

# Polymer Solutions: a Geometric Introduction\*

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Long hydrocarbon chain polymers dissolved in a liquid qualitatively alter the way the liquid moves and transmits forces. The basic origins of this behavior can be understood geometrically by recognizing that a polymer chain resembles a random walk. The spatial distribution of atoms may be described by scaling properties and quantified using the notion of fractal dimension and dilation invariance. The strong thermodynamic and hydrodynamic interactions of polymers may be accounted for in terms of the intersection properties of fractal objects. These intersection properties show why polymers exclude flow as well as one another from their interiors, despite their arbitrarily small interior concentration. Self avoidance decreases the fractal dimension of a polymer. The origin of this decrease and conditions for its occurrence are explained. From these geometric properties, scaling laws describing how osmotic pressure, diffusion and stress relaxation depend on molecular weight and concentration are explained.

## I. INTRODUCTION

Why should a physicist be interested in polymers? They do not hold the key to vast sources of energy as atomic nuclei do. They do not defy the intuition with ultrasmall dissipation as superconductors and superfluids do. They do not reveal subtle new nonabelian symmetries as do subatomic particles. Nor do they hold secrets about the origin or fate of the universe. Polymers are just ordinary matter—just insulating organic molecules. These molecules are merely larger than usual and are in the form of chains of small subunits. Yet these chain molecules have ways of interacting unmatched in other forms of matter. The study of polymers over the last few decades has forced us to broaden our notion of how matter can behave—how it can organize itself in space, how it can flow, and how it can transmit forces. These new behaviors arise from a few qualitative features of the polymer molecule’s structure. The potential for shaping these phenomena is just beginning to be realized as the power of synthetic chemists to control the molecular structure increases.

The purpose of this introductory essay is to convey an understanding of how polymer liquids differ from other liquids and from other forms of condensed matter. Excellent treatments exist already (Jannink *et al.* 1992), notably *Scaling Concepts in Polymer Physics* by P. G. deGennes (DeGennes 1979). Here we adopt a geometric approach, exploiting the “fractal” structure of the poly-

mers. This enables us to provide an economical and unified overview of the phenomena treated in greater depth in these books. As much as possible we shall attempt to account for the interaction of polymers with their surroundings by the mathematical laws describing the intersections between two fractal structures. We begin by recalling the scaling properties of any flexible chain of randomly-oriented links, noting that such a random-walk structure has the spatial scaling properties of a fractal object as defined by Mandelbrot (Mandelbrot 1982). We shall then survey the important ways in which fractal structures, including polymers, interact with their environments. This leads to a discussion of the thermodynamics and hydrodynamics of a polymer solution. With the fractal properties in mind we discuss the interaction of a random-walk polymer with itself, finding that these interactions change the spatial arrangement of the molecule considerably. Having described the behavior of individual polymer molecules, we can discuss the behavior of solutions, notably those where the polymer chains interpenetrate strongly. The spatial, energetic and dynamic behavior of these solutions can be understood in its major outlines from the fractal properties of isolated polymers treated earlier. We collect in Table I the main quantities used for this discussion.

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## II. RANDOM-WALK POLYMER

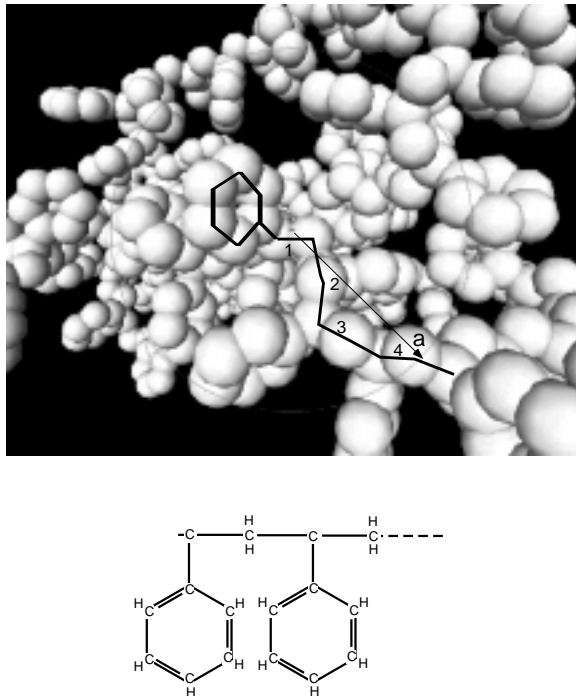


FIG. 1. Top: Detail of a polystyrene molecule  $((\text{CH}-\text{C}_6\text{H}_5)-\text{CH}_2)_n$  as it might appear in a good solvent. Each sphere represents a carbon atom and one or two small hydrogen atoms attached to it. The distance between connected atoms is about 1.4 Angstroms. The chemical bonds are superimposed on one repeating unit or monomer, and on a section of the chain backbone. The backbone bonds may rotate freely. A few successive backbone repeat units are labeled 0, 1, 2, ... . The vector  $\vec{a}$  for a four-monomer segment is shown. This structure was generated by a Monte Carlo computer simulation (Mondello *et al.* 1991), which simulates the random rotations of the bonds as they might occur in solution. The simulated molecule has about 1/20 the mass of a polymer in a typical styrofoam cup. Bottom: Chemical diagram of two repeating units of polystyrene.

Figure 1 shows a close-up of polystyrene, the best studied polymer molecule and one of the most common. The picture suggests the many intricacies controlling the structure and interactions of these molecules with themselves and with their solvent environment. From these

intricacies we note two simple features. First, the carbon-carbon bonds along the chain backbone can rotate. Second, the successive bond angles of the backbone chain are bent, so that the chain is flexible. This means that the vector  $\vec{a}$  linking the first and last atoms of the segment shown is nearly unaffected by the direction of the preceding segment along the chain. This means that the overall shape of the polymer can be represented as a sequence of  $n$  vectors  $\vec{a}_i$  that vary randomly and are statistically independent of each other<sup>1</sup>. A typical polystyrene molecule might have a hundred segments of this size; one can make polystyrene molecules containing 10,000 or more such segments. Thus the overall structure of the molecule is apparently that of a long, random walk in space.

To gauge the overall size of a large polymer, we recall familiar properties of random walks. We expect longer polymers to extend over larger distances in space. For random walks we can find this relationship in a quantitative way. The root-mean squared distance  $\sqrt{\langle r_n^2 \rangle}$  gives the typical size of a walk:  $\sqrt{\langle r_n^2 \rangle} = \sqrt{na}$ . The typical size is proportional to the square root of the chainlength  $n$ . Since a random-walk polymer of  $n$  segments is like a random walk of  $n$  steps, the same scaling law applies to these polymers<sup>2</sup>.

The random-walk structure of flexible polymers has an important consequence that accounts for many of the distinctive properties of polymers: they are *tenuous*. To explain this notion, we consider a sphere of radius  $R$  much larger than our elementary segments  $a$  but much smaller than the entire polymer coil. The sphere contains monomers and solvent; since the liquid has a well-defined density, the amount of matter inside is proportional to  $R^3$ —*i.e.*, the volume of the sphere. But the fraction  $\phi_i$  of this volume occupied by monomers is very small. The piece of chain in the sphere varies in length as the chain fluctuates. But the *average* number  $n(R)$  of segments is roughly that number whose typical size  $\sqrt{\langle r_n^2 \rangle}$  is the sphere radius  $R$ . Thus,  $n(R) \simeq (R/a)^2$ . Knowing how  $n$  varies with  $R$ , we can readily deduce how the volume fraction  $\phi_i$  depends on  $R$ . If each of the  $n$  polymer segments displaces volume  $v$  in the solution then  $\phi \simeq vn/R^3$ . Since  $n$  grows as  $R^2$ , the volume fraction  $\phi$  scales like  $1/R$ : as the sphere is made larger, the density of polymer within it decreases *indefinitely*. If the sphere is several hundred Angstroms in size, the proportion of polymer inside may be only a fraction of a percent. We describe objects with such arbitrarily low density as “tenuous”. Large polymers in a solution often amount to no more than a dilute impurity, whose volume fraction is as small as in this

<sup>1</sup>Though the statistical independence of the segments is not quite complete, it becomes rapidly more so as one considers longer segments. For the time being we shall suppose that the segments fluctuate completely independently.

<sup>2</sup>In what follows, we shall see that real polymers are often not exactly random-walk polymers, so that this proportionality is somewhat altered. For the time being, we’ll confine our discussion to random-walk polymers.

sphere. But as we shall see below, this vanishingly small amount of polymer can exert a major influence on certain liquid properties.

These tenuous polymers fit the definition of a *fractal* object. A fractal object is an assembly of particles distributed in space in such a way that the average number of particles  $n(R)$  within a sphere of radius  $R$  surrounding an arbitrary particle varies as  $R$  to some fixed power  $D$  called the “fractal dimension” (Mandelbrot 1982)<sup>3</sup> Any fractal object is tenuous: the average volume fraction  $\phi(R)$  in the sphere is  $v n(R)/R^3$ , which varies as  $R^{D-3}$ . Whenever  $D$  is smaller than 3, as it is in a fractal, the power is negative and  $\phi$  becomes arbitrarily small. Our reasoning from the last paragraph implies that random-walk polymers are fractal objects with fractal dimension  $D = 2$ . One may deduce several important features of how polymers behave in a liquid using only their fractal property.

### III. FRACTALS IN SOLUTION

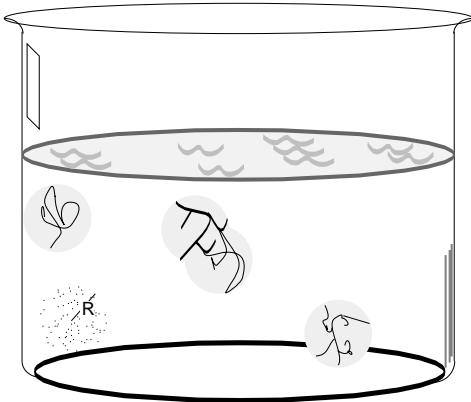


FIG. 2. A liquid containing fractals. Represented are two linear polymers, a branched polymer and a colloidal aggregate. Each has been trimmed to fit into a spherical pervaded volume of radius  $R$ , shown as shaded regions. For comparison a cloud of dispersed monomers from one of the polymers is also shown.

We now imagine many fractal objects floating in solution as sketched in Figure 2. In this section we shall find that depending on their  $D$  values, two fractals in this solution show one of two qualitative different types of interaction. They may be “mutually transparent” and readily interpenetrate each other, or they may be “mutually opaque” and strongly resist interpenetration. Our

main interest is the case where these objects are polymers. But we shall try to make our reasoning applicable for any connected fractal structures, with general dimension  $D$ . In this way our conclusions will be applicable to several types of fractal structure that impart special properties to liquids: random-walk and rigid linear polymers (Elias 1984), branched polymers (Daoud 1995), and colloidal aggregates (Witten *et al.* 1986).

We shall suppose that the constituent particles have size  $a$ , and that all the fractals have the same size  $R$ . For definiteness we can imagine that these had been made by cutting out spherical volumes from a fractal much larger than  $R$ . The region within each sphere is often called the *pervaded volume* of the object. For the time being we shall treat each fractal as a frozen object with no internal motion. We may apply the fractal law  $n(r) = (\text{constant})r^D$  for  $r = a$  to deduce  $n(R) \simeq (R/a)^D$ . Each type of fractal has its own value of the fractal dimension  $D$ , so that the  $n(R)$  for different types of object may be quite different. We imagine that the concentration of objects is roughly as suggested in Figure 2: the distance between objects is somewhat larger than their size  $R$ . Since each of these objects is tenuous, the overall volume fraction of particles is very small. In what follows we shall focus on the limiting behavior as  $R$  becomes *indefinitely* large compared to the particle size  $a$ .

Our problem is to gauge how much these few fractals influence the macroscopic properties of the liquid. One basic influence is their thermodynamic effects, seen. *e.g.*, through the *osmotic pressure* (Reif 1965). If the objects are confined in part of the solution by some membrane that allows the solvent but not the objects to pass, the objects exert an outward average force on the membrane. The force per unit area is the osmotic pressure. Osmotic pressure measurements of polymer solutions are a routine laboratory procedure. Even if the objects exerted no influence on each other, there would be osmotic pressure, just as there is pressure in an ideal gas of noninteracting atoms. But just as the pressure in a real gas differs from the ideal gas pressure, so the osmotic pressure in our solution of objects is not quite the ideal pressure. The difference reflects the influence of the objects upon each other.

These objects influence each other because no two particles can be in the same place at the same time. That means that the objects cannot be positioned arbitrarily in the solution. If we did position them arbitrarily, we would sometimes create illegal configurations in which two or more constituent particles intersected. One way to construct a valid state of the solution is to start by positioning the objects completely at random within it and

<sup>3</sup>The sphere must be much larger than the size of a particle and much smaller than the overall size of the object. One cannot hope to meet both of these conditions arbitrarily well unless the object contains arbitrarily many particles.

then simply removing all the objects that make illegal intersections. When the illegal configurations have been discarded, each object has in effect been pushed out of the excluded volume around the other objects. This reduction of accessible volume increases the osmotic pressure exerted by the objects. The fraction of objects removed for this reason is just the fractional increase in osmotic pressure due to interactions. Thus to gauge the importance of interactions, we may look at an arbitrary object in the solution, and ask what is the probability that it will be discarded because it intersects another.

A convenient way to treat the discarding process is via the “pair distribution function”  $g(r)$ . To define  $g(r)$  we arbitrarily designate a “home particle” near the center of each fractal object. Then  $g(r)$  means the probability that two objects whose home particles are  $r$  apart are in a legal, nonintersecting configuration, which survives the discarding process. If two *solid* spheres of radius  $R$  were placed at random in a very large volume  $\Omega$ , *all* separations  $r < 2R$  would be illegal and all larger separations would be legal. That is,  $g(r) = 0$  for  $r < 2R$  and  $g(r) = 1$  for  $r > 2R$ . The probability of an illegal intersection is simply the illegal volume  $\frac{4}{3}\pi(2R)^3$  divided by the total volume  $\Omega$ . This all-or-nothing picture is not true for fractals. When they are placed close to each other they may nevertheless avoid each other:  $g(r)$  is greater than zero even for  $r < 2R$ . The overall discarding probability is simply that for the solid spheres times the average<sup>4</sup> of  $(1 - g(r))$ , *i.e.*,  $[\langle 1 - g(r) \rangle_{r < 2R} (\frac{4}{3}\pi(2R)^3)]/\Omega$ . The numerator in [...] is called the mutual *excluded volume*  $V_t$  of the two objects in question. If the solution contains a large number of objects  $N$ , the fractional increase in osmotic pressure is simply half the fractional volume excluded to each one: *viz.*,  $\frac{1}{2}NV_t/\Omega$ . Two neighboring fractals have nearly empty solvent in the overlapping regions. Yet the probability of intersection  $(1 - g(r))$  can still be important. Whether this probability is high or low depends on how the particles are arranged. To illustrate this point, let us consider two extreme arrangements with contrasting intersection behavior. In the first arrangement, the  $n$  particles of each object are distributed completely at random within a sphere of radius  $R$ . Thus each fractal is replaced by a structureless cloud with the same

small internal volume fraction  $\phi_i$  as the original fractal. If the separation  $r$  between the clouds is near zero, the two clouds overlap completely. The probability that a given particle of the first cloud intersects is essentially the volume fraction of the second cloud<sup>5</sup>  $\phi_i$ . This probability is much less than unity in a fractal object, as we have seen. But the average number of particles in the first cloud that intersect is the sum of this small probability for each of the  $n$  particles in the first cloud. The average number  $I$  is thus  $n$  times the single-intersection probability, *i.e.*,  $I \simeq n\phi_i \simeq n^2(a/R)^3$ . Using the fractal law:  $n \simeq (R/a)^D$ , the average number of intersections is roughly  $I \simeq (R/a)^{2D-3}$ . If  $D > 3/2$ ,  $I$  becomes arbitrarily large for sufficiently large  $R$ . Random-walk polymers, with  $D = 2$ , are in this category.

Naturally the probability  $g(r)$  of *no* intersection is very small for such clouds<sup>6</sup>. The same reasoning holds if the two clouds are displaced by some distance  $r < 2R$ : the average number of intersections is still arbitrarily large compared to 1. Thus the survival probability  $g(r)$  remains much smaller than 1 for all  $r < 2R$ . These clouds must create osmotic pressure in the solution just as though they were solid spheres of radius  $R$ . This solid-sphere behavior emerges no matter how tenuous the clouds are, provided  $R$  and thence  $n$  are large enough and provided  $D > 3/2$ . Even if we halve the size of the constituent particles of a large cloud, there is no corresponding decrease in the excluded volume  $V_t$ . This volume changes arbitrarily little. There are so many illegal intersections that even when their number is cut by a large factor, the chance of escaping from all of them remains negligible.

This solid-sphere behavior can be greatly weakened by re-arranging the  $n$  particles of our original fractal objects. To show this, we now arrange our particles into solid square rods. Each rod must thus have a width  $w$  such that the volume of the rod is equal to that of all the particles:  $2Rw^2 \simeq a^3n$ . Naturally, this width is much smaller than the length  $2R$ . We may take the home particle to be at the center of each rod. If the two rods are spaced at separation  $r < w$ , then of course  $g(r) = 0$ . But if  $r$  is any fixed fraction of the radius  $R$ ,  $g(r)$  is close to 1. To see this, we consider Figure 3, a picture of the

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<sup>4</sup>Explicitly, we mean the average over all separations  $R$ :

$$\langle 1 - g(r) \rangle_{r < 2R} \equiv \frac{\int_{r < 2R} d^3r (1 - g(r))}{\int_{r < 2R} d^3r 1}.$$

<sup>5</sup>More precisely,  $\phi_i$  is the probability that a given point is occupied by a particle. The probability that some particle intersects a given particle is  $8\phi_i$ .

<sup>6</sup>Specifically, the probability of no intersection for a *given* particle of the first cloud is  $(1 - \phi_i)$ . The probability that all  $n$  particles do not intersect is the product of the (independent) probabilities for each of the  $n$  particles: *i.e.*,  $(1 - \phi_i)^n$ . For large  $n$  and small  $\phi_i$  this product becomes  $\exp(-n\phi_i) \simeq \exp(-I)$ . When the average number of intersections  $I$  is large, the survival probability  $g(r)$  is very small.

two rods with  $r = R/2$ .

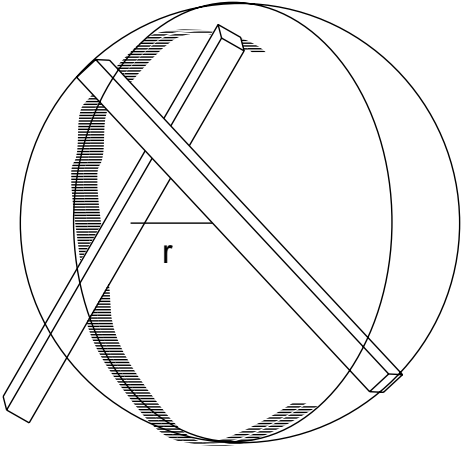


FIG. 3. Two rods of length  $2R$  whose centers are separated by  $R/2$ . The sphere indicates the possible orientations for the rod on the right. The shaded area suggests forbidden orientations which would intersect the other rod.

From the picture it is clear that the rods may easily avoid each other. For any typical orientation of the first rod, the second rod may have almost any orientation without hitting it. Since all orientations are equally likely *a priori*, the probability that the second rod would have a forbidden orientation is proportional to the shaded fraction of the sphere in the Figure. This fraction is small; thus the probability  $g(r)$  that two randomly oriented rods would not intersect is near unity. It is much larger than it was for the two clouds. Accordingly, the excluded volume is much smaller than for the clouds. To work out the allowed orientations and thus the excluded volume is a classic exercise (Onsager 1949). The result is that  $1 - g(r) \simeq w/r$ , compared with 1 for the clouds. The average  $\langle 1 - g(r) \rangle$  is roughly  $w/R$ . Thus  $V_t \simeq (w/R)R^3$ , compared with  $R^3$  for the clouds.

The above examples show that it is a subtle task to gauge the strength of osmotic interactions of our fractal polymers. Even simple rearrangements of the particles can have a big effect on the interaction strength. Happily, though, the intersections of fractals (without any rearrangements) can be readily analyzed. Thus we consider the  $g(r)$  of two fractals with dimensions  $D_1$  and  $D_2$ , both made from particles of radius  $a$ . One way to infer this  $g(r)$  is by analyzing its effect on the number of intersections  $I(r)$ . In fractals, unlike clouds, these intersections are not statistically independent. If one intersection occurs at some point, many others must occur near it. We denote the number of extra intersections by  $M$ . That is,  $M$  is the number of intersections for those objects which have at least one intersection.

This  $M$  can be used to find information about our desired probability  $g(r)$ . We consider two fractals sepa-

rated by a distance  $r$  of order  $R$ . Since they have been placed completely at random, the average number of intersections  $I(r)$  is no different than if they were uncorrelated clouds. But since these objects are fractals, these intersections occur in large groups, and there is some probability—namely  $g(r)$ —that there is no intersection at all. The average number of intersections can be expressed as the probability of an intersection  $(1 - g(r))$  times the number intersections, given that there is at least one. We call this  $M(r)$ ; thus  $I(r) = (1 - g(r))M(r)$ .

This scheme allows us to understand the  $g(r)$  of the clouds and the rods discussed above. For the clouds there is no difference between  $I(r)$  and  $M(r)$ . The average number of intersections  $M$  if there is known to be one is virtually the same as the overall average  $I$ . Thus  $I(r) = (1 - g(r))M(r)$  becomes  $I(r)/M(r) = 1 - g(r)$ . Since the left side is nearly one,  $g(r)$  must be much less than one, as found above. For the rods,  $I(r)$  is unchanged. But the number of extra intersections  $M$  is different. For example if the two rods cross at right angles, the number of intersections is  $(w/a)^3$ . Since intersecting rods typically intersect at some finite angle, the average  $M$  is also of order  $(w/a)^3$ . Now, we recall that  $w^2 \simeq na^3/R$ , and  $I \simeq n^2/R^3 \simeq w^4/(a^3R)$ . Thus  $(1 - g) = I/M \simeq w/R$ , in agreement with our previous conclusion. Intersections must be rare, since any intersection that does occur implies a number of extra intersections that is much larger than the average.

For two general fractals  $M$  and  $I$  are of the same order of magnitude, but not identical. Extending the reasoning above,  $I \simeq n_1 n_2 / R^3 \simeq (R/a)^{D_1 + D_2 - 3}$ . If this exponent is negative, then the average number of intersections decreases indefinitely as  $R$  increases. Then the probability of intersection  $1 - g(r)$  is also indefinitely small. The fractals interfere with each other hardly at all for most  $r < R$ . We say that fractals with  $D_1 + D_2 < 3$  are mutually *transparent* in three-dimensional space. On the other hand if  $D_1 + D_2 > 3$ , the average number of intersections  $I$  is large. The probability of intersection, though smaller than for two random clouds, is still substantial. For example if  $r = \frac{1}{2}R$ , the legal probability  $g(r)$  is a *fixed* number that does not go to zero or to unity as  $R \rightarrow \infty$ . Thus non-transparent fractals can interpenetrate much less than transparent fractals, where  $g(r) \rightarrow 1$ . But they can interpenetrate much more than if their particles were rearranged into random clouds; there  $g(r) \rightarrow 0$ .

The mutual excluded volume of two objects of size  $R$  is the solid-sphere excluded volume times the average  $\langle 1 - g(r) \rangle$ , as noted above. Since  $g(r)$  neither approaches 0 or 1 for most of the sphere volume, its average must also be some finite, nonzero fraction. Thus these fractals have an excluded volume that is a finite, nonzero fraction of the solid-sphere excluded volume, despite their tenuous structure. We term such fractals mutually *opaque*. We conclude that two fractals may interact in one of two qualitatively different ways. If  $D_1 + D_2 < 3$  they are transparent, and have a mutual excluded volume much

smaller than their pervaded volume. If  $D_1 + D_2 > 3$ , they are opaque and have a mutual excluded volume that is a fixed fraction of their pervaded volume<sup>7</sup>.

Whenever two fractals are mutually opaque, their specific fractal dimensions  $D_1$  and  $D_2$  are not important in determining their excluded volume  $V_t$ . The size of their constituent particles is also unimportant. Only their overall size  $R$  is important. The ratio  $V_t/R^3$  must approach a finite limit as  $R$  goes to infinity. Another way to express this scaling is to consider the solid spheres that would produce the same osmotic pressure as the fractals in question. Thus every population of fractals of size  $R$  also has a “thermodynamic radius”  $R_t$ . This  $R_t$  is defined to be radius of solid spheres that have exactly the same excluded volume as the fractals—by definition,  $V_t = \frac{4\pi}{3}(2R_t)^3$ . Since for opaque fractals  $V_t \simeq R^3$ , this means that their “thermodynamic size”  $R_t$  is comparable to their geometric size  $R$ . The ratio of  $R_t$  to  $R$  is an important characteristic of any given type of mutually opaque fractals, including polymers; we shall return to it below.

With these properties of fractal intersection in mind, we may readily determine the order of magnitude of the interactions in a polymer solution, as measured, *e.g.*, by osmotic pressure. We have noted that the excluded volume  $V_t$  directly influences this pressure. Specifically, we may express the pressure described above in terms of the number of fractals per unit volume,  $c_p = N/\Omega$ . As noted above, the osmotic pressure  $\Pi$  for small  $c_p$  is given by  $\Pi \simeq c_p kT [1 + \frac{1}{2} V_t c_p]$ . The front factor, proportional to the absolute temperature  $T$ , is simply the osmotic pressure of an ideal solution of noninteracting objects. Since the coefficient  $V_t$  is roughly the volume within a polymer coil,  $R^3$ , the interaction term becomes comparable with the ideal term when the volume per coil,  $1/c_p$ , is comparable to the pervaded volume within a coil,  $\frac{4}{3}\pi R^3$ . This behavior is well documented in practice. The concentration at which the interaction term becomes equal to the ideal pressure is often called the “overlap concentration”  $c_p^*$ . Qualitatively, our dilute solution of polymers generates much more osmotic pressure than if the chains were collapsed into a compact mass of monomers. Our random-walk polymers produce osmotic pressure qualitatively as though the large pervaded volume within each coil were completely filled with monomers. Gram for gram, the fractal structure of a polymer makes it interact qualitatively more strongly with its neighbors than it would in a compact, nonfractal form. Analogous strong interaction occurs with the fluid solvent itself, as we now explore.

#### IV. DIFFUSION AND FLOW NEAR A FRACTAL

One fundamental way a polymer interacts with its fluid surroundings is by modifying the flow of this fluid. This modification is important. It leads to the thickening of fluids like motor oil, shampoo or salad dressing. The same principles control a simpler phenomenon: the absorption of a diffusing substance by the polymers or other fractal absorbers. The diffusing substance might be a small-molecule solute that sticks to the fractal on contact. It might be some electronically excited molecule that diffuses through the liquid and de-excites when it encounters the fractal (DeGennes 1982). All of these diffusers can be described as a substance with concentration  $u(r)$  initially distributed uniformly throughout the solution at some concentration  $u_0$ . Whenever a particle of this substance encounters the fractal, it disappears. We wish to know how the fractal structure influences the rate of disappearance.

The motion of a diffusing particle is a random walk. Thus the track that such a particle follows has the same fractal properties as a random-walk polymer: both have  $D = 2$ . The encounters between a diffusing particle and a fractal may thus be viewed as the intersection of two fractals. In this view, the tracks of the diffusing particles are a tangle of intersecting random walks whose lengths increase steadily with time. These walks would fill space uniformly were it not for the fractal absorber. But with this adsorber, any particle that touches the fractal must disappear. Thus the random walk representing its future motion must be removed. The remaining random walks are no longer uniform; instead, their density near the fractal is depleted. By analyzing this density we may understand the rate of adsorption. If there is little modification of the diffusing density, there is little adsorption. The most efficient adsorber that can fit within a distance  $R$  of a given center is a perfectly absorbing sphere of radius  $R$ .

As before, it is convenient to designate a home particle on the fractal adsorber. We now consider an arbitrary point at a distance  $r$  from the home point. Despite the absorption we expect some of the walker’s tracks to remain at  $r$ , as shown in Figure 4. The density of such walkers relative to the initial density is the probability that the walker at  $r$  has not been removed by adsorption. This probability is the probability that the random walk representing its past has not intersected the fractal. This probability is precisely the  $g(r)$  discussed in the last section. The fractals in this case are the adsorbing fractal, with dimension  $D$ , and the random walk, with dimension 2. As we saw above, this  $g(r)$  depends on the fractal dimensions. If  $D + 2$  is less than 3, the

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<sup>7</sup>“Borderline” fractals, with  $D_1 + D_2 = 3$ , are neither transparent nor opaque in general and must be treated on a case-by-case basis.

two are mutually transparent:  $g(r) \simeq 1$ . virtually all the walkers in the pervaded volume of the fractal never touch the fractal. Their density  $u$  is thus virtually unaffected:  $u(r) \simeq u_0$ . But if  $D + 2$  is greater than 3, the two are mutually opaque, and  $g(r)$  is substantially smaller than 1 for most points  $r$  within the absorbing fractal. All connected fractals have  $D \geq 1$  and thus show opaque behavior. For all such fractals, including random-walk polymers, the diffusing density is substantially depleted throughout the volume of the absorber.

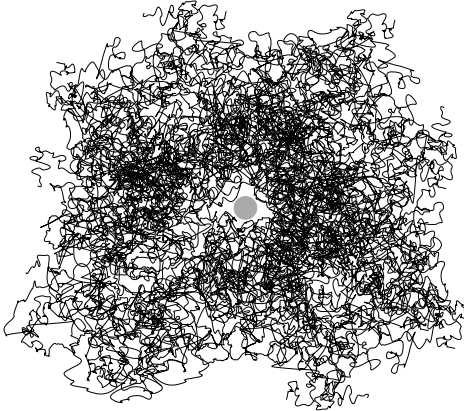


FIG. 4. An absorbing sphere in a uniform sea of random walkers. The density of walkers in the central region was initially uniform. Then all walkers that intersected the absorber were removed. This results in a depletion of density in the vicinity of the absorber. A fractal absorber with dimension  $D > 1$  produces a similar depletion region.

This depletion implies a high rate of adsorption. To see this, we focus on that distance  $r$  such that  $g(r) = \frac{1}{2}$ . The fractal must absorb at least as fast as a sphere of radius  $r$  that absorbs half the particles that hit it<sup>8</sup>. But this sphere adsorbs at a rate comparable to that of a perfectly absorbing sphere of radius  $r$ . Moreover, this  $r$  is some fixed fraction of the fractal's radius  $R$ . These comparisons lead to the conclusion that our fractal adsorbs at a rate comparable to that of a perfectly absorbing sphere of the same size as the fractal. As with the mutual interactions discussed previously, this strong absorption must emerge for a large enough fractal regardless of how small (or how weakly absorbing) its constituent particles are. The indefinitely large number of intersections between mutually opaque objects compensates for any such weakness. A fractal of sufficient size  $R$  adsorbs at the same rate as if it were a perfectly absorbing sphere of some

fixed fraction of  $R$ .

The interaction of a fractal with a gentle flow in the surrounding liquid is similar to its interaction with a diffusing density. If the flow is sufficiently gentle, it has a negligible effect on the shape of even a flexible polymer. A fractal can generate such flows to produce hydrodynamic drag when an external force like gravity is exerted on the fractal. More importantly, the fractal perturbs an imposed flow, thus increasing the dissipation and increasing the effective viscosity of the fluid. The cases considered above lead us to suspect that fractals are especially effective at modifying flow. We shall see below that this is true.

We imagine a fractal held stationary as the surrounding fluid gently flows upward at a speed  $v_0$ . The fractal influences the fluid, because at any point on the (fixed) fractal the adjacent flow velocity must be zero. At some given distance  $r$  from the fractal's home particle there is some average velocity  $v(r)$ . In general, the velocity at  $r$  need not be upward as the flow at large distances is. But for our qualitative purposes it is sufficient to consider only the vertical part of the velocity. The velocity field around the fractal is controlled by the laws of hydrodynamics; these express the balance of forces and accelerations on each fluid element. But in the present situation, the meaning of the hydrodynamic laws can be summarized in a phrase: momentum moves through the fluid by diffusion. The fluid infinitely far from a fractal has a given fixed momentum per unit volume, proportional to its speed  $v_0$ . Each fractal particle absorbs all the momentum density adjacent to it, so that the fluid next to it is motionless. In steady flow, each particle absorbs momentum at some constant rate, and thus experiences a steady force. Momentum absorbed from the fractal particles is replaced by diffusion of momentum from the fluid outside. Thus the velocity field plays exactly the role played by the diffusing field  $u$  treated above. We may view the vertical momentum as being carried by a tangle of random walkers, as with any other diffusing substance (Roux 1987).

Any fractal that is transparent to a diffusing substance is also transparent to flow. Though the fluid is stationary near each particle of the fractal, still  $v(r) \simeq v_0$  throughout most of the fractal volume. The fluid passes right through the fractal. On the other hand, any fractal that is opaque to a diffusing substance is also opaque to a flow. The speed  $v(r)$  throughout the interior is substantially reduced relative to the distant speed  $v_0$ . Since the fluid cannot flow through the fractal, it mostly flows around it. The force on our fractal due to the flow can be expressed in terms of an equivalent hard sphere—which would feel the same force. The radius of this equivalent sphere is

<sup>8</sup>The actual rate is proportional to the sphere's radius, the distant concentration and the diffusion constant of the diffusing substance.

called the “hydrodynamic radius”  $R_h$  of the object. Since the fractal is opaque to flow, this  $R_h$  is comparable to the geometric radius  $R$ , as seen above for the thermodynamic radius  $R_t$ . This means that the fractal absorbs momentum at a rate comparable to that of a solid sphere with the same size as the fractal<sup>9</sup>. The force on the fractal is thus similar to the force on the sphere. Any object moved through a fluid exerts a force depending on its size. By reducing the radius of our solid sphere by a finite factor, we can achieve the same force that the fractal exerts. The radius of this equivalent sphere is defined as the hydrodynamic radius  $R_h$ . Evidently, if the object is a large fractal, the hydrodynamic radius is a fixed fraction of its geometric radius  $R$ .

Hydrodynamic drag on an object also controls the Brownian motion of that object in the solution. Brownian motion is caused by random thermal forces in the surrounding solvent. These forces, like imposed forces, produce a proportionate velocity  $v_0$ , given by the hydrodynamic drag ratio ( $F/v_0$ ) characteristic of the object and solvent. Knowing the velocity resulting from the random thermal forces allows one to calculate the diffusion constant  $\zeta$ . This  $\zeta$  gives the mean-squared distance  $\langle x^2 \rangle$  covered in a given time  $t$ :  $\langle x^2 \rangle = \zeta t$ . Einstein (1905) discovered that the diffusion constant  $\zeta$  of any object at absolute temperature  $T$  is determined by its drag ratio<sup>10</sup>:  $\zeta = kT(v_0/F)$ . Given the drag ratio of our fractals, this means  $\zeta = kT/(6\pi\eta R_h)$ . Thus opaque fractals diffuse in a solution at about the same rate as solid spheres of the same overall size.

This opacity holds for other flow conditions, notably shear flow. In a shear flow, like that in a pipe or a glass of swirling water, the velocity  $\vec{v}(r)$  near the wall runs parallel to it and is proportional to the distance from it. In a shear flow a small cubical region of the fluid distorts into a rhomboidal box as shown in Figure 5. The fractional movement of the top of the box relative to the bottom is called the shear  $\gamma$ ; this shear increases at a constant rate in time; the shear rate is called  $\dot{\gamma}$ . From the point of view of a fractal moving with the fluid, there is right-moving fluid above it and left-moving fluid below it. The fractal particles disturb this flow much as they did the uniform fluid treated above. And again the disturbance is substantial. The flow within an opaque fractal is reduced by a finite factor regardless of how large (and tenuous) the fractal becomes. And as with uniform flow, the change in

the velocity far outside the fractal is comparable to that of a solid sphere whose radius is a fixed fraction of  $R$ .

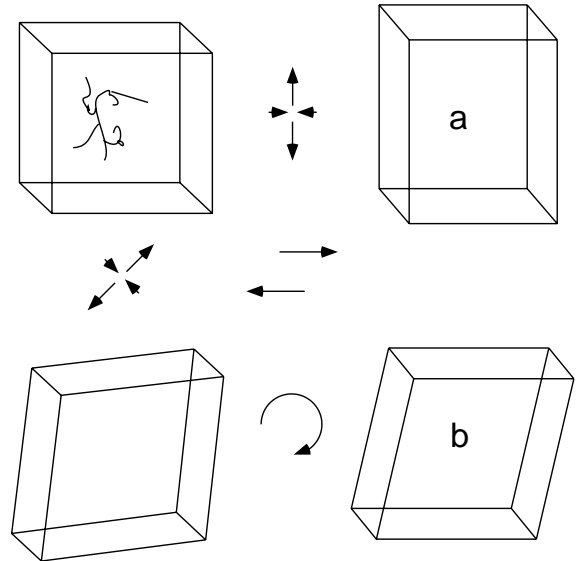


FIG. 5. Two types of flow: a) elongational flow; b) shear flow. The elongational flow shown amounts to a vertical stretching of the upper left picture, as indicated by the arrows. Shear distortion, indicated by opposed arrows at center, can also be effected by a diagonal stretching (lower-left picture) followed by a rotation, to obtain the lower-right picture.

One consequence of the disturbed flow is an increased dissipation of the fluid’s kinetic energy as heat. The power dissipated per unit volume in a small region is equal to the viscosity  $\eta$  times the square<sup>11</sup> of the shear rate,  $\dot{\gamma}^2$ . A solid sphere in a fluid has none of this dissipation within the sphere. But there is extra dissipation outside it: the fluid must flow faster in order to pass around the sphere. The overall effect is to increase the dissipation moderately in a volume comparable to the sphere volume (Happel *et al.* 1973). The extra power  $P$  is 2.5 times that which would have occurred in the sphere volume  $V$  if the sphere had been absent:  $P = 2.5\eta\dot{\gamma}^2V$ .

An opaque fractal produces dissipation much like a solid sphere of the same size. It cannot dissipate more, since no solid object confined within a spherical volume

<sup>9</sup>The actual force  $F$  is proportional to the sphere radius  $R_h$ , the distant speed  $v_0$  and the viscosity  $\eta$  of the fluid. Specifically  $F = 6\pi\eta v_0 R_h$ .

<sup>10</sup>The Boltzmann constant  $k$  is a conversion factor from conventional temperature units to energy units. At room temperature,  $kT$  is roughly 1/40 of an electron volt—a hundred times smaller than the energy needed to break a polymer chain.

<sup>11</sup>The work done per unit time on a cubical volume element of side  $L$  like that of Figure 5b is the (lateral) force on the top (or bottom) of the element, times the speed of the top face relative to the bottom face. In a viscous fluid this force is the product of the viscosity  $\eta$ , the shear rate  $\dot{\gamma}$  and the area  $L^2$ . The speed is the shear rate  $\dot{\gamma}$  times the height  $L$ . Combining, the power  $P$  dissipated in the cube is proportional to its volume  $L^3$ :  $\eta\dot{\gamma}^2L^3$ .



can produce more dissipation than a sphere filling the volume. It cannot dissipate much less since the exterior flow and dissipation are like that of a solid sphere. By shrinking our solid sphere by some moderate factor, we may find a radius  $R_v$  such that the sphere and the fractal have the *same* dissipation. This  $R_v$  is called the “viscometric” radius. Regardless of how large and tenuous an opaque fractal becomes,  $R_v/R$  remains a fixed number, as with  $R_t/R$  and  $R_h/R$  above. We shall return to discuss the value of this fraction and other related ones.

Figure 5a depicts an *elongational* flow, in which a small cube is elongated into a rectangular box. The effect of a fractal on a weak elongational flow is the same as in shear flow. Indeed, a shear flow is equivalent to an elongational flow, as the figure shows. Thus each fractal produces dissipation like a solid sphere with the same radius  $R_v$  in elongational or in shear flow.

Since fractals increase dissipation, they increase the effective viscosity of the fluid: more external work—more force or pressure—is required to maintain a given flow when the fractals are added to the liquid. The macroscopic viscosity  $\eta$  is that required to account for the power dissipated in a volume  $\Omega$ . This power  $P$  is  $\eta\dot{\gamma}^2\Omega$ . On the other hand, this power can be expressed in terms of the power  $P_0$  without the fractals and the extra power dissipated by the  $N$  fractals added. If the viscosity of the pure solvent is  $\eta_s$ , then  $P_0 = \eta_s\dot{\gamma}^2\Omega$ . Each fractal causes a dissipation  $\eta_s\dot{\gamma}^2(2.5V_v)$ , where  $V_v = \frac{4}{3}\pi R_v^3$  is the volume of the equivalent sphere. Adding the dissipation from the  $N$  fractals in the solution volume  $\Omega$  we have  $P = \eta_s\dot{\gamma}^2\Omega[1 + 2.5V_v(N/\Omega)]$ . Here we imagine a solution dilute enough that the flows around the fractals don’t interfere with one another. We recognize the  $N/\Omega$  as the concentration of fractals  $c_p$ . The macroscopic viscosity is increased by the same factor as the power  $P$ :  $\eta = \eta_s[1 + 2.5V_v c_p]$ .

This increase in viscosity is quite similar to the increase in osmotic pressure  $\Pi$  discussed in the previous section:  $\Pi = kTc_p[1 + \frac{1}{2}V_t c_p]$ . Both osmotic pressure and viscosity are increased in proportion to the concentration of fractals. For both quantities the amount of increase per fractal is expressed as a volume,  $V_t$  or  $V_v$ . And for opaque fractals both of these volumes are of the order of the pervaded volume  $\frac{4}{3}\pi R^3$ .

A small amount of fractal material increases the viscosity noticeably just as it increases osmotic pressure noticeably. The same concentration  $c_p^*$  that doubles the osmotic pressure is roughly the concentration that doubles the viscosity. As we noted above, this is the “overlap concentration” at which the distance between fractals  $c_p^{-1/3}$  is comparable to their size  $R$ , and the overall volume fraction  $\phi$  in the solution is comparable to the (small) internal volume fraction  $\phi_i$  within a fractal. Fractals, including polymers, are potent viscosifiers. Many thick fluids in everyday life such as motor oil, or bottled sauces owe their thick consistency to a small proportion of polymers.

In this section we have seen how fractals can modify flow and diffusion in a liquid. In our discussion we have idealized the fractals. We have treated them as completely rigid objects of a fixed size  $R$ . Polymers, though they are fractals, are not rigid and do not have the same size. Each polymer, as it moves through a liquid by Brownian motion, changes its size and shape continually. It is only its average size and shape that stay fixed. Still the laws of flow and diffusion discussed above are applicable. One must simply replace the size  $R$  by an appropriate average size, such as the average distance between two arbitrary monomers. Another effect of a polymer’s flexibility is that the polymer can be readily distorted by flow. In order to have the properties described above the fluids must flow gently enough that this type of distortion can be neglected.

We have seen that polymers, like all opaque fractals, have a number of characteristic effects on a fluid. They produce osmotic pressure and viscosity in the fluid, and they individually experience hydrodynamic drag. Each of these effects can be quantified by a *length*. For the osmotic pressure this was the thermodynamic radius  $R_t$ , the radius of a sphere with the same excluded volume as the polymer. For the viscosity it was the viscometric radius  $R_v$ . For the drag coefficient it was the hydrodynamic radius  $R_h$ . All these radii have roughly the same size, and like the geometric size  $R$  they grow with the molecular weight  $M$  as  $M^{1/D}$ , where  $D$  is the fractal dimension. In the next section, we shall encounter effects that alter the fractal dimension of a polymer from the random-walk dimension of 2. But since our conclusions apply to arbitrary opaque fractals, they apply also to these altered polymers.

## V. HOW SELF-INTERACTION CHANGES THE FRACTAL DIMENSION

The conceptual random-walk polymers we’ve considered up to now are different from real polymers in an important way. A random-walk polymer typically intersects itself many times, while real polymers cannot intersect themselves. A real polymer is “self-avoiding”: two of its atoms cannot be in the same place at the same time! Thus instead of treating polymers as random walks, it would seem more realistic to treat them as *self-avoiding* random walks. The subtleties of self avoidance can lead to large changes in a polymer’s size and hence viscosity with a few-degree shift in the temperature, as explained below. The differences between random walks and self-avoiding random walks also form an important subject in mathematical polymer physics. Our goal here is to give some account and some feeling for these differences.

If we consider all the possible bond angles of a polymer, we will generate a large set of configurations. Many of these configurations have monomers that intersect each other, and are hence unrealistic. One way to arrive at the proper set of realistic configurations is to start with

the full set of random-walk polymers and then discard the self-intersecting ones. (This is the same discarding process we used above in our discussion of interactions between fractals.) The fraction of the original configurations remaining is the probability that the polymer is self-avoiding. We wish to know how much the remaining self-avoiding polymers differ in their properties from the full set of random-walk polymers.

We may begin with the full set of random-walk configurations and then start examining them for self-intersections. For convenience we imagine that our polymer contains a number of monomers  $n$  that is an integer power of two:  $n = 2^K$ . We group the  $n$  monomers of the chain into  $n/2$  pairs. We group each two adjacent pairs into a quartet, thus forming  $n/4$  quartets. Then we group each two adjacent quartets into an octet, to form  $n/8$  octets. We continue in this way ( $K$  times) until we've made one final pairing containing the first half and the last half of the monomers. Now we discard self-intersecting configurations in stages. First we discard those in which a monomer intersects with its paired monomer. Non-intersecting pairs are somewhat larger on the average than unrestricted pairs. But since intersections are still freely allowed for other monomers, the overall structure of our chain is still a random walk. It is merely expanded by some factor because all the elementary pairs within it have been expanded by the same factor as a dimer. We call this factor  $\alpha_1$ . Next we discard configurations in which a dimer intersects with its paired dimer. Figure 6 shows the result for two dimers making a quartet. The effect on an isolated quartet is to expand it by some modest factor  $\alpha_2$ . The overall chain is expanded by the same factor, leading to a cumulative expansion from both stages of  $\alpha_1\alpha_2$ . After many such stages, we must consider chain-sections with  $m$  monomers. Each half of the section already avoids itself, but the two halves do not avoid each other. We now discard all configurations in which the first half intersects the last half. We have seen above that the probability of intersection is substantial if the two halves are fractals with  $D > 3/2$ . Configurations with a smaller size will be more likely to intersect than those of a larger size. Thus when the intersecting ones are discarded, the remaining ones have a larger average size. The expansion factor  $\alpha_k$  at the  $k$ -th stage is finite and limited even for arbitrarily large segments. *i.e.*, it is insensitive to the stage  $k$ . Accordingly, we replace it by  $\alpha$  with no subscript.

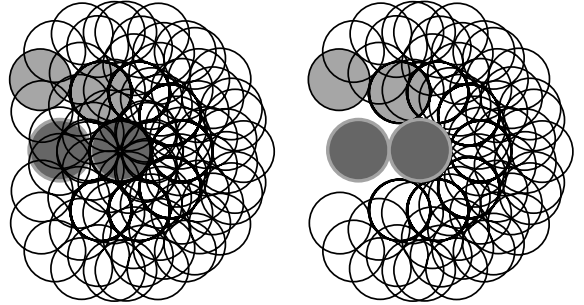


FIG. 6. A two-dimer chain with no avoidance between the two dimers (left) and with avoidance (right). Some possible positions of the right half are sketched. The average end-to-end distance is a factor  $\alpha_2$  larger in the self-avoiding case.

After all the intersections from the various stages above have been discarded, we have a completely self-avoiding chain. On the other hand, each stage has expanded the overall size by a factor  $\alpha$ . This expansion factor is (except perhaps for the earliest stages) independent of the stage  $k$ . Thus the overall expansion factor is  $\alpha^K$ , where  $K$  is the total number of stages. We conclude that the final size  $R$  is related to the original random-walk size  $R_0$  by  $R = R_0\alpha^K$ . Using  $R_0 = (\text{constant})n^{1/2}$  and  $K = \log n / \log 2$ , we have  $R = (\text{constant})n^{1/2 + \log \alpha / \log 2}$ . Since a fractal obeys  $R = \text{constant} n^{1/D}$ , our self-avoiding chain acts like a fractal of dimension  $D = 1/(1/2 + \log \alpha / \log 2)$ . This argument leads us to expect that self-avoidance maintains the fractal nature of a polymer, but decreases its fractal dimension. These arguments are borne out by more detailed work (Jannink *et al.* 1992).

The fractal dimension  $D$  must not decrease too much. If it became smaller than the dimension of mutual opacity,  $D = 3/2$ , the consistency of our arguments would break down. For then, when we imposed self avoidance between the two halves of a segment, these two halves would not be mutually opaque. Their probability of intersection would be indefinitely small. Accordingly, the fraction discarded would be small, and the discarding process would have virtually no effect on the size of the segment. The expansion factor  $\alpha$  would approach 1. This would be true for virtually all the stages  $k$ , so that the above formula would lead to an unmodified  $D$ .  $D$  would remain 2 as in a simple random-walk polymer. That is, the assumption that  $D < 3/2$  leads to the conclusion that  $D = 2$ : a contradiction. We are thus forced to the conclusion, first noted by Des Cloizeaux (Des Cloizeaux 1970), that  $2 > D > 3/2$ . The actual properties of self-avoiding polymers have been studied by detailed calculations, by computer simulations, and by measurements on real polymer solutions. All these approaches confirm that these polymers, like random-walk polymers, are fractals. They have a  $D$  very close to  $5/3$ —a value consistent with Des Cloizeaux's inequality.

Since real polymers are fractals just as random-walk polymers are, the properties we deduced for general fractals apply to real polymers. Since  $D > 3/2$ , they are opaque to one another. Thus they increase osmotic pressure as though they were hard spheres of radius  $R_t$  comparable to their average geometric size  $R$ . Since real polymers have  $D > 1$ , they are also opaque to diffusing substances and to flow. They experience hydrodynamic drag and enhance viscosity as though they were solid spheres roughly as large as their geometric size  $R$ . Large real polymers have hydrodynamic radii  $R_h$  and viscosimetric radii  $R_v$  that is a fixed multiple of the geometric size  $R$ . These multiples depend only on the fractal structure, and not on the specific polymer: they are the same for all sufficiently large polymers. Measurements on a number of polymers and solvents have established the ‘‘Graessley ratios’’<sup>12</sup> (Davidson *et al.* 1987)  $R_t : R_h : R_v : R = 1.01 : 1 : 1.03 : 1.9$ .

A real polymer must always avoid itself in any solvent. Yet a real polymer need not always behave as a self-avoiding walk with  $D \simeq 5/3$ . This is because the basic effect of self avoidance can be modified by other effects. In some solvents the monomers feel an effective attraction for each other: they are more likely to be near each other than if they were placed in the solution at random. We must take account of this attraction as well as the self avoidance when we consider the expansion of a polymer. For example, in the tetramer of Figure 6, we saw that throwing out the self-intersecting configurations makes the average size expand. But because of the attraction, monomers which are close together like the shaded ones in Figure 6 should be given extra weight compared to monomers that are far apart. This extra weight tends to reduce the average size of the pair. It can happen that the reduction in size caused by the attraction just compensates for the increase in size caused by the self-avoidance, so that the expansion factor  $\alpha$  is 1. When this happens for many stages  $k$ , the attraction completely compensates for the repulsion and the fractal dimension  $D$  remains 2 like a random-walk polymer. Naturally, this compensation requires a very specific amount of attraction between the monomers. Thus even a small change in temperature can destroy the compensation. A solvent and temperature for which the compensation is perfect is called a ‘‘theta solvent’’. For example, for the polystyrene

pictured in Figure 1, the solvent cyclohexane near  $35 \pm 1$  degrees Centigrade is a well-known theta solvent (Janink *et al.* 1992). In practice, an increase of temperature by only 10 degrees from the theta temperature can double the volume of a long polymer and thus increase the solution viscosity significantly. Solvents with attraction weaker than this compensating amount are called ‘‘good solvents.’’ All good solvents show some net self repulsion. Since the self repelling pieces are mutually opaque, the probability of discarding becomes independent of the repulsion strength. The expansion factors  $\alpha_k$  reach the same value for large segments (large  $k$ ) even when some attraction is present. Thus for all ‘‘good solvents’’ the large-scale behavior<sup>13</sup> is that of a self-avoiding walk, with  $D \simeq 5/3$ .

If this cyclohexane is *cooler* than 35 degrees, the attraction becomes stronger than the compensating value. Polymers in such a solvent become progressively smaller than the random-walk size: they have a  $D$  that is larger than 2. Such polymers attract one another in solution as well as attracting themselves. Thus it is difficult to isolate them and measure their  $D$  definitively. Such solvents are called ‘‘poor solvents’’.

## VI. SOLUTIONS OF MANY POLYMERS

The properties of individual polymers are strongly determined by their fractal structure, as we have seen above. This is even more true as we increase the concentration of our polymer solution from the dilute limit studied above. As we shall see, the fractal structure accounts for the oozing, springy flow of substances like mucus and silly putty. For simplicity in what follows we shall consider only good solvents, containing polymers with  $D = 5/3$ . As the number of polymers per unit volume  $c_p$  increases, so does the osmotic pressure  $\Pi$ . As we have seen,  $\Pi/(kTc_p) \simeq 1 + \frac{1}{2}V_i c_p$ . We saw that the concentration  $c_p^*$  at which the second term becomes equal to the first is the concentration at which the pervaded volumes of the different coils begin to overlap. It was thus called the overlap concentration. The associated volume fraction  $\phi^*$  is roughly the internal volume fraction  $\phi_i \simeq (R/a)^{-4/3}$  within a coil. The work done to

<sup>12</sup>The geometric measure  $R$  used here is the radius of a solid sphere that would have the same root-mean-square distance between arbitrary monomers that the polymer has. The values reported are for high-molecular-weight polystyrene in benzene. Reported values for other polymers in good solvents differ from these by several percent; this variation is consistent with experimental error. Several of these lengths are equal within experimental error, but there is no theoretical reason to believe they are exactly equal.

<sup>13</sup>Naturally, chains in solvents close to the theta state must become very long in order to attain the asymptotic self-avoiding behavior. The chain size required for self-avoidance to become significant is called the ‘‘thermal blob’’ length  $\xi_t$  (Daoud *et al.* 1976). Chains smaller than a thermal blob size are approximately random-walk chains. Even chains much larger than this size behave as simple random walk fractals with  $D = 2$  on length scales  $r \lesssim \xi_t$ . This  $\xi_t$  goes to infinity as theta-solvent conditions are approached.

compress a solution to  $\phi^*$  is roughly the osmotic pressure times the volume  $\Omega$ . Thus a sizeable fraction of this work is due to the interactions between polymers. This work is called the free energy. Since  $\Pi \simeq kT c_p^*$ , the free energy is roughly a thermal energy  $kT$  for each chain. For typical polymers, with a molecular weight of  $10^5$ , this characteristic pressure is of the order of  $10^{-3}$  atmosphere.

The overlap concentration  $c_p^*$  is an important dividing line in polymer solutions. Solutions much less concentrated than  $c_p^*$ , are effectively dilute and interactions between the polymers are unimportant. Solutions much more concentrated than  $c_p^*$  have strong interactions between the polymers. They are strong enough to distort the polymer coils substantially and to bring about cooperative motions of many chains.

As the volume fraction increases above  $\phi^*$ , the chains interpenetrate. Concentrations much larger than  $\phi^*$  but still much smaller than unity are called “semidilute.” A chain in the semidilute regime interacts strongly with many other chains. Accordingly, its structure is much altered from the self-avoiding walk structure of a dilute chain. To understand this structure, it is convenient to build the semidilute solution by joining chains originally at the overlap concentration  $\phi^*$ . These primary chains have an internal volume fraction  $\phi_i$  roughly equal to the overall volume fraction  $\phi$  of the solution. This means they have a particular size  $\xi$  satisfying  $\phi \simeq \phi_i \simeq (\xi/a)^{-4/3}$ . We choose an initial  $\xi$ -chain at random and then connect one of its ends to the nearest available end from another chain. Since the initial chains were at  $\phi^*$ , the two ends to be joined are no farther apart than about a chain-size  $R$ . Thus the joining does not distort the two chains very much. After doubling all the chains in this way, we repeat the process so that each chain is quadrupled in length. With sufficient repetitions we may increase the chain length as much as desired, while keeping the volume per chain constant. This joining process thus takes us further and further above  $\phi^*$ .

These chains interpenetrate strongly, with many chains occupying the pervaded volume of each. All these chains must avoid each other and not intersect. But unlike dilute chains, these interpenetrating chains gain nothing by expanding into a self-avoiding-walk structure. To see this, we consider doubling one of the chains by joining two nearby ends together. The two pieces joined have no special alignment with each other; their end-to-end vectors are unrelated to each other—they must each avoid many other chains as well as avoiding each other. Thus when the two are joined, the two halves remain uncorrelated, as in a random walk discussed in the first section. The mean-squared end-to-end distance is just double that of each half. This argument holds for all subsequent doublings, as well. Thus the long, interpenetrating chains are like simple random walks, with  $D = 2$ . This contrasts with the situation in a pure solvent. There, if two chains are joined, the two halves tend to be aligned, and the mean-squared end-to-end distance is significantly

more than doubled, in accordance with self-avoiding walk behavior.

Though our interpenetrating chains have the overall structure of a simple random walk, the original  $\xi$ -chains that were joined to create the final chains have their original self-avoiding structure. Semidilute chains thus obey two different fractal laws. The amount of chain  $n(r)$  enclosed in a radius  $r$  grows as  $r^{5/3}$  if  $a \ll \xi$ . But for  $\xi \ll r \ll R$ ,  $n(r)$  grows as  $r^2$ . The  $\xi$ -chains are often called “blobs” (Daoud *et al.* 1975). The density of monomers around a given monomer is shown in Figure 7. The chains of a semidilute solution each come in contact with arbitrarily many others. The various chains are strongly entangled with one another. The result resembles a network of random strands.

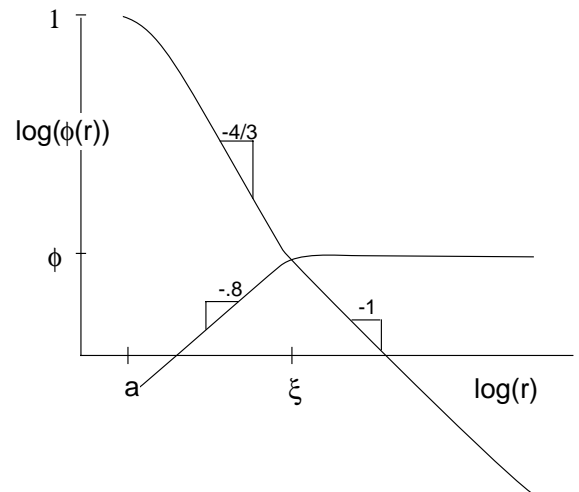


FIG. 7. Local volume fractions of monomer  $\phi(r)$  at distance  $r$  from an arbitrary monomer in a semidilute solution of very low concentration  $\phi$ . Solid curve, monomers from the chain going through the origin. Dashed curve, volume fraction of other chains. Scales are logarithmic, so that power laws appear as straight lines. Within a blob size  $\xi$  the total volume fraction is dominated by the chain passing through the origin. Beyond the distance  $\xi$  the total volume fraction is dominated by other chains.

From the joining construction above we can also understand the osmotic pressure in a semidilute solution. As noted above, the pressure is important because it counts the amount of free energy stored in the solution. Before the joining process, we have seen that this energy is about  $kT$  per chain. When the first two chains are joined together, the distance to the surrounding chains is not much changed. Thus the interaction energy with these chains is about the same before and after joining. This continues to be true as the joining process continues. Thus after this process, the interaction energy remains about  $kT$  per joined segment, as it was originally. That

is, the interaction free energy and osmotic pressure are of order  $kT$  per blob<sup>14</sup>. Expressed in terms of the volume fraction  $\phi$ , we may write  $\Pi \simeq kT/\xi^3 \simeq (kT/a^3)\phi^{3/(3-D)}$ . This prediction that  $\Pi \sim \phi^{9/4}$  and is independent of chainlength is well verified experimentally, as shown in Figure 8. We may readily remove *all* the solvent from our solution and increase the volume fraction to unity. Sometimes removing the solvent causes crystallization of the polymers, or it immobilizes them in a glassy structure. But at high enough temperature the chains in this solvent-free state remain in the liquid state called the melt. In this melt state the blob size has been reduced to a monomer size  $a$ . The density at all distances from a given monomer is as uniform and constant as in a small-molecule liquid. The chains are then simple random walks at all length scales much larger than a monomer. The osmotic pressure in this state is difficult to define, since all the solvent has been removed. It is progressively more difficult to remove the last traces of solvent; in this sense the osmotic pressure becomes large on the scale of  $kT$  per monomer.

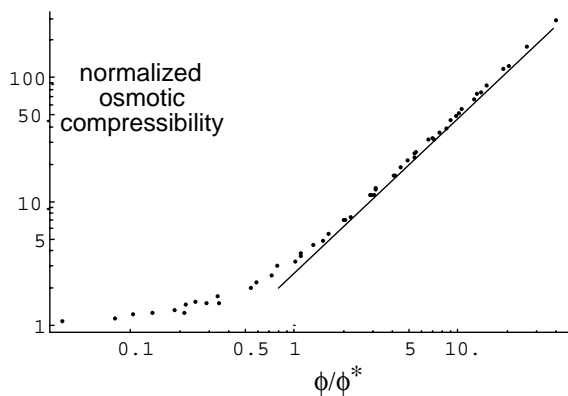


FIG. 8. Osmotic compressibility *vs.* volume fraction for various polymers and solvents. Osmotic compressibility means change of osmotic pressure with volume fraction. Horizontal scale is volume fraction  $\phi$ , relative to  $\phi^*$ . Vertical scale is osmotic compressibility relative to its value in the dilute limit. The scales are logarithmic. Points are combined data on three samples of poly  $\alpha$ -methyl styrene in toluene, differing by a factor of five in molecular weight (Noda *et al.* 1981), and one sample of polyisoprene (natural rubber) in cyclohexane (Adam 1988). The superposition of this data suggests that all long polymers in good solvents have the same osmotic-pressure behavior. The line indicates the expected  $\phi^{5/4}$  behavior in the semidilute regime.

## VII. DYNAMIC RELAXATION IN POLYMER SOLUTIONS

The most important and obvious property of a polymer solution is the way it flows. A polymer solution flows in a springy, syrupy way quite different from the flow of a simple liquid like water or gasoline. To understand these distinctive flow properties, we must understand how the polymers move through the liquid.

In a quiescent dilute solution a polymer, like any other molecule, moves via diffusion: the motion is a random walk, whose mean squared distance  $\langle x^2 \rangle$  covered is the diffusion constant  $\zeta$  times the elapsed time  $t$ , as noted in Section IV. The various chains are far apart and thus they do their random motions independently. As the concentration approaches  $\phi^*$ , this ceases to be true. The random currents moving one polymer are also felt by its neighbors, so that nearby chains have similar motions. To characterize the motion we must specify two diffusion coefficients: the self-diffusion coefficient and the cooperative diffusion coefficient. The self diffusion coefficient  $\zeta_s$  is defined by the motion of an individual chain.  $\zeta_s \equiv \langle x^2 \rangle / t$ , as introduced above. Neighboring chains impede the random currents near a given chain; thus  $\zeta_s$  decreases as the concentration increases. The other important aspect of diffusion is the spreading of extra local concentration in the solution. The extra material spreads over a distance  $x$  whose square is proportional to time. The “cooperative diffusion coefficient”  $\zeta_c$  gives the constant of proportionality:  $\zeta_c = x^2 / t$ . A small region of extra concentration is under extra osmotic pressure. This extra pressure, due to the repulsive interaction between the polymers, tends to spread the chains in the concentrated region apart faster than they would otherwise

<sup>14</sup>In this argument we ignored the interactions between the segments being joined. It is correct to ignore these, because the osmotic pressure and the work to compress the solution to the given concentration  $\phi$  are both expressed relative to the dilute state. In the dilute state the final chains have already been joined together. Thus it does not contribute to the work of compression and should not be counted.

spread. Thus the interactions increase  $\zeta_c$ . And thus as the concentration increases from zero,  $\zeta_c$  increases from its limiting value of  $\zeta$ , just as  $\zeta_s$  decreases.

At semidilute concentrations, these two diffusion constants become qualitatively different. If the chains in a semidilute solution are more concentrated in a given region, the extra concentration can spread by having the solvent move into the region through the entangled network of polymers. This flow is impeded by the polymers just as it is near an isolated polymer. The flow must go around the chains rather than going uniformly through them, as we saw above. This impeded flow depends on how the monomers collectively produce drag. This drag is about the same in the semidilute solution or in a similar one obtained by cutting the blobs apart from one another. But with the blobs cut apart in this way, the solution is now at the overlap concentration  $\phi^*$ . Here we can readily estimate the cooperative diffusion coefficient. It is not greatly different from the dilute diffusion constant of an isolated blob. We saw in Section IV that this diffusion constant is inversely proportional to the radius  $\xi$ :  $\zeta_{blob} = kT/(6\pi\eta_s\xi)$ . We have deduced in the last section that the blob size  $\xi$  decreases as the concentration increases:  $\xi \simeq a\phi^{-3/4}$ . Combining, we infer that  $\zeta_c \simeq kT/(\eta_s a)\phi^{3/4}$ . The cooperative diffusion becomes faster as the concentration increases. But joining the chains to make them longer has no effect on the cooperative diffusion.

To deduce the *self*-diffusion coefficient  $\zeta_s$  we must ask how a given polymer coil moves in the semidilute environment. Its motion is strongly impeded because it is entangled with many other chains. To understand the diffusion, we must understand the disentanglement process. There is one way for a chain to move that does not require the motion of other chains. It may simply move along its own contour as a worm does. This “reptation” motion arises from the independent Brownian motions of the different blobs composing it. It is simplest to visualize this motion of a chain along its contour by imagining that the sequence of  $K$  blobs making up the chain lie in a straight line. Each blob is subjected to independent random forces. Considering the combined effect of all of these, there is some net tendency at a given moment for the chain to move to the left or to the right. It is simplest to consider the motion of the center of mass, since this center can only depend on the external forces on the chain. The total external force is the sum of  $K$  independent random forces, one for each blob. The external forces are the same whether the blobs are connected or not. If they are not, then each blob diffuses independently with diffusion constant  $\zeta_{blob}$ . The center-of-mass has position  $x = \sum_k x_k/K$ . The mean-squared center-of-mass position  $\langle x^2 \rangle$  is the average of those of its blobs:  $\langle x^2 \rangle = \langle x_k^2 \rangle/K$ . Thus the diffusion constant of the center of mass is reduced from that of a blob by a factor of the number of blobs in a chain  $K$ . Now we may readily account for the effect of connecting the blobs. The

connections generate internal forces amongst the blobs. But such forces don’t affect the center-of-mass motion. Thus they don’t affect the diffusion constant. The self diffusion along its contour is  $K$  times smaller than that of a disconnected blob.

From this contour diffusion constant, we may deduce the time for a chain to diffuse its own contour length  $\xi K$ . This time is called the “reptation time”  $\tau_{rep}$ . We may express it as  $\tau_{rep} \simeq (\xi K)^2 K/\zeta_{blob}$ . This  $\tau_{rep}$  is evidently proportional to the cube of the chainlength; it can easily reach tens of seconds, even without especially large molecular weights. From this  $\tau_{rep}$  we can deduce the self-diffusion constant. In the time  $\tau_{rep}$  the chain moves its own size  $R \simeq \sqrt{K}\xi$  as it moves its own length along the contour. The self-diffusion constant can thus be written  $\zeta_s \simeq R^2/\tau_{rep} \simeq \zeta_{blob}/K^2$ . It is much smaller than the cooperative diffusion constant  $\zeta_c$ , which is roughly the size of  $\zeta_{blob}$ . It is also much smaller than the diffusion constant  $\zeta$  in the dilute state where the chain has size  $R_0$ :  $\zeta = \zeta_{blob}(\xi/R_0)$ .

With these dynamical responses in mind, we can account for the most important type of relaxation in a polymer solution: the relaxation of mechanical stress. This stress arises, *e.g.*, when the solution is stretched along some axis as it would be if poured from a vessel. When this stretching is done more rapidly than  $\tau_{rep}$ , the polymer chains cannot disentangle during the stretching. Each chain is obliged to elongate with the sample as a whole, and thus becomes distorted. With each successive blob, a given chain encounters other chains that constrain it. Thus if the sample is stretched by a factor of two, each blob is obliged to elongate by roughly a factor of two as well. The force exerted to cause the stretching supplies the energy to distort these blobs. The work required to pull the ends of any free polymer a distance comparable to the chain size is of the order of the thermal energy  $kT$ . Since each blob is elongated to this degree, each blob stores about  $kT$  of energy under a unit elongation. If our solution is rapidly released from this stretched position, the restoring forces on the chains bring them back to their undistorted shape; the sample springs back elastically to its original shape, like a solid. This is the origin of the elasticity of rubber. It is also the cause of the springy behavior of a raw egg white, of viscous fluids in our body, and of many other liquids in daily life.

Now if the sample is not released but is held in its stretched position, the chains move by the same reptation responsible for self diffusion. As they move, they are able to disengage from each other. The entanglements that initially constrained the chains unravel and the chains become undistorted again. The time required for this is the time for a chain to reptate out of its initial constraints: *i.e.*, the reptation time  $\tau_{rep}$ . Thus the initial applied force relaxes on this time scale. Now if the sample is released, there is no restoring force and it keeps its distorted shape. Over this time scale it has flowed like a liquid rather than springing back like an elastic solid.

## VIII. CONCLUSION

In their atomic makeup the polymer solutions we have considered differ very little from a simple liquid like water. Water consists of a mass of small molecules that may move about freely, subject to the lenient constraints of the liquid state. In a polymer solution almost all of this freedom remains. Only a small fraction of the atoms are linked in sequence so that their mutual separations are fixed. These sequences are the flexible polymer chains. We have seen that even a small fraction of these chains changes the macroscopic properties of the liquid dramatically. It creates large spatial structures which are very effective at modifying flow, transmitting stress and increasing viscosity. In addition these structures store mechanical energy in a convenient form over macroscopic times.

The polymer phenomena sketched here now constitute a mature field of science. Most of the phenomena are well documented experimentally and are understood theoretically. They reveal a type of matter that is distinctive, controllable, and understandable from a few basic principles. This understanding now forms the basis for a wealth of new phenomena involving polymers. Polymer chains in new architectures such as branches, combs, and loops change the nature of entanglement and disentanglement. Polymers in confined geometries—adsorbed or grafted to surfaces, in thin wetting layers, or in adhesive layers—produce new types of flow and interaction with bulk fluid. Heterogeneous polymers with mutually immiscible parts phase separate on a molecular scale, forming controllable, periodic patterns. The elements of fractal structure, interpenetration, and deformability that make simple polymers interesting and useful promise also to create further surprising behavior in these new situations.

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## IX. KEY TO SYMBOLS (IN ORDER OF APPEARANCE)

- $n$  Number of elementary segments in a polymer.
- $\langle \dots \rangle$  Means average over some fluctuating quantity:
- $a$  Length of a step in a random-walk polymer.
- $R$  Radius of imaginary sphere used in defining fractal properties. Radius of the truncated fractal objects defined in the text.
- $n(R)$  Average number of chain segments within distance  $R$  of an arbitrary segment.

- $\phi$  Volume fraction: the fraction of the fluid's volume occupied by polymers or other solutes.
- $D$  Fractal dimension from the formula for the distribution of matter in a fractal object:  $n(R) \propto R^D$
- $g(r)$  Pair distribution function describing the number of particles at a displacement  $r$  from a given particle.
- $\Omega$  Volume of the solution being studied.
- $N$  Number of solute objects in the solution being studied.
- $V_t$  Thermodynamic volume or excluded volume: the volume rendered inaccessible to the solute objects in a solution by the addition of one further solute object.
- $R_t$  Thermodynamic radius: radius of a sphere whose volume is  $V_t$ .
- $c_p$  Number concentration of solute:  $N/\Omega$ .
- $\Pi$  Osmotic pressure in a solution.
- $kT$  Boltzman constant times temperature.
- $c_p^*$  Overlap concentration, at which the osmotic pressure rises to twice its ideal-solution value.
- $\eta$  Viscosity of a solution.
- $R_h$  Hydrodynamic radius: radius of a sphere with the same drag coefficient as a given solute object.
- $\zeta$  Diffusion constant.
- $\gamma$  Shear strain or shear.
- $\dot{\gamma}$  Shear rate: rate of increase of shear per unit time.
- $R_v$  Viscometric radius: radius of here that increases the fluid viscosity the same amount as given solute object does.
- $\xi_t$  Size of a segment of a polymer above which self-avoidance effects become important.
- $\phi^*$  Overlap volume fraction: Volume fraction of a solution whose solute particles are at a concentration  $c_p^*$ .
- $\xi$  Blob size: geometric size of polymers that would be at their overlap concentration in a solution of given volume fraction.
- $\phi(r)$  Local volume fraction at a distance  $r$  from an arbitrary monomer.
- $\zeta_s$  Self-diffusion constant defined from measurements of a single object's displacement over time.

$\zeta_c$  Co-operative diffusion constant defined from measurements of the density of solute objects over time.

$\tau_{rep}$  Reptation time: time for a polymer to move a distance equal to its radius through the tangle of other polymers constraining it.

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