{6.22}$$

In the limit of weak localization, a similar formula holds, i.e.,

$$r_{\mathrm{loc}} = q^{-1} \propto \Lambda_0^{2(3 - D_s)} \tag{6.23}$$

The localization length has to be small to be significant. In both cases it can be seen that the localization length decreases when the surface fractal dimension increases. At this stage, it is useful to compare the localization length to the radius of gyration of the chain (mesh). This comparison shows the range of localization inside the chain in the melt (rubber) near the fractal surface. Since only the strong localization case is physically significant, we restrict ourselves to this issue. To do this we consider the ratio of the localization length and the radius of gyration, i.e., $\Lambda_R = r_{\mathrm{loc}}/l\mathrm{N}^{1/2} = 1/(q\ell\mathrm{N}^{1/2})$. This ratio scales with the molecular weight as

$$\Lambda_{\mathrm{R}} \propto \Lambda^{5/2(3-D_{\mathrm{s}})} N^{-1/2} \tag{6.24}$$

For the case of $D_{\mathrm{s}} = {}^{5}/_{2}$ (which corresponds roughly to the case of cb), we find that this ratio scales as $L_0{}^{5/4}N^{-1/2}$, which is always less than the chain length itself; the chains are localized. It is noticeable that the case $D_{\mathrm{s}} = 2.5$ corresponds to Brownian surfaces.[20]

To be more specific, consider now the special cases of flat surfaces, $D_{\mathrm{s}} = 2$, and irregular surfaces, $D_{\mathrm{s}} = 2.5$. These lead to the two cases

$$D = 2\text{:}\ \ \sigma^2 = \frac{1}{2} K^{(2)} L_0^2 \tag{6.25a}$$

$$D = 2,5\text{:}\ \ \sigma^2 = K^{(2,5)} L_0 \tag{6.25b}$$

In the case of $D_{\mathrm{s}} = 2.5$, the topethesy $K = K^{(2,5)}$ has the dimension of a length, $S(f) = Kf^{-2}$, which was proposed by Sayles and Thomas.[23] Using these results for carbon black, i.e., $D_{\mathrm{s}} = 2, 5$,[13] and the ratio for the cutoffs to be $\mathrm{L}_0/\ell \cong \mathrm{N}$, we can make predictions for the strong and weak localization limits discussed above. The results can be summarized as follows:

Strong localization:

$$\Lambda \equiv \frac{q^{-1}}{\ell} \cong w^{-1/2} \left(\frac{K}{\ell}\right)^{5/4} \Lambda_0{}^{5/4} \tag{6.26}$$

Weak localization: $$\Lambda \cong w^{-2} \left(\frac{K}{\ell}\right)^{2} \Lambda_0{}^{2} \tag{6.27}$$

For comparison it is useful to consider the ratio between the two cases, i.e.,

$$\frac{\Lambda^{(\mathrm{weak})}}{\Lambda^{(\mathrm{strong})}} \cong w^{-3/2}\, (K/\ell)^{3/4}\, \Lambda_0{}^{3/4} \tag{6.28}$$

The results become also more clear if the change of the localization length with the surface fractal dimension in the two different cases is calculated. Consider first the lower limit, $D_{\mathrm{s}} = 2$. This does not seem to make sense since it corresponds to the case of the flat surface, where no variational calculation is needed. Nevertheless it serves as an interesting bound that corresponds to the case where the adsorption Hamiltonian is treated by a variational principle. The error which is made is known from the treatment of the excluded volume effect.[24] Consider the two cases, weak and strong localization.

1. Weak Localization:

$$D_{\mathrm{s}} = 2\text{:}\ \ \Lambda^{(D_{\mathrm{s}}=2)} = w^{-2} \left(\frac{K^{(2)} L_0^2}{2\ell^2}\right)^2 \propto \Lambda_0^4$$

$$D_{\mathrm{s}} = 2, 5\ \Lambda^{(\mathrm{D_s}=2,5)} = w^{-2} \left(K^{(2,5)} \frac{L_0}{\ell^2}\right)^2 \propto \Lambda_0^2$$

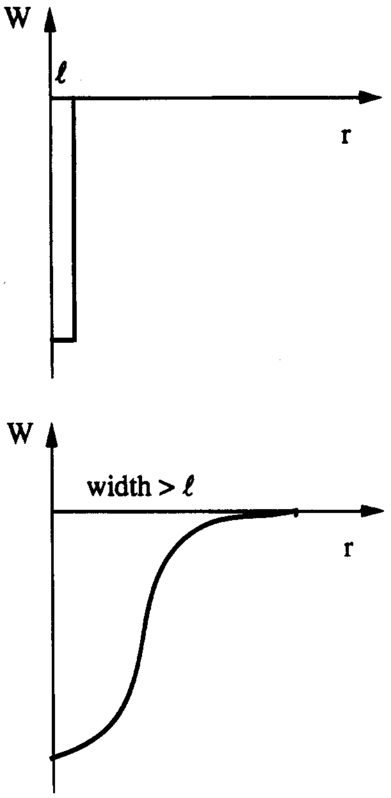

Figure 4. The adsorption potential on a rough surface is always broader than the initial short range potential. This is only an illustration, and the precise form of the potential has to be calculated for the case under consideration.

$$\frac{\Lambda^{(\mathrm{D_s}=2,5)}}{\Lambda^{(\mathrm{D_s}=2)}} \cong \left(\frac{K^{(2,5)}}{K^{(2)}}\right)^2 L_0^{-2} \propto \Lambda_0^{-1}$$

i.e., a dramatic decrease of the localization length with increasing fractal surface dimension.

2. Strong Localization: Similar considerations for the strong localization can be made and yield

$$\frac{\Lambda^{(D=2,5)}}{\Lambda^{(D=2)}} \cong \left(\frac{K^{(2,5)}}{K^{(2)}\,\ell}\right)^{5/4} \left(\frac{\ell}{L_0}\right)^{5/4} \sim \Lambda_0{}^{-5/4}$$

which also shows a strong increase of the localization effect. It is noteworthy that in this approximation the chains show localized configurations, $R \propto$ *constant*, i.e., the radius of gyration is independent of the molecular weight. This, however, is a consequence of the mean field variational approximation. It has been shown earlier, e.g., as in eq 3.14, that this is not always the case, and a more sophisticated analysis has to follow. Such considerations are not the subjects of this paper and will be discussed in a subsequent study.

7. Discussion

The purpose of this paper is to show that disordered surfaces lead to an induced adsorption polymer enrichment on surfaces. Although this effect has been discussed qualitatively before,[7,25–27] a more detailed discussion has been provided here. The aim of this paper was not to solve the problem in detail but to use various possibilities of surface characterization and to discuss the effect of attraction. From a pictorial point of view, the situation can be summarized in Figure 4. As long as any disorder is present, the effective adsorption potential becomes stronger. Short range potentials may become long ranged, but in most cases their widths

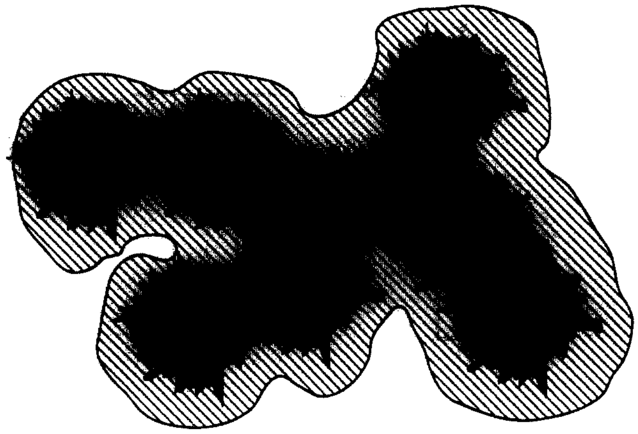

Figure 5. Schematic illustration of the bound rubber phase (shaded area) around a cluster formed by fractal filler particles. The length scales in this figure are not represented correctly. Polymer chains are not drawn since their size is of the order of the surface roughness. Due to clustering of the single filler particles, a huge surface in the rubber is formed. At this entire surface, bound rubber is formed by localization. The bound rubber is schematically shown by the shaded area.

become larger, so that the probability for adsorption becomes much larger. For a detailed calculation of the size of the chains at such rough surfaces, different methods have to be employed. These have been discussed in the literature. The more applicative result of this paper is also that such concepts can be applied to industrial questions such as the filler polymer interaction in filled rubbers. Such materials are widely used in applications. The typical example is the car tire industry. The effect of reinforcement by fillers is one of the outstanding problems in this field. The presence of strongly bound rubber (see Figure 5 for an illustration) in technical rubbers is essential for dynamic mechanical material properties, wet skid behavior, and frictional properties. Of course, this paper does not solve real "down to earth" questions for improving such materials. It provides, however, new ideas to this complex field, which have, so far, not been used for applicative questions.

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