Polymers: Their Movement and the Transition to Reptation Motion as a Function of Polymer Length

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Polymers

Polymer is a term for large organic molecules that consist of a small number of repeated structural units, called monomers, strung together to form a long, usually flexible chain. Polymers are ubiquitous in industry, as they make up the plastics, resins, and other commercial products. They are also critical to biological systems, as the most important classes of biological molecules, proteins and nucleic acids, are polymers. Understanding polymers and their properties is thus vitally important to industry and biology. Several textbooks discuss polymers, including the text by Doi,[1] and there is a good introduction to the subject at wikipedia. A picture of a typical polymer, poly(2-vinylpyridine) taken with an atomic force microscope, taken from the paper by Roiter and Minko,[2] can be seen in Figure 1.

In this paper, we are primarily interested in understanding the diffusion properties of polymers, as these properties determine such properties of polymers as the behavior and appearance of polymer melts and the diffusion of

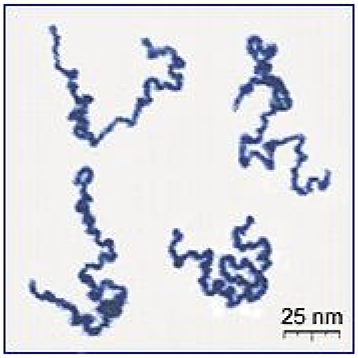

Figure 1: Poly(2-vinylpyridine) image taken with an atomic force microscope.

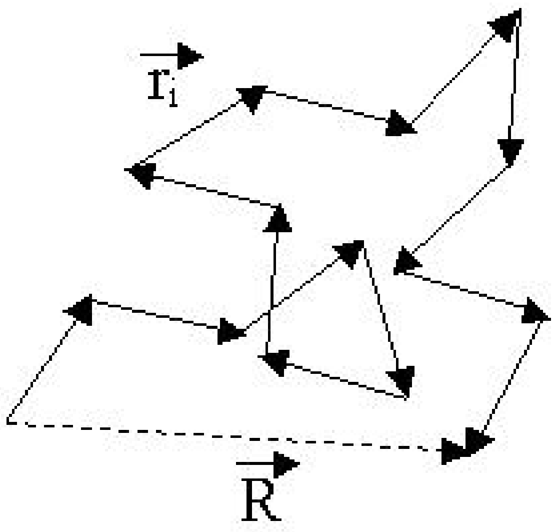

Figure 2: Gaussian chain model

polymers through electrophoresis gels. These phenomena are described by the theory of reptation, and we will now discuss several preliminary ideas in polymer physics and modeling.

Gaussian chain model

One of the first polymer models was the Gaussian chain model, or random coil model, introduced by Flory,[3] which models the polymer as a chain of monomers with a total unfolded length of

$$L = Nl \tag{1}$$

where N is the number of monomers in the chain, and l is the length of a single monomer. Flory assumed that the distance and direction between adjacent monomers would be distributed as a Gaussian. This is a reasonable assumption for some real chains in the absence of interactions between the monomers, although some important polymers, like proteins and DNA do not agree well with this model because the monomers of these polymers react strongly because they are charged. The Gaussian chain model is illustrated in Figure 2.

Under these assumptions, the probability, ω, of finding the end of a polymer chain whose first monomer is at the origin of the coordinate system within a sphere of radius r around the origin is given by a Gaussian distribution

$$\omega(x, y, z)dxdydz = \left(\frac{b}{\pi^{1/2}}\right)^3 \exp\left(-b^2r^2\right) dxdydz \tag{2}$$

More details of this model can be found at Chapter 3.

Persistence length and the worm-like chain

Unfortunately, the Gaussian chain model does not include some aspects of real polymer chains that are known from experiment. For example, the Gaussian chain model gives a finite probability for the polymer chain to be much longer than L, which is obviously problematic because the lengths of real polymers are rarely variable. Also, the direction of connections between monomers is not normally independent of the connections that came before, as is assumed in the Gaussian chain model. Instead, the monomers cooperate over short distances, where they tend to all point in the same direction. In fact, many polymers appear more like a rubber tube than the loose, flexible coil postulated by the Gaussian chain model. These considerations led to the development of the worm-like chain model, or the Kratky-Porod worm-like chain model.[4]

In this model, the polymer is represented as a rubber tube, rather than a chain of monomers, with a relaxed length of L, as given above. To give the tube rigidity at short distances, it was assumed that curvature in the tube gives an energy penalty to the polymer. This enforces the observed behavior of real polymers that neighboring monomers are aligned in the same direction. Because the curvature is proportional to the square of the tangent vector to the tube, the energy can be defined to be

$$E = k_b T \int_0^L \frac{A}{2} \left| \overrightarrow{t}\,(s) \right|^2 ds \tag{3}$$

where $\overrightarrow{t}(s) = \frac{d\overrightarrow{r}(s)}{ds}$ with $\overrightarrow{r}\,(s)$ the position of the chain a tangential distance s from the beginning of the chain. Many real polymers, like DNA, can be modeled as worm-like chains. A is defined as the persistence length, and it is the length over which the tangent of the chain remains correlated. With this energy definition, $\overrightarrow{t}\,(s)$ is correlated with $\overrightarrow{t}\,(s')$ with a correlation function given by

$$\left\langle \overrightarrow{t}\,(s) \centerdot \overrightarrow{t}\,(s') \right\rangle = \exp\left(- \left| s' - s \right| / A\right) \tag{4}$$

The mean square distance between the ends of the chain, $\langle R^2 \rangle$, is given by

$$\left\langle R^2 \right\rangle = 2AL \left[1 - A/L \left(1 - e^{-L/A} \right) \right] \tag{5}$$

An illustration of a worm-like chain can be viewed in Figure 3, and more information about the worm-like chain model is available from worm-like chains and this paper by Bouchiat et al., which focus on using a worm-like chain model to describe experiments with pulling forces applied to polymer chains.

Diffusion Properties

For many applications of polymer science, the diffusion properties of polymers are vitally important. For example, in polymer melts, which are used for plastics, rubbers, resins, and other industrial applications, the diffusion properties

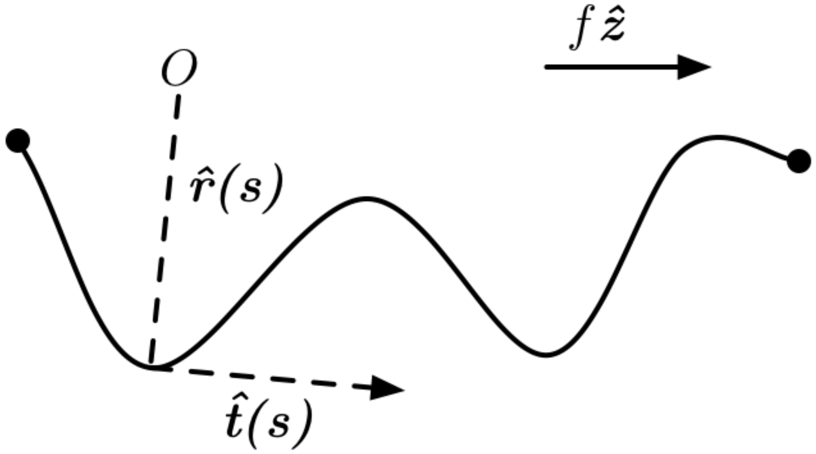

Figure 3: Worm-like chain being stretched by an applied force f. The chain has an inherent directionality formed by the cooperative behavior of the monomers in the chain.

of individual polymers determine the properties of the bulk substance. For example, it was found that polymers smaller than a critical size formed waxy substances in their semi-crystalline state, while longer polymers tended to form more solid, usable plastics, such as nylon and polyethylene. Also, when gel electrophoresis was being developed to identify DNA by separating a mixture of DNA segments by size, it was found that small segments of DNA could not be separated by this method while segments that were longer than the critical length could be. To understand these behaviors, theoretical models of polymer diffusion that included a phase transition had to be developed. The eventual explanation of this problem was the reptation theory, but other models were developed first, and some details of one of these, the Rouse model, is required to understand reptation.

Rouse model

This is a simple model of polymer diffusion that attempts to combine the features of the Gaussian chain model and the worm-like chain model to obtain an accurate description of how polymers diffuse through their environment. The model assumes that the polymer chain can be described as a series of stiff spherical segments, reflecting the stiffness of the polymer at short distances, which are connected by springs whose length can be described as a Gaussian. Friction with the environment is experienced by the small spherical stiff segments. Figure 4 from the book by Strobl[5] represents this model, and a general introduction to the model can be found at Rouse Model. For the purposes of understanding the reptation model later, one result of the Rouse theory that is required is the

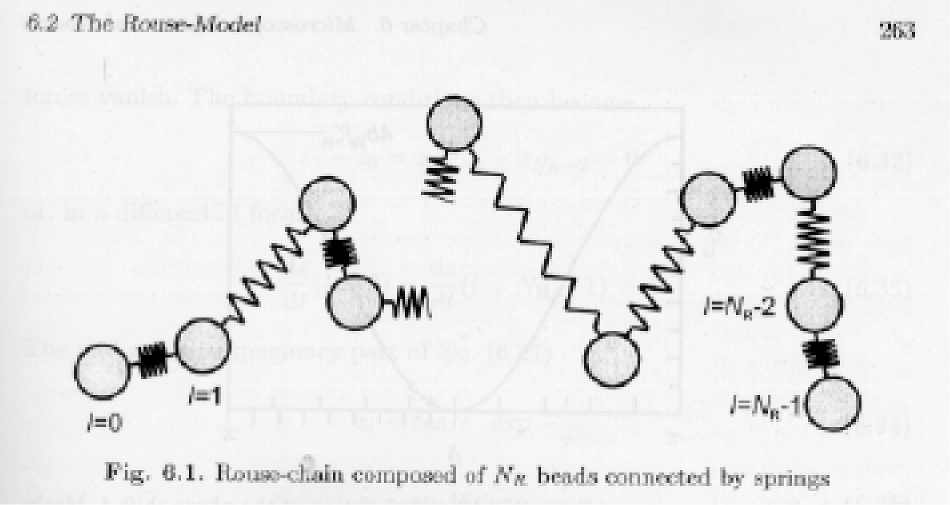

Fig. 6.1. Rouse-chain composed of N_R beads connected by springs

Figure 4: Rouse model for polymer motion. The segments of the chain are connected by springs. The total friction between the polymer chain and the environment is proportional to the number of segments.

friction factor, z_p of a Rouse chain:

$$z_p = N z_r \tag{6}$$

where N is the number of monomers in the polymer chain and z_r is the friction factor of the individual units of the polymer chain. The friction factor is in turn related to μ, the ratio, v/f of the velocity, v imparted to a polymer by an external force f by

$$\mu = 1/z_p \tag{7}$$

From this expression, the diffusion constant of a Rouse polymer chain can be derived using the Einstein relationship,

$$D = k_b T \mu \tag{8}$$

D is therefore inversely proportional to N in the Rouse model.

Reptation model

The Rouse model above works fairly well at describing the motion of small polymers through small solvents and melts made up of small polymers. However, as mentioned above, it was found that several properties change abruptly once the length of the polymer exceeds a minimum length, about 10 M_e where M_e is the length of the rigid sections in the Rouse model. The theoretical model that explains this behavior is the reptation model. By assuming the existence

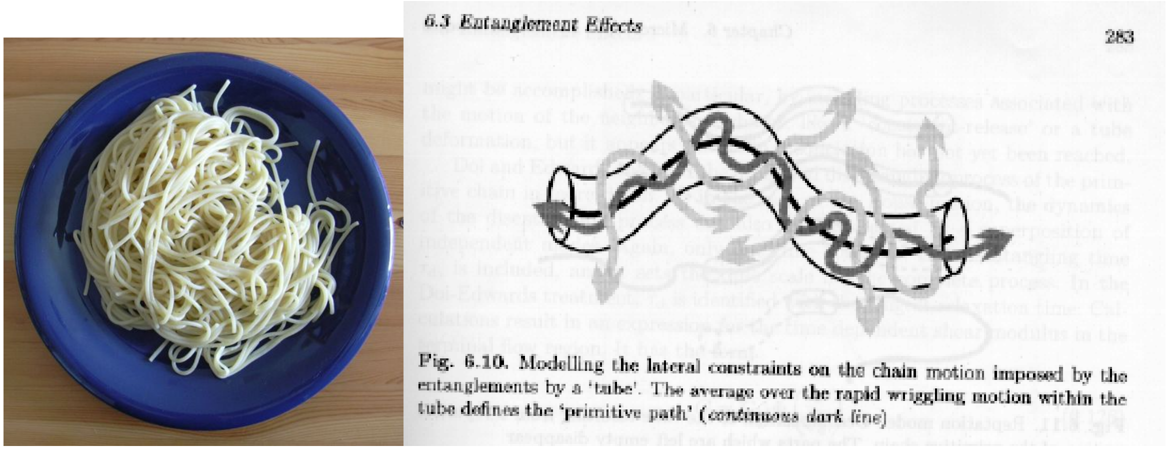

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Fig. 6.10. Modelling the lateral constraints on the chain motion imposed by the entanglements by a 'tube'. The average over the rapid wriggling motion within the tube defines the 'primitive path' (*continuous dark line*)

Figure 5: Reptation model: Polymers are entangled, like pasta, confined to move in a tube.

of entanglements that trap the polymer and allow it to move less freely, the observed diffusion behaviors of larger polymers can be explained. This model was first discussed by de Gennes,[6] and he wrote a simple, popular discussion in Physics Today.[7] There is also a good introduction at reptation. Figure 5 illustrates the model. The polymers in a polymer melt become entangled with each other, and this causes the diffusion rate to slow. The basic idea of this model is that, when a polymer is moving through crowded conditions, it is constrained to move in a tube. As the polymer moves, its tube moves. The longer the polymers in the melt, the more entanglements form between neighboring polymers. This type of motion resembles that of a snake and thus gave rise to the term reptation. Figure 6, again from the Strobl text, illustrates this type of motion.

To compute the diffusion rate of a reptating polymer, de Gennes assumed that inside the tube there was a gas of defects, or small loops that can diffuse parallel to the tube while diffusion perpendicular to the direction of the tube behaved as in the Rouse model. Within the tube, the diffusion constant, D', for this one-dimensional motion along the direction of the tube can be derived from the Einstein relationship:

$$D' = k_b T \mu_{tube} \tag{9}$$

where μ_{tube} is the ratio, v/f of the velocity, v, induced on a polymer by a force f. If we assume that the diffusion of the molecule in the direction of the tube length is given by the Rouse results in equation , then we find that

$$D' \propto 1/N \tag{10}$$

Because this motion obeys Brownian motion, we can relate the relaxation time, t_d that it takes the polymer to travel its own length, L, to this diffusion

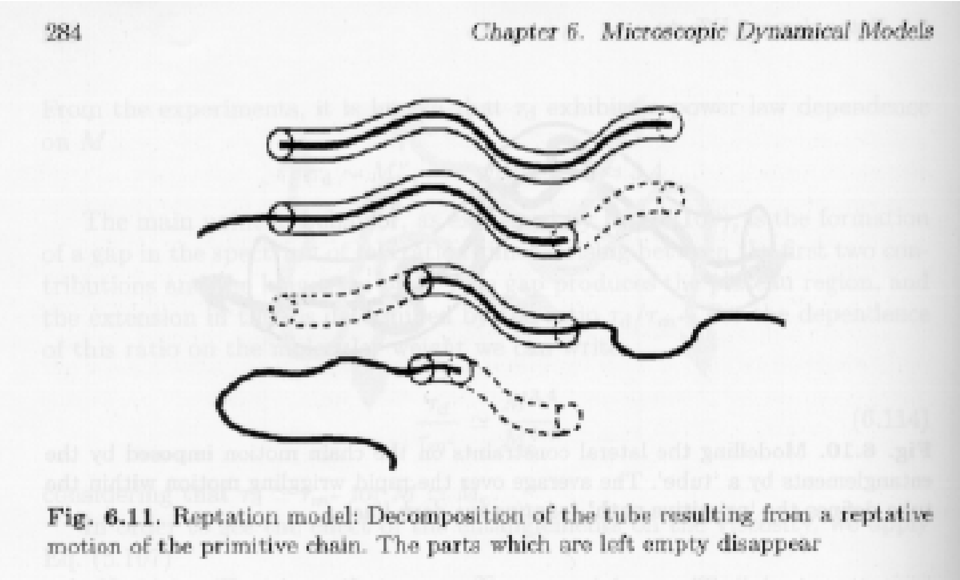

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Fig. 6.11. Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

Figure 6: Reptation motion of a DNA polymer. As a polymer moves, it must create new tube for it to move through, and the back parts of the polymer must move through the forward parts of the tube.

constant.

$$t_d = L^2/D' \tag{11}$$

Because L is proportional to N, we find the result

$$t_d \propto N^3 \tag{12}$$

The value of this expression has been determined experimentally to be

$$t_d \propto N^{3.4} \tag{13}$$

so the results are fairly good. This behavior is significantly different than that predicted by the Rouse model, as can be seen by comparing this equation to equation . This yields a diffusion constant, D, that is proportional to $1/N^2$, rather than the Rouse prediction that it is proportional to $1/N$. More sophisticated theories, including attempting to include the intersecting of neighboring chains through the topology of knots, but none of them have proven to be clearly superior to this relatively simple theory of reptation. This is still an active area of research.

Diffusion constants

As mentioned before, mixtures of short polymers do not behave according to the predictions of reptation, but rather obey the predictions of the Rouse model.

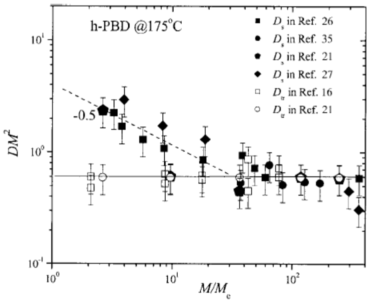

Figure 7: Experimental data from Wang illustrating the transition to reptation motion of the polymer chains at $M_e \approx 10M$.

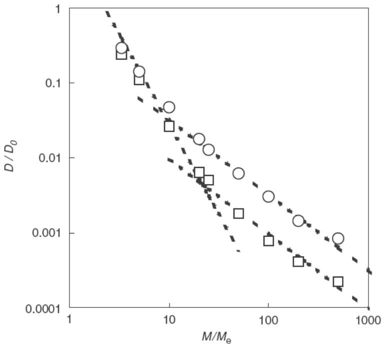

Figure 8: Simulation results for D taken from a paper by Pokrovskii. The results clearly show the expected result that for small polymers, $M_e \lesssim 10M$, D obeys the Rouse model, while larger polymers follow the reptation predictions. These results agree with experimental observations.

This phase transition occurs at about $M_e \approx 10M$, as can be predicted by the methods in a paper by Pokrovskii.[8] This agrees roughly with the available experimental data, as can be seen in figure 7from work by Wang.[9] It is further illustrated in figure 8 from Pokrovskii's paper which shows the behavior of D given by a simulation.

This is a different sort of phase transition than the phase transitions that we are examining in class, like magnetic phase transitions. Here, it is not possible to approach infinitesimally to the critical length because the number of monomers in a chain is a discrete number. It is thus difficult to talk of critical exponents and similar quantities that we have examined in class. Furthermore, it is not possible to change the chain length of the polymers in a polymer melt by adding monomers to a melt. Instead, a new melt with longer polymers must be created.

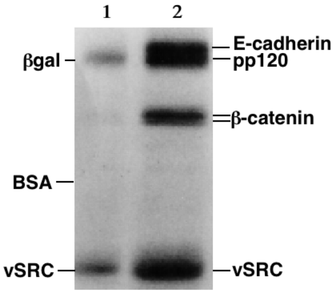

Figure 9: Gel electrophoresis separating different proteins from a mixture. Larger polymer chains travel farther than their smaller counterparts.

Gel Electrophoresis

Gel electrophoresis is a technique frequently used to separate different length DNA fragments and mixtures of different sized proteins. The fragments are placed in a gel and driven to diffuse in a certain direction by the application of an electric field. Generally, larger DNA fragments will travel less distance and so be separated from their shorter counterparts. The amount of fragments of different lengths in a DNA sample can be used as a method of identifying a particular DNA sample. An illustration of this technique is given in figure 9where this technique was used to separate proteins of different lengths rather than DNA fragments. A good introduction to the uses of this technique can be found at wikipedia, and de Gennes discusses the importance of reptation to electrophoresis in his paper in Physics Today. The phase transition between Rouse motion and reptation motion is vital in understanding the behavior of DNA during electrophoresis. For example, it was found experimentally that segments of DNA that are shorter than a critical threshold value do not separate from one another, while above this cutoff level separation is observed. This can be explained by realizing that if a DNA fragment is shorter than the critical length, it will behave as a Rouse chain, with a friction factor proportional to the length of the chain, N, as given by the Rouse model. The force on the chain will be proportional to the charge on the DNA, which, because each monomer of a DNA polymer contains a charge of -1 electron, will be proportional to N as well. The result is that the distance that the molecule travels will be independent of N because these two N dependencies will cancel out. On the other hand, if the DNA is longer than the critical length to trigger reptation, the friction constant will be proportional to N^2, as described above, while the force will still be proportional to N. This means that the distance traveled by these longer DNA fragments will be proportional to N^{-1}, and they will separate during electrophoresis.

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