Connectivity selection by porous media: “spectral chromatography”
T. Vilgis

To cite this version:
Short Communication

Connectivity selection by porous media: "spectral chromatography"

T. A. Vilgis (*)

Institut Charles Sadron, CRM-EAHP, 6 rue Boussingault, F-67083 Strasbourg, France

(Received 30 July 1992, accepted in final form 2 September 1992)

Abstract. — This note discusses the behavior of polymers with arbitrary connectivity in small pores. For simplicity only cylindrical pores are considered. In contrast to linear polymers (spectral dimension = 1) which fit into very small pores, branched chains with larger spectral dimension require a minimum pore size, which is a function of the molecular weight. This special situation allows for a connectivity selection of mixtures of differently branched and linear molecules by specially designed chromatograph.

During the last decade much attention has been given to the behavior of linear polymers in porous media on the scaling level [1, 2]. Despite the formal and theoretical complications which arise naturally in studying statics and dynamics of linear polymer chains in complex porous media, modelled by a chain within random obstables [3, 4] the simplest approach to the problem is to consider the size of a linear polymer in small pores of different geometries, such as spheres, wedges, cylinders, or of more complicated shapes by use of scaling techniques. This is, of course, not a very precise treatment of a porous medium, and many important and very interesting theoretical problems are neglected, but the main features, even beyond mean-field, can be found. A useful restriction is the discussion of the shape of a linear polymer in a small cylindrical pore to find the typical behavior including non-classical exponents [5].

The problem has been treated in three basic ways, one uses a simple Flory argument, the other is the blob model, and the third is a scaling theory [1]. In the Flory argument the elastic part and the confinement part of the free energy is balanced and the result is a basically stretched configuration of the chain in the cylindrical pore. The blob picture introduces a new scale in the problem, i.e. the blob size. The portion of the chain inside one blob in the pore takes its natural dimensions and shows, however, good solvent behavior. The size of the blobs is entirely determined by the diameter of the pore. Such results for linear chains

(*) Permanent address: Max-Plank-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Germany.
are reasonable and well established [1, 2]. The question we would like to answer in this note is the equivalent problem of predicting the size of higher dimensionally connected polymers, such as branched polymers, or more generally \(D\)-dimensional manifolds in porous media. Such problems are basically of the same complication, since the manifold finds itself in a quenched random environment. Such complications are here neglected also and we restrict ourselves to the scaling limit, to predict the main features without paying too much attention to formal matters. These are hoped to be left to an extended work.

First a proper description of such polymers is needed and it has been found useful to characterize them by their connectivity. Linear polymers are one dimensional objects, surfaces are of two dimensional connectivity, and randomly branched polymers can be approximated as polymeric fractals with a spectral dimension of about 4/3, which is the mean field limit of percolation clusters, i.e. not exact in \(d < 6\), but reasonably close to the real values obtained numerically [6]. Nevertheless for the purpose of our study based on a Flory estimate only the mean field values are of relevance. In the following the formulation and the study of the problems will be given in terms of the fractal concept, where the spectral dimension is the parameter classifying the polymeric objects of different connectivity, and providing a "unique" description of the differently connected selfsimilar polymers [7].

One problem obviously present is that, at first sight, no appropriate blob description of such polymers is possible, and one has to rely on Flory arguments. Such arguments can be made more rigorous if a generalization of the Edwards Hamiltonian for linear polymers is introduced for polymeric fractals in the following way:

\[
H = \int_{0}^{L} d^{D}x (\nabla \cdot \mathbf{R})^{2} - v \int_{0}^{L} d^{D}x \int_{0}^{L} d^{D}x' \delta^{D}(\mathbf{R}(x) - \mathbf{R}(x'))
\]

(1)

where \(D\) is the spectral dimension, i.e. \(D = 1\) for linear polymers, \(D = 2\) for random surfaces, and \(1 < D < 2\) for any polymeric fractal of arbitrary connectivity. \(x\) is a \(D\)-dimensional vector of the manifold embedded in \(d\)-space dimensions described by the vector \(\mathbf{R}\), and \(L\) is the linear dimension in one arbitrary direction. The first term is the connectivity and the second term the usual excluded volume interaction. Throughout the paper only objects with \(D < 2\) are considered for simplicity. Of course the Hamiltonian (1) does make little sense for fractional \(D\), without defining fractional differentials and integrals properly. Here it is used crudely as an analytic continuation for the purpose here in the paper. Indeed (1) has been applied successfully to other problems earlier [8].

Transforming the Hamiltonian into a Flory Free Energy by dimensional analysis, the usual Flory exponent for the size can be found to be

\[
\nu = \frac{D + 2}{d + 2}
\]

(2)

Note that this exponent is for the linear size \(L\) and not for the total mass \(M\). For the size of the object in terms of the total mass \(M\) the fractal dimension has to be used. It is naturally \(D_{f} = D/\nu\) which agrees with the usual fractal dimension of swollen polymeric fractals [9].

When such selfsimilarly branched, non-linear objects are put in cylindrical pores the simple dimensional analysis from above has to be modified in the usual sense, i.e. the \(d\)-dimensional Dirac function becomes anisotropic and the lateral dimensions are given by the pore size. Thus we estimate it to be

\[
\delta^{d}(\mathbf{R}(x) - \mathbf{R}(x')) \propto \frac{1}{D^{d-1}} \frac{1}{\mathbf{R}_{||}}
\]

(3)
where $D$ is the pore size and $R_{||}$ is the direction parallel to the pore. Thus the excluded volume term becomes, as usual, anisotropic and the corresponding Flory free energy is given by

$$F = R_{||}^2/L^{2-D} + L^{2D}/(D^{d-1}R_{||})$$

Minimization yields the result for the parallel exponent

$$\nu_{||} = \frac{D + 2}{3}$$

which agrees for $D = 1$ with the standard formula. So far, nothing new has been derived, but the problems start at this point. For any polymer with higher connectivity than $D = 1$, i.e. for any branched molecule, the parallel exponent $\nu_{||}$ is larger than one, and is, therefore, unphysical. The linear dimension of the polymer cannot be larger than one, i.e. more than fully stretched. It is known that there exists a minimum fractal dimension for any polymer which is $D_{f\text{min}} = D$, which is indeed the spectral dimension. This has been noticed earlier by Lhuillier [10] on an intuitive basis and shown more explicitly by the present author [7]. It can also be seen simply from the following: the Gaussian size is given by $R_{||} \propto L^{(2-D)/2}$, and the maximum extension is $R_{||} \propto L$. Hence the maximum stretching ratio is given by $\lambda_{\text{max}} = L^{D/2}$ and is determined by the spectral dimension. Therefore the parallel extension by the exponent derived in equation (5) cannot be reached for any connectivity larger than 1, since the polymer would be more stretched than physically allowed.

Thus, a minimum pore size has to be defined through which the polymer is able to pass through. This can be seen by minimizing equation (4) as before which yields

$$R_{||} \propto \frac{L^{(D+2)/3}}{D^{d-1}}$$

Thus the absolute minimum pore size, which can be defined by $R_{||} \propto L$, is then given by

$$D_{\text{min}} \propto L^{(D-1)/(d-1)} \equiv \frac{M^{(D-1)/D(d-1)}}{(d-1)}$$

$M$ is the total mass of the polymer. This is the central result of this note. It can be seen that for linear polymers the pore size is independent of the molecular weight. Thus linear polymers ($D = 1$) find their way even through a very small pore, if $D_{\text{min}}$ is of the order of the Kuhn length, but with a low probability and in a very long time. The time the linear polymer needs to pass through the pore will be exponentially large, i.e. its diffusion constant is of the order of [1]

$$D \propto \frac{kT}{(6\eta D_{\text{min}})} \exp\{-N/(g - 1)\}$$

where $\eta$ is the viscosity of the solvent and $g$ is the number of monomers in one blob, which is very small ($O(1)$) for small pores. The limiting factor which decides whether the polymer goes through the pore or not is therefore given by its diffusion coefficient, which is for linear polymers exponentially small if the pore size is of the order of the Kuhn length.

In branched polymers another important limitation is present: the connectivity. The larger the connectivity, the larger the minimum pore size. Thus it would be possible to construct a porous medium which is able to separate in a mixture of branched and linear molecules on a basis of their connectivity by an appropriate minimum pore size. For the construction of such a chromatographer dynamical aspects have to be taken into account, since the other selection constraints is the finite time to pass through a pore, as mentioned in equation (8). Such aspects are left for the moment, since an analogous equation for the diffusion coefficient in terms of
blobs is still lacking. It can be expected, however, that the diffusion constant shows a similar behavior as given in equation (8) for pores larger than the minimum pore size.

The question whether a blob picture in branched systems makes sense has to be considered open. Speculatively it can be suggested that the linear size L be considered as a basis for a blob construction. We assume that the branched polymer is squeezed in a pore of appropriate size. As long as the lateral direction is large enough, a blob picture can be built up as long as the linear size L is considered. It is found that the branched chain is swollen within the blobs and stretched out in direction of the cylindrical pore. To obtain that situation the pore size has to be much larger than Dmin. The interesting situation is given whenever the pore size is of order of the minimum size. Then this modified blob picture breaks down and a new situation occurs since the polymer becomes saturated in the lateral direction. This means, however, that two limiting cases occur for branched polymers, either the amount of polymer in the blobs, determined by the pore size, is swollen (large pores) or the amount of the branched polymer in the blob will become saturated [11]. This “transition” occurs at the minimum pore size computed above. Another interesting point is that at the minimum pore size the internal concentration (or filling factor) cint = N/D/D/D/D becomes independent of the molecular weight M = N/D. The essential point to be made is that the minimum pore size is entirely defined by the spectral dimension and the molecular weight. Therefore the pore selects the objects with respect to their connectivity, i.e. their spectral dimension. We call this new possibility – to distinguish classical chromatography, which selects only with respect to molecular weight – spectral chromatography.

All these complications come from the severe restriction in space imposed by the pore. There is essentially no serious problem in putting branched polymers between two plates. This can be seen by employing a similar Flory argument. The excluded volume energy is given by vN/D/D/D/D, hence the exponent for the extension of the polymer between two plates is given by

\[ \nu = \frac{D + 2}{4} \] (9)

The limit \( \nu = 1 \) is trivially reached for membranes \( D = 2 \) where they are flat between two squeezed plates. Branched polymers \( D \approx 4/3 \) between two plates behave as \( \nu \approx 5/6 \). When, for example, a membrane is put into a pore it cannot flatten out in the remaining space but has either to crumble, if the pore is large enough, or to saturate (collapse) in smaller pores in the lateral direction. Whether one finds the crumpled or collapsed case it is determined by the value of the minimum pore size Dmin.

This (non-uniform) “blob model” will be elucidated in more detail in a subsequent extended paper, which will use the results obtained here for problems which are deeply related to this one. For example, the problem of grafting branched polymers on a surface (where we find a maximum grafting density and a singularity in the grafting free energy) or the problem of charged fractals, charged membranes and branched polyelectrolytes, recently analyzed by Daoud [12] and closely related are charged fractals or charged membranes, where a maximum charge fraction \( f < 1 \) can be found, which already stretches the fractal or membrane out completely. Such situations can be discussed in the framework of scaling and with more sophisticated path integral methods using self consistent fields and Hartree approximations.

Acknowledgements.

The author is very grateful to the Université Louis Pasteur Strasbourg, France, for financial support in the form of a two month visiting professorship, and the members of the Institut
Charles Sadron, especially Jean-François Joanny and Henri Benoît, for providing a stimulating and friendly atmosphere with many useful discussions.

References