CHAPTER 6
Scaling, Exponents, and Fractal Dimensions

Mohamed Daoud,* H. Eugene Stanley, † and Dietrich Stauffer‡

* Laboratoire Léon Brillouin (CEA-CNRS), CE Saclay; Gif-sur-Yvette, Cedex, France
† Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215
‡ Institute of Theoretical Physics, Cologne University, D-50923 Köln, Euroland

6.1 Linear Polymers ........................................................... 83
6.2 Gelation for Branched Polymers ............................................. 86
Acknowledgments ......................................................... 89
References ............................................................. 89

6.1 LINEAR POLYMERS

Textiles, much of living matter, plastics, and many other materials consist of linear or branched polymers. Each polymer usually is a carbon chain consisting of many monomers like -CH2-. We emphasize here the modeling of such polymers and compare the theoretical results with experiments.

First, we consider the conformation of a random linear chain, which is a model for a dilute solution of a polymer in a solvent [1–6]. Typical examples are polystyrene in benzene or polydimethylsiloxane in toluene or cyclohexane. We assume that the macromolecules are made of \( N \) statistical units which are randomly oriented with respect to each other. Because the actual monomers have to respect chemical bond angles, independent units can be regarded as made of several monomers. It is possible to define such independent units which will be used in all cases. This procedure was first presented by Kuhn, who defined the concept of local rigidity of a polymer [1]. Here, we consider the chains as completely flexible, and we do not distinguish between actual monomers and statistically independent units.

6.1.1 The Random Walk

The simplest model to describe the structure of a linear chain made of \( N \) units of length \( l \) each is the random walk. This is an ideal chain where no interactions are present between monomers. The distribution function \( P(r,N) \), which is the probability that a chain made of \( N \) steps starts at the origin and ends at point \( r \), is a Gaussian. In three-dimensional space,

\[
P(r, N) = (3/2\pi N l^2)^{3/2} \exp \{-3r^2/2N l^2\}.
\]

From the second moment we define the fractal dimension \( d_f \) of the walk by \( \langle r^2 \rangle^{d_f/2} \sim N \). For any spatial dimension \( d \), the second moment \( R_0^2 \equiv \langle r^2 \rangle \) of \( P(r, N) \) is

\[
R_0^2 \sim N l^2.
\]

Thus the fractal dimension [6] is

\[
d_f = 2
\]

for any \( d \). It is important to stress that any definition of a characteristic length for the random walk leads to this result.

What is a fractal and its dimension? A long spaghetti is one dimensional since its mass increases linearly with the length. A pizza has a mass proportional to the square of the radius, if its thickness is constant, and thus is two dimensional. A glass of red wine has a volume and mass proportional to the third power of the length, and is three dimensional. Thus an object with mass proportional to \((\text{radius})^d\) has a dimension \( d_f \). It is called a fractal with the fractal dimension \( d_f \) if \( d_f \) differs from the Euclidean dimension (usually 3) of the space into which the object is embedded. The apple-like Mandelbrot set is perhaps the most famous deterministic fractal, whereas the random walks of Eq. (6.2a) are random fractals with mass \( \propto N \propto (\text{radius})^2 \).

In deterministic fractals, small parts are mathematically similar to suitably chosen large parts; in random fractals this “self-similarity” (a large branch of a tree looks similar to a small twig on it) is often described but seldom defined in any precise way.

For a polymer chain, it is possible to use the mean square end-to-end distance, as we did above. It is also possible to
define the average radius of gyration. One finds that these
lengths are proportional to each other if both are long, and
that the fractal dimension is 2 (for a discussion, see Chapter 1
in [7]). This is the reason for using the sign $\sim$, which denotes
asymptotic proportionality, and scaling laws are assumed to
be valid only asymptotically. It is important that the precise
way the length is defined will change the prefactor, but not
the exponents. In this sense, we can say that there is only one
characteristic length, and we will not be interested in the
differences between the prefactors.

The fractal dimension may be observed experimentally
by light or neutron scattering [8]. The scattered intensity
$S(q)$ is the Fourier transform of the pair correlation function

$$S(q) = \sum_{i,j=1}^{N} \langle \exp[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \rangle,$$

(6.3)

where the brackets $\langle \cdots \rangle$ represent an average over all
configurations, and $\mathbf{q}$ is the momentum transfer in the scattering
experiment: for a neutron with wavelength $\lambda$ elastically scattered with an angle $\theta$, we have

$$q \equiv |\mathbf{q}| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}. $$

(6.4)

Because Eq. (6.1) is valid for any pair of units in a random
walk, Eq. (6.3) may be calculated exactly. This was done by
Debye [1] some years ago. He found

$$S(q) = \frac{2}{X} (e^{-q^2} - 1 + X), $$

(6.5)

with

$$X = q^2 R_0^3/3. $$

(6.6)

Here, $R_0$ is the radius of gyration of the ideal chain. In the
intermediate range, $l^{-1} \gg q \gg R_0^{-1}$, where the fractal na-
ture of the walk appears, relation (6.5) may be approximated by

$$S(q) \sim q^{-2}. $$

(6.7)

This relation provides a convenient way to measure the
fractal dimension of a single polymer, whenever the inter-
mediate range may be reached experimentally. Neutron
scattering is an excellent technique for this: The available
wave vector range is particularly well suited for polymers;
since the typical unit size is around 10$\text{A}$, and the radius of
gyration is several hundred Angströms. Linear chains be-
have actually as random walks in two cases: in a melt, when
no solvent is present, and in a theta solvent [9]. The latter is
introduced in Section 6.1.2 when we discuss the actual
interactions between monomers.

6.1.2 The Self-Avoiding Walk

Random walks are ideal chains in the sense that there is
no interaction between monomers. For actual polymers,
there is an interaction between any two monomers. The
interaction consist of an attractive part for large distances,
goes through a minimum at intermediate distances, and
becomes a repulsive core at short distances. Because of
this “steric” constraint, two monomers cannot be in the
same location.

At high temperatures, the repulsive core is dominant, and
the local minimum may be neglected completely. This is the
excluded volume effect, and corresponds to what is called a
good solvent [10,11]. There exists a critical temperature
called the Flory theta temperature, where the excluded vol-
ume effect and the attractive part compensate each other.
Such solutions are said to be in a theta solvent [12–14]. For
still lower temperatures, the attractive part of the potential
becomes dominant, and although two monomers are not
allowed to be in the same location, they tend to be in the
vicinity of each other. As a consequence, the chain tends to
collapse on itself [15–17]. Solvents in which this happens
are known as poor solvents.

As mentioned above, at the theta temperature, because of
the compensation between attractive and repulsive parts of
the potential, the random walk model gives an adequate
description of a chain in three-dimensional space [1–6].
Actually, there are still logarithmic corrections, but they
may be neglected. In two dimensions, a chain at theta
temperature is still not equivalent to a random walk [18].
In what follows, we will be concerned with solutions in a
good solvent. It was realized by Edwards [10] that the exact
shape of the potential is not important, and that it could be
described by a parameter $v(T)$, where $T$ is the temperature,
called the excluded volume parameter, defined as

$$v(T) = \int \{ 1 - e^{-v(r)/kT} \} dr, $$

(6.8)

like the classical second virial coefficient, where $V(r)$ is the
effective monomer–monomer potential. This parameter is
positive in a good solvent, vanishes at the theta temperature
and becomes negative in a poor solvent.

In the good solvent, steric interactions are dominant, as
mentioned above, and the polymer is swollen compared to
the ideal chain. This swelling corresponds to a change in the
fractal dimension of the chain, which now becomes smaller
than 2.

The fractal dimension was calculated by various renor-
malization group techniques and by computer simulations
[19,20]. Here, we describe the Flory approximation which,
athough being wrong [1–6], gives the fractal dimension
within a very good accuracy for all dimensions. In this
approximation one assumes that the free energy can be written as

$$F/kT = \frac{R^2}{R_0^2} + N^2 \frac{R}{R_0}. $$

(6.9)

The first term is the elastic energy, in which one considers
the chain as a spring with spring constant $1/R_0^2$, where $R_0$ is