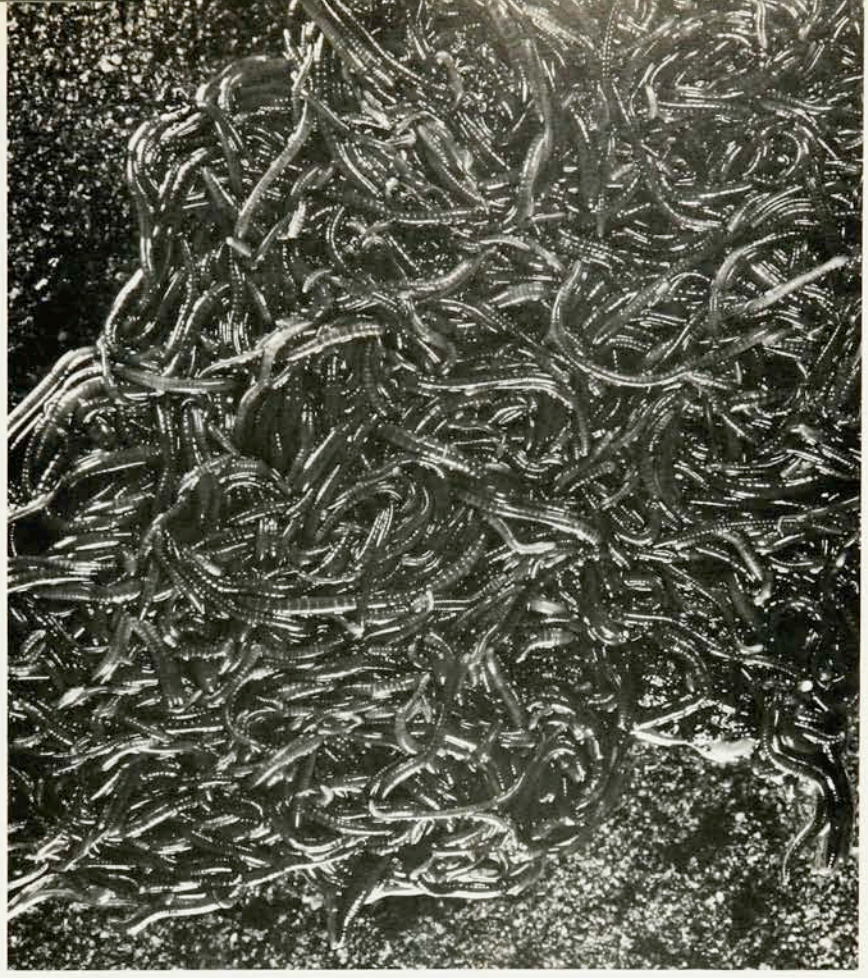

Tangle of long earthworms. The motion of these "Red Wigglers" through the snarl suggests an analogy with the motion of long polymer molecules in the melt. (Photograph of *Lumbricus rubellus* by Runk/Schoenberger; from Grant Heilman, reproduced by permission.)

Entangled polymers

A theory based on the snake-like motion by which chains of monomers move in the melt is enhancing our understanding of rheology, diffusion, polymer–polymer welding, chemical kinetics and biotechnology.

Pierre-Gilles de Gennes

Most of us have played with lumps of "silly putty," the strange substance shown in the photographs on page 34. Given a bit of time, this material flows like a viscous liquid. Forced to respond quickly, it bounces like rubber. We can trace this "viscoelastic" behavior,[1] which shows up in all polymer melts, to the knotting of the chains of "monomers" that make up the polymers. Shearing forces tend to undo certain knots, but this takes a finite time τ. In a time greater than τ the original knots fade out, and the melt flows. Over shorter times the original knots are all present, and the melt behaves like an elastic network.

A major question—and the subject of this article—is how to transform these qualitative ideas into a theory. The most natural approach would involve a detailed analysis of knot structures and knot statistics, and many researchers have tried this. However, they have met with limited success for a number of reasons:

- To define topologically a knot between two curves, each curve must be closed. However, the essential behavior of chains at times close to τ depends directly on the fact that they are open, and can modify their knots.
- The theory of knots is far from complete. Mathematicians know explicitly only a few topological invariants characterizing knots.[2]
- As we will see, the scaling law for the time τ is expected to be the same for different dimensionalities of space. Of course, this is a very formal statement, but it suggests that the specific features of knot invariants in three dimensions are not very relevant.

In this article we will concentrate on a different approach, whose development was prompted by these problems. As we will see, with this approach one focuses on the situation of the individual polymer chains as they move in the complex polymer melt by "reptation" (from the Latin *reptare*, to creep), much as snakes would move through a set of fixed obstacles.

Reptation

Before we look at the details of the reptation theory,[3] let us look at an important example of the type of parameter that it predicts. A polymer melt at a given temperature has a measurable characteristic frequency $1/\tau$ separating the viscous domain from the elastic domain.[1] The time τ is extremely sensitive to the length of the polymer chains in the melt. If we specify this length in terms of the

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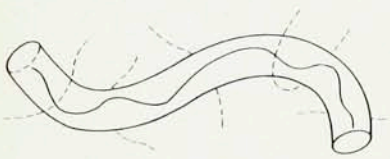
number N of monomers in the chain, we find

$$\tau = \tau_0 N^a$$

where τ_0 is a microscopic time on the order of 10^{-10} seconds in melts, and experimental values of the exponent a are about 3.3. We will see shortly that the theory based on the idea of reptation, through a very straightforward argument, gives 3 for the exponent a.

Because the number N of repeat units in the chain can be of order 10^4, the characteristic time τ can be very long—on the order of minutes. The characteristic time may be very long even when the polymer melt is far above its glass transition temperature, the temperature at which polymer molecules first begin to move globally in the melt.

In a polymer melt, the chains can change their shape, and move, by local Brownian motion, but they cannot intersect each other. Sam Edwards was the first to point out[4] that under these conditions, each chain is confined to a "tube," as this schematic diagram shows (and the photograph on the previous page suggests).

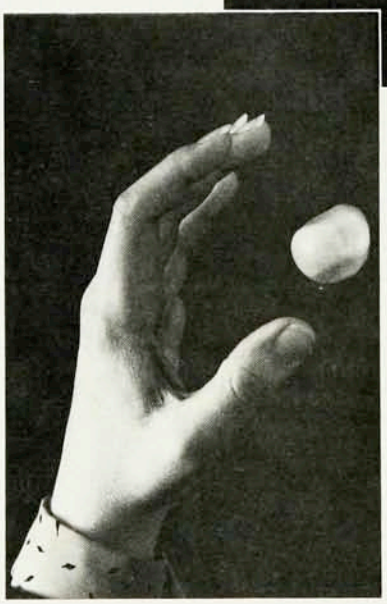


The diameter of this tube is related to the minimum size of a knot, and is of order 50 Å for conventional melts.

If we follow one chain in the melt—call it a "test chain"—we will see it moving by snake-like motion inside its own tube.

Let us consider time intervals that are comparable to τ. For such long intervals we may ignore the details of the test chain's "reptation" and take a macroscopic point of view, in which the test chain moves as a whole, like a wet rope in a pipe. One essential parameter is then the chain's "tube mobility" μ_{tube}, defined as v/f, where v is the velocity with which the chain moves along the tube when it is pulled by a force f. This mobility is inversely proportional to the chain's length, for which N is our measure.

Silicone putty, a viscoelastic polymer derived from dimethyl silicone oil. The particular formulation shown here is sold as "Silly Putty." (Photographs courtesy of Dow Corning Corporation, Midland, Michigan.)



Now we can use the Einstein diffusivity relation to calculate the chain's Brownian motion along the tube

$$D_{\text{tube}} = kT\mu_{\text{tube}}$$

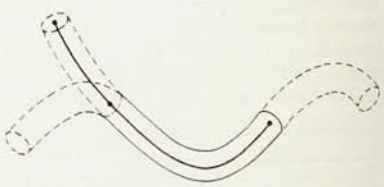
Thus, the diffusivity is also inversely proportional to the chain length N. Along a fixed tube, then, a polymer chain's mean square displacement $s^2(t)$ due to Brownian motion has the standard form

$$s^2(t) = 2D_{\text{tube}}\, t \qquad (1)$$

We are now fully equipped to understand the nature of the relaxation time τ. The sketch at right illustrates the basic process of relaxation, in which the chain generates new tube portions at random as it advances. The original tube is completely wiped out after a time τ for which $s(\tau)$ is comparable to the original tube length L. Thus

$$\tau \simeq L^2/D_{\text{tube}} \sim N^3$$

Here we have used the fact that L is linear in N while D_{tube} is inversely proportional to N. The proportionality of the relaxation time to the cube of the chain length is the fundamental result of the reptation model. Only recently, computer model calculations have confirmed[5] the general picture and the transition from local wiggling motions to an overall Brownian motion along the tube.



These ideas led Masao Doi and Edwards to develop[6] a precise theory of

viscoelastic effects in melts. For small perturbations, that is, for linear viscoelasticity, their major result is the detailed form of the "memory function," which gives the stress at time t as a function of the strain rates at earlier times t'. It turns out that the memory function $M(t-t')$ is exactly proportional to the "tube memory" that the above sequence of sketches illustrates—the average fraction of the chain length that, at time t, is still trapped in the tube that was defined at time t'. Computations[3] of this fraction show that it decreases exponentially at large times:

$$M(t) \to \alpha \exp(-t/\tau)$$

More generally, the Doi–Edwards analysis appears to give a good description of the rheology of entangled polymers provided that the distribution of polymer chain lengths N is narrow and the molecular weight is high enough that the macroscopic description given by equation 1 is valid at all relevant times. A detailed study on polystyrene solutions, at Kyoto University in Japan, indicates that the Doi–Edwards equations work even in the nonlinear regime, provided that the above conditions are well satisfied.

Self diffusion

Consider one test chain, or "coil," suitably labeled to be recognized in the melt. After a time t very large compared with the tube lifetime τ, this chain's center of mass will have moved a distance x, of mean square

$$x^2 = 2D_{\text{rep}}t \qquad (t \gg \tau) \qquad (2)$$

The self-diffusion coefficient D_{rep} is much smaller than the tube diffusivity D_{tube}. This is because each tube is very much contorted, so that any movement of the chain along the tube produces a much smaller movement of the chain's center of mass.

It is relatively simple to estimate the self-diffusion coefficient. We divide the interval t into pieces of duration τ. Successive pieces are then statistically independent. During one piece the coil has moved by something like its own statistical size R_0. In these melts $R_0 = aN^{1/2}$, where a is the size of the monomer.[7] Thus we may write

$$D_{\text{rep}} \approx R_0^2/\tau \sim N^{-2}$$

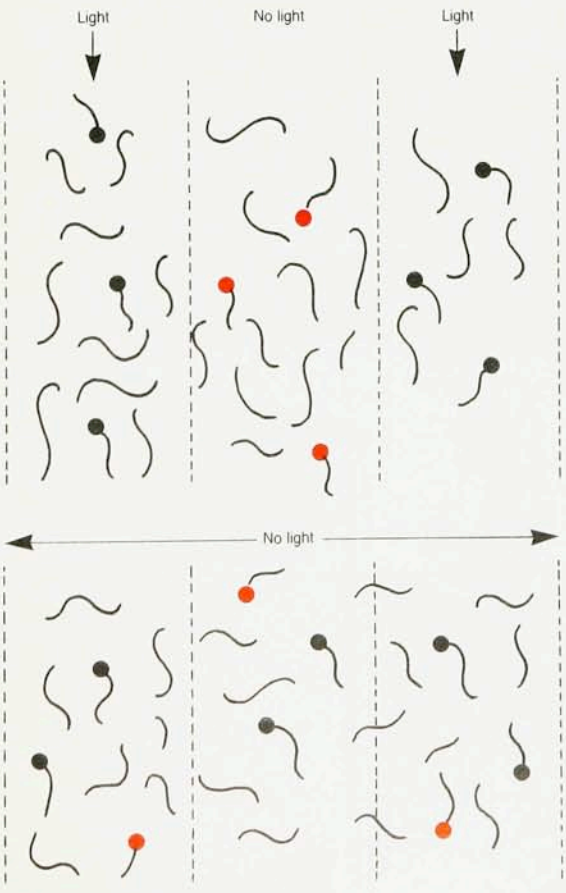
The self diffusivity is very small, typically 10^{-11} cm^2/sec, so that to measure it requires either very long times t, or the ability to measure relatively short spatial intervals x. Researchers at Cambridge carried out the first group of systematic experiments[8] measuring $D_{\text{rep}}(N)$. In these experiments the labeled species was deuterated polyethylene, which was allowed to diffuse in a protonated polyethylene melt. The local fraction of deuterated polyethylene was measured by infrared spectroscopy on thin slices of a nearly glassy polymer. The spatial resolution was about 100 microns and the times involved were roughly one month.

Forced Rayleigh scattering[9] mandates a very different choice of diffusion time and distance. With this technique the labeled chain carries a photochromic group; this is a cyclic molecule that opens up its cycle upon irradiation, thereby changing its absorption. The sample is illuminated with an optical fringe pattern, which creates a spatially periodic distribution of photoexcited molecules, as indicated in the figure below. The net result is an absorption grating inside the sample. After one cuts off the illumination, the grating fades out by diffusion of the labeled species, and this fading out is monitored by a probing laser, which measures as a function of time the Bragg scattering intensity due to the grating. Here the diffusion length is the spatial period of the grating—a few microns—and the decay times are rather short—on the order of minutes.

A third technique[10] is based on proton resonance in a pulsed field gradient, which measures the mean-square self-diffusion distance $x^2(t)$ directly. For very long times, one does find that x^2 is linear in time as expected from equation 2.

All these techniques appear to converge and give a self-diffusion coefficient $D_{\text{rep}}(N)$ that decreases as N^{-2}; thus the reptation model appears to work, and it gives good results even for surprisingly small values of the chain length N.

Most of the above considerations hold not only for melts, but also for polymer solutions in good solvents. (What the physical chemist means by a "good" solvent is one in which the polymer chains *repel* each other. In a bad solvent, they attract each other and ultimately precipitate.) Entanglement effects are still observed in solutions, provided that the concentration c is not so low that the chains fail to overlap each other. Increasing the concentration increases the number of entanglements, and the self diffusivity decreases. A rather naive scaling theory predicts that the self-diffusion coefficient is proportional to $c^{-1.75}$, which appears to fit data from the forced



Forced Rayleigh effect. A polymer melt or solution containing a few chains that are labeled with a photochromic dye (circles) is exposed to a spatially periodic pattern of intense light. In the illuminated regions the dye becomes dark; elsewhere it remains transparent. The successive dark and transparent slabs fade out by diffusion. This fading is monitored through the Bragg reflection of light from a low-power laser.

Rayleigh-scattering experiments.[9]

It is important to realize that in a binary system—polymer and solvent—we can define *two* macroscopic diffusion coefficients. One of these is the self diffusion coefficient D_{rep}. The other one, called the cooperative diffusion coefficient D_{coop}, is measured by probing the fluctuations of the global concentration and seeing how they fade out in time.[11] We call this diffusion cooperative because the concentration profile relaxes by motions where all chains drift together in the solvent—they do not have to disentangle. Cooperative diffusivity is an *increasing* function of concentration because at high concentration the osmotic forces, which tend to make the system uniform, are stronger.

Some practical problems

Many problems of polymer engineering stem from reptation effects. Viscoelastic behavior is an obvious example, with many consequences for the molding and extrusion of plastics. Here, however, we shall focus our attention on a couple of more recent questions.

Polymer dissolution is an important (and delicate) industrial process. One starts with droplets of a certain radius r_0 and concentration c_0 immersed in pure solvent. Of course, the smaller the radius of the droplets, the faster they dissolve, but one is limited in practice because preparing very small droplets requires more time and more energy. What is the optimum radius? Recent theoretical work[12] based on reptation concepts gives a partial answer to this question. The dissolution occurs in two steps. In the first step, the solvent causes the transient polymer network to swell as in a gel. The rate for this step is controlled by the cooperative diffusion coefficient D_{coop}. In the second step the transient network yields; the knots are removed in a time $\tau(c_0)$, the reptation time of the original network. A crucial parameter is the length

$$l = (D_{coop}\tau)^{1/2}$$

The dissolution of large droplets, that is, droplets for which $r_0 > l$, is limited by the first step. The time required for swelling is the diffusion time ${r_0}^2/D_{coop}$, and is larger than the reptation time τ. On the other hand, the dissolution of small droplets, that is, those for which $r_0 < l$, is limited by the second step. This takes a time τ, the reptation time, which is independent of the radius. Thus one gains nothing by choosing $r_0 < l$. The optimal droplet size, then, is $r_0 = l$. This leads to interesting scaling laws for the optimal droplet size as a function of molecular weight, and as a function of the concentration c_0.

Another important practical question is chemical. One of the major methods for synthesizing polymers is by radical polymerization. Each growing polymer chain carries one free radical, and the reaction ends when two such radicals recombine. How does the recombination rate depend on chain length? We can analyze this for long chains by a detailed study of the Brownian motion of a single monomer at times t less than, but close to, the reptation time τ. In this time range, equation 1 gives the displacement $s(t)$ along the tube, but the displacement $x(t)$ of the long chain's center of mass is much smaller. Because the shape of the tube is contorted as in a random walk, its rms displacement is

$$x(t) \sim [s(t)]^{1/2} \sim t^{1/4}$$

This explains the strange behavior of the displacement $x(t)$ observed by proton resonance in a pulsed field gradient at times less than τ, that is, for very long chains.[10]

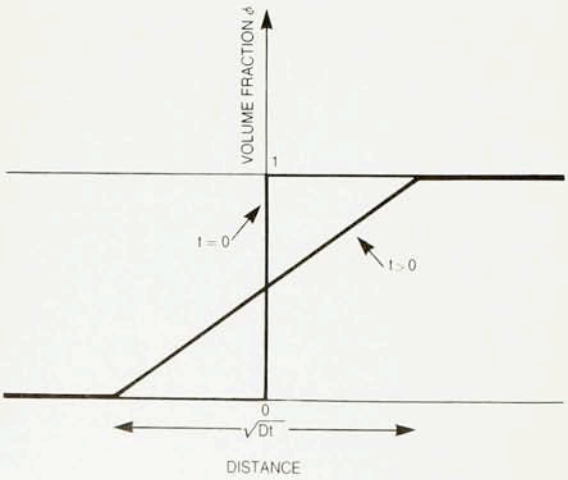
The rule that the displacement x is proportional to $t^{1/4}$ leads to very remarkable laws of approach for reactants carried by polymer chains.[12,3] It will take some time to check these laws with systems having highly uniform distributions of reactants. However, with the aid of suitable photophysical techniques such as excitation transfer and fluorescence quenching, the prospects are rather good.[13]

Polymer–polymer interdiffusion

In most cases, chemically different polymers are not miscible. However, there are a few interesting exceptions to this rule. For example, if we put a block of polyvinylchloride (PVC) in contact with a block of polycaprolactone (PCL) we find that they tend to mix at temperatures slightly above that of the glass transition. Researchers at the University of Massachusetts, Amherst, have studied[14] the shape of the diffusion profile using electron-induced x-ray fluorescence, a sophisticated technique that allows them to probe very locally the chlorine concentrations inside the mixing region.

It turns out that the diffusion laws here are very different from what is observed in ideal mixtures such as those we described earlier. Recall that in the ideal case, we found that the diffusion constant is proportional to N^{-2}. In the miscible case, the diffusion is a slower function of the chain length, being proportional to N^{-1}. This slower function was a surprise at first, but now we see that the basic reason for it is relatively simple. The enthalpy of mixing of the pure PVC and PCL is negative; in more familiar terms, PVC monomers like to be surrounded by PCL and rush to the PCL side. This introduces a driving force on each polymer molecule proportional to the number of monomers it contains, and thus explains the change from N^{-2} to N^{-1}.

The shape of the polymer–polymer interdiffusion profile is not classical. In conventional diffusion, we see rather smooth profiles (they are related to error functions). But for "compatible mixtures" such as PVC/PCL, the diffusion constant is very sensitive to the local concentration or volume fraction ϕ. When this volume fraction is about $\frac{1}{2}$, we have the fast process described in the preceeding paragraph. But when the volume fraction is near 0 or 1, the diffusion constant is very small. For instance, when we have a single PVC chain floating in PCL, it has the optimal environment and is not pushed strongly towards the PCL side. Thus the diffusion constant $D(\phi)$ nearly vanishes at both ends of the concentration range. Solving the resulting nonlinear diffusion equation leads to the profile



Diffusion profile. This is the simple but unusual profile predicted for the interface between two miscible polymers in contact. Instead of the usual smooth profile, one expects two well-defined boundaries. (From reference 21.)

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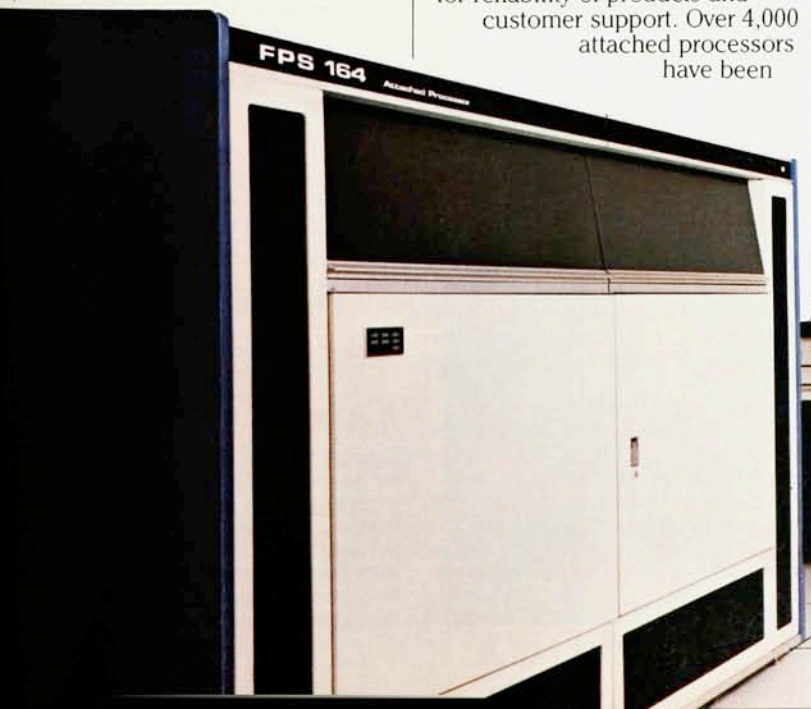


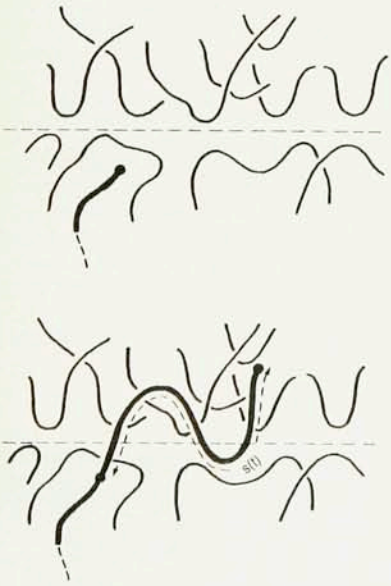
plotted in the figure on page 36, which shows that the mixing region has two sharp boundaries. The thickness of the mixing region does increase like the square root of the diffusion time, but the shape, while simple, is quite unusual.

Polymer–polymer welding. One can weld a pair of polymer blocks by bringing them into close contact and maintaining them slightly above the glass transition temperature for a certain time t. Interdiffusion takes place, and the junction develops mechanical strength. The essential difference with the preceding case is that for the purposes of welding, the interesting time interval t is *smaller* than the reptation time τ. In other words, the thickness of the mixing layer is smaller than the size of a coil.

In some experiments[15] carried out in Lausanne, Switzerland, researchers monitored the state of the mixing layer by fracturing the junction and measuring the fracture energy per unit area, G, as a function of the welding time. Experimentally $G(t)$ saturates after one reptation time τ, and increases at earlier times according to

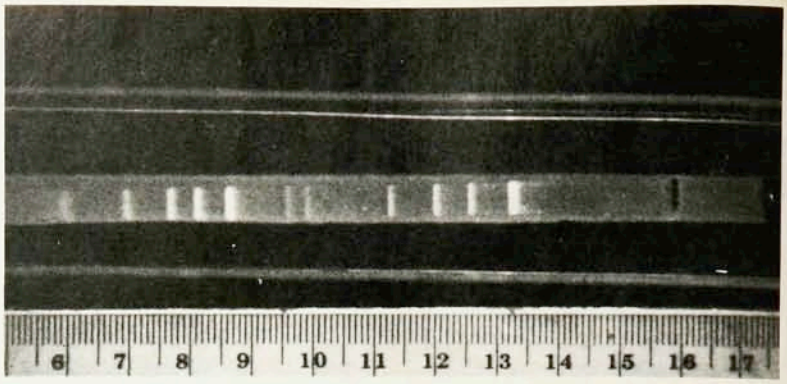
$$G \simeq G_{max}(t/\tau)^{1/2} \qquad (t < \tau)$$

The following sketch suggests a microscopic picture of the welding process.



The chains from the bottom half migrate by reptation over a curvilinear distance $s(t)$ given by equation 1. The fracture energy G is approximately the product of the migration distance s and the local stress σ at the fracture tip. This means that the work required to "pull out" a chain portion of length s is proportional to s and to the local force.[16] It is plausible to think of the stress as reaching at fracture a certain yield stress that is a material constant of the glassy polymer. Then the fracture energy G should increase like $t^{1/2}$, as observed. A group at the University of Illinois in Urbana has developed[17] a somewhat different, but related, argument that leads to the same final laws.

We have restricted our discussion here to two blocks of the same polymer. With different polymers that are miscible, the situation is more complex because there is a thermodynamic force favoring the mixing. This situation is not completely understood.



Gel electrophoresis of DNA. A solution containing about one quarter of a microgram of eleven different lengths of double-stranded DNA, ranging from 310 base pairs to 23 600 base pairs, was loaded in a well (at the right in the picture) that was cast in a gel. An electric field of a few volts/cm, maintained for a few hours, caused the DNA molecules to migrate to the left. Those with the smallest molecular weights moved the farthest. The DNA fractions are made visible by allowing them to adsorb a fluorescent ion, ethidium. When irradiated with ultraviolet light, the bands of DNA give off an orange glow. (Courtesy of Charles P. Bean and Hubert Hervet.)

Molecules drifting in gels

Polyacrylamide gel electrophoresis is an important technique used to select various biomolecules, such as DNA fragments, according to their molecular weight. The charged macromolecules are incorporated into a water-swollen gel, where they drift under the influence of an electric field E, with a velocity μE. The electrophoretic mobility μ is found to decrease with the molecular weight M, and this allows for the separation, an example of which appears in the figure above.

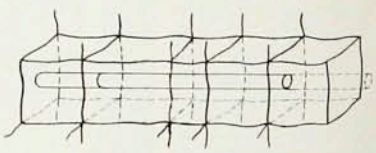
Charles P. Bean of the General Electric Research and Development Center in Schenectady, New York, and Hubert Hervet of the Collège de France have studied[18] in great detail the laws for $\mu(M)$ in agarose, a different but comparable gel.

Two simple limits emerge:

▶ When the chain is short, it behaves like a rigid rod. Here the friction coefficient f, the ratio of force to velocity, is proportional to the chain length, and the force is proportional to the charge Z. This gives a mobility that is independent of chain length, so that in this limit there is no electrophoretic separation.

▶ When the chain is long, it appears as a flexible object, and reptation prevails. From the Einstein relation, the friction coefficient f is related to the self diffusivity by $D_{rep} = kT/f$, and thus the friction coefficient is proportional to N^2. Then the mobility μ, which is Z/f, is proportional to N^{-1}, and there is a strong selection effect.

Bean and Hervet have derived an exact interpolation between these two limits, and this fits the data remarkably well. Some problems remain, however: The chain rigidity required to fit $\mu(N)$ is anomalous, and it may be that the rigid-rod limit for short chains is more complex than expected.[19] The essential point, apparent in the following sketch, is that the rod moves in *one* dimension for times long compared with τ, because it cannot rotate easily in the gel.



Because the gel is a random medium, we are dealing with one-dimensional motion in the presence of random barriers, for which the simple laws of friction do not hold. On the average, a high barrier will be hit many times before being passed. This leads to very strange mobility laws, which have been

studied in the completely different context of one-dimensional conductors.[20]

Although these last remarks are very specific to rigid chains, they may serve as a general warning; while the reptation ideas that we have examined in this article have helped us reach a simple vision of motion in melts, they may well need some deep revisions in the future.

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