

SUBJECT

Generalized Modulus-Temperature Curve for Polymeric Materials

JOB NO.

SHEET

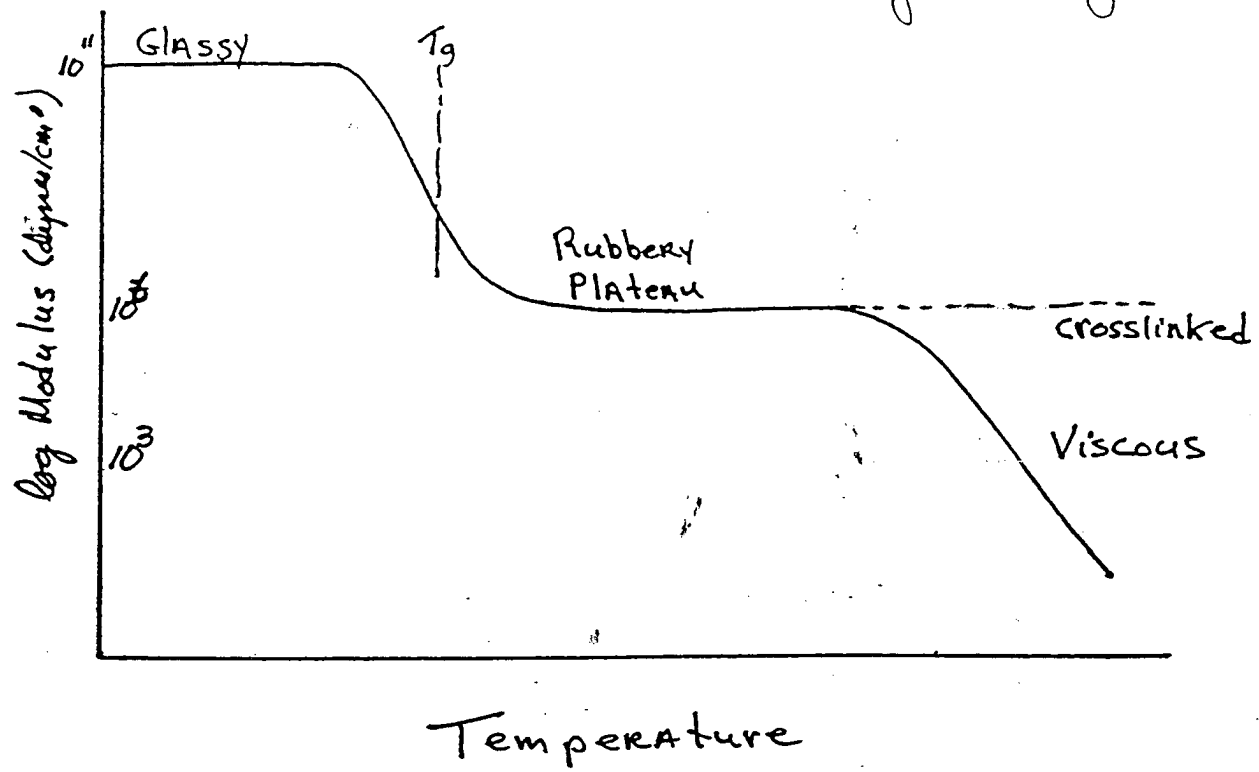
OF

FILE

BY

DATE

Silly Putty



Everything Flows

"... the mountains flowed before the Lord..."

From the song of the prophetess Deborah

Judges 5:5

Time - Temperature Superposition [Silly Putty]

• $E(T, t) = E(T_2, t/a_T)$ where a_T = shift factor

• WLF Equation: $\log a_T = \frac{-C_1(T-T_g)}{C_2 + T-T_g}$

where T_g = glass transition temperature
 C_1, C_2 = constants for a polymer system

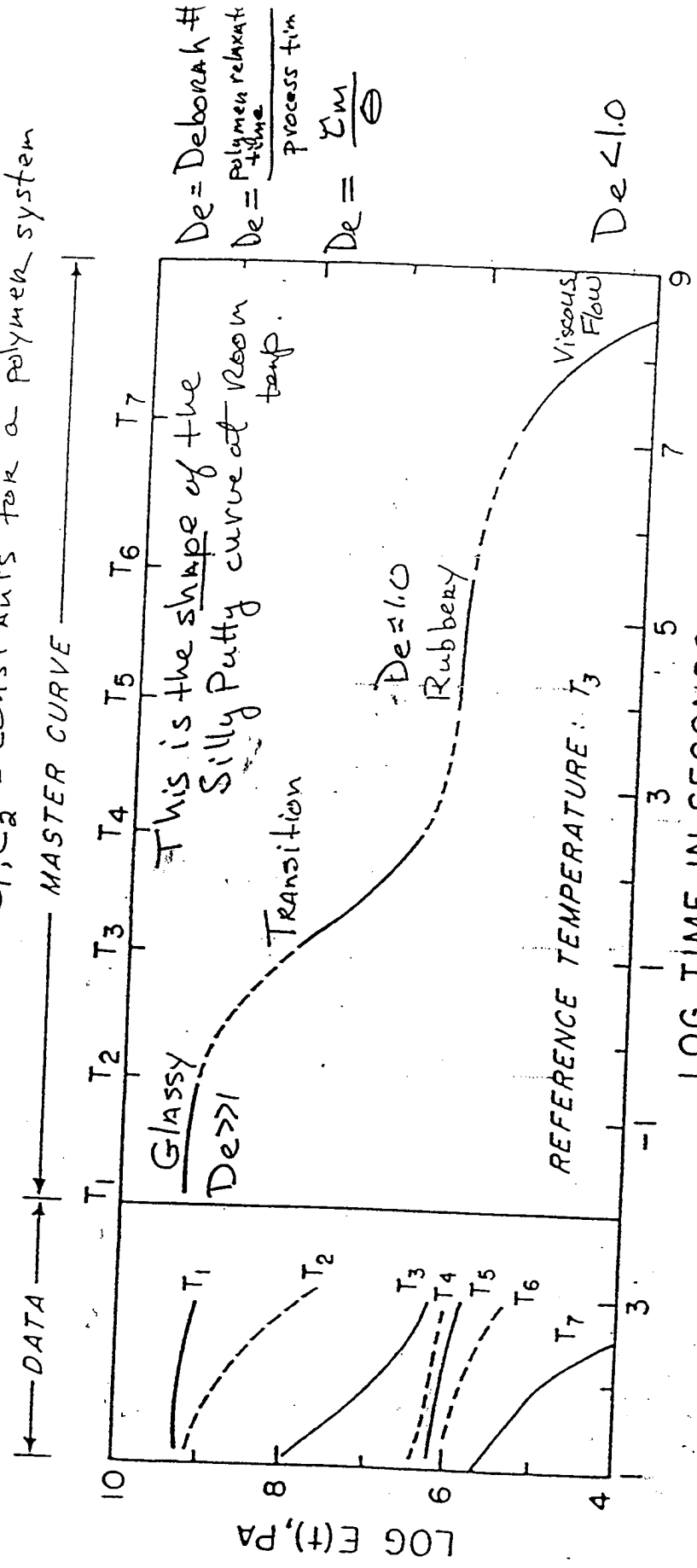


Figure 3-5. Preparation of a stress relaxation master curve from experimentally measured stress-time curves at various temperatures.

SUBJECT

Dimensionless #'s to Describe Viscoelasticity

JOB NO.

SHEET

FILE

BY

DATE

OF

Skip R.

Deborah #: $De = \frac{\lambda}{t_D}$

- unsteady flows

t_D = time-scale of the deformation (experiment)

λ = polymer relaxation time

Weissenberg #: $We = \lambda \dot{\gamma}$

- steady flows

$t_D = 1/\dot{\gamma}$ \Rightarrow shearing time scale

De (or We) $\rightarrow \infty$

solid-like response (elastic)

De (or We) $\rightarrow 0$

liquid-like response (viscous)

$0 \leq De \leq \infty$

Viscoelastic

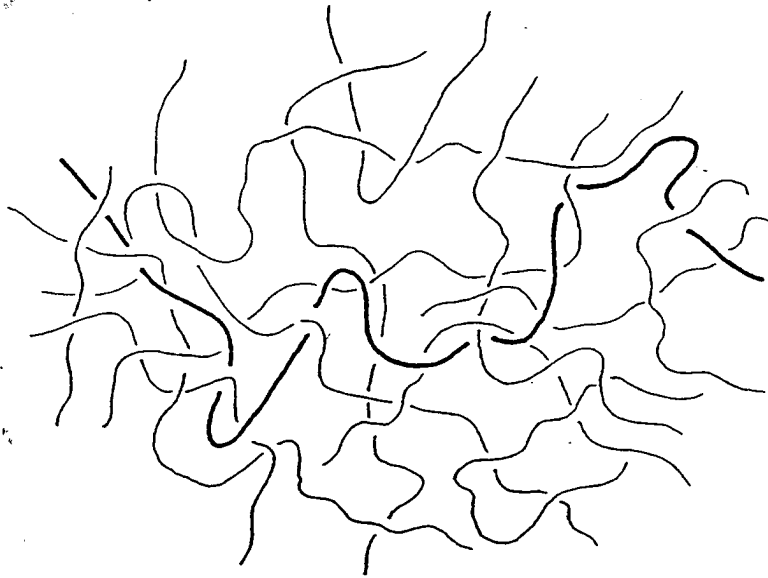
$De < 1$

typically linear viscoelastic (LVE)

$De \approx 2-5$

typically non-linear viscoelastic

Reptation



Polymer molecule
"entangled"
in a matrix of
other polymer chains

- concentrated solution or melt
- $M > M_c$
(high molecular weight)

Fig. 4-6 Polymer molecule entangled in a mesh of other polymer chains (from Graessley,¹⁸ reprinted with permission from Advances in Polymer Science).

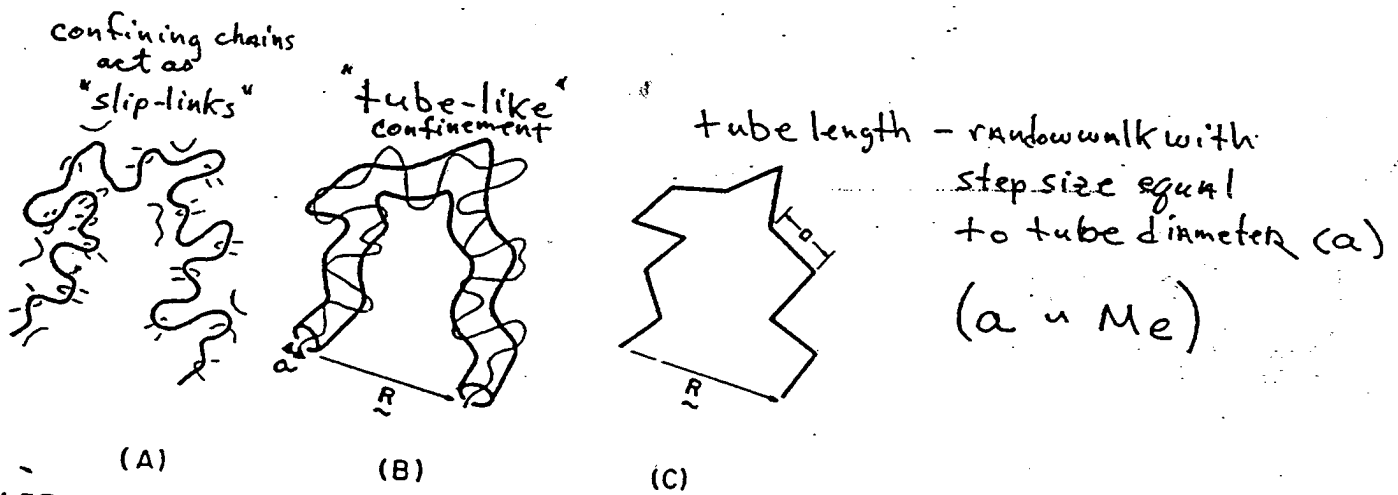


Fig. 4-7 Polymer molecules with which a given molecule is entangled (A) confine the given chain to a tube-like region (B). The tube contour (C) is roughly that of a random walk with step size equal to the tube diameter a . This random walk is called the primitive path; its contour length is much less than the contour length of the chain (From Graessley¹⁸ reprinted with permission from Advances in Polymer Science).

Q. What is the appeal of Reptation Theory?

A. It is the first theory that allows for the formulation of predictive flow models (constitutive equations) based on Molecular Parameters.

Reptation Theory

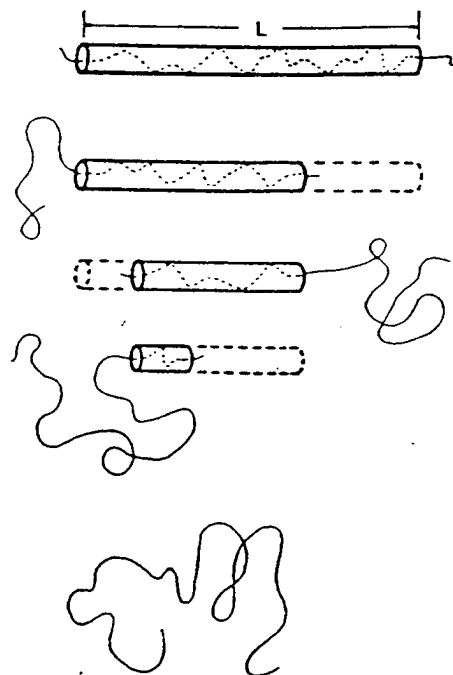


Fig. 4-8 Reptative diffusion of a polymer molecule out of its tube. For simplicity of visualization, the tube of Fig. 4-7 has been straightened out (From Graessley¹⁸).

Predictions

Diffusivity $D \propto M^{-2}$

Maximum Relaxation time $\tau_R \propto M^3$

Zero-shear viscosity $\eta_0 \propto M^3$ ($\eta_0 \propto M^{3.4}$ observed)

Plateau Modulus $G_N^0 \propto M^0$ (observed)

CHEMICAL ENGINEERING 445/545 Polymer Engineering and Science
LITERATURE REVIEW - Example of an ANOTATED BIBLIOGRAPHY for an article
from a Journal, Monograph, or Book.

"Entangled Polymers"

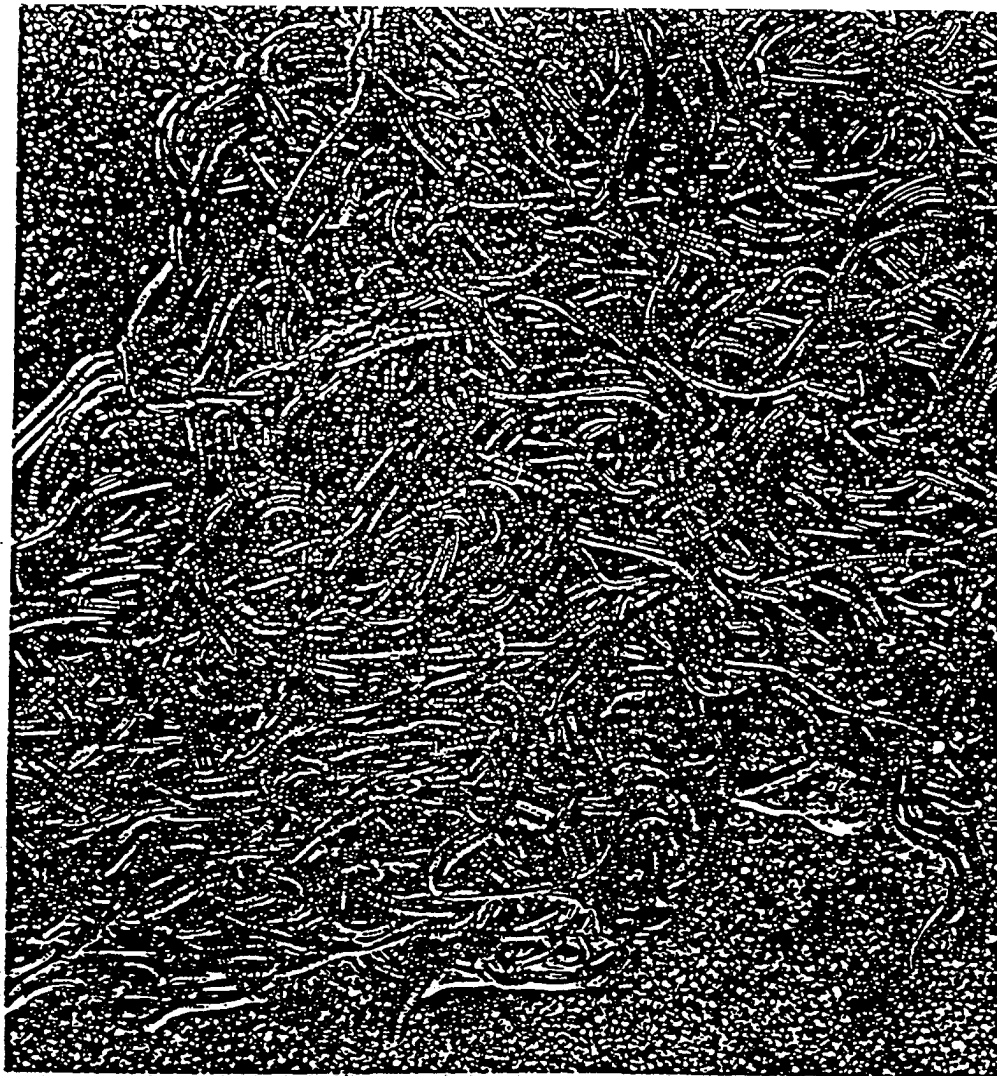
Pierre-Gilles de Gennes, *Physics Today*, p. 33-34 (June, 1983)

- Discussion of a new theory (*reptation*) to describe the way polymer molecules move in a melt. The theory can be applied to enhance the understanding of rheology, diffusion, polymer-polymer welding, and many other phenomena of long molecules.
- REPTATION: the "snake-like" motion of long molecules in the melt state. de Gennes suggest that the motion of a tangle of earthworms is analogous to the movement of polymer molecules in the melt state.
- Describes the theory in a qualitative manner which emphasizes the physical aspects ("snake-like" motion) rather than the mathematical development.
- Uses "silly putty" as an example of a "viscoelastic" fluid whose viscous flow and rubbery bounce are due to the "knotting" of the chains of monomers that make up the polymer.
- Development of a theory from the qualitative ideas of "snake-like" motions and knot structures is the main subject of the article.
- Discusses the major physical components of the theory by showing schematic diagrams of the construction of the "tube" which constrains the polymer chain (this was first noted by Sam Edwards), and the "reptation" of the chain in the tube.
- Discusses "tube renewal" as the basic process for relaxation of macroscopic stress in the melt.
- The main fundamental result of the "reptation" model is that it predicts that the dominant relaxation time is proportional to the cube of the chain length (molecular weight).
- de Gennes states that recent computer simulations confirm the general picture of reptation.

Comments:

- An excellent article (the first two pages of which are given here) for the introduction of the concepts of reptation to the uninitiated student. The "wriggling worm" analogy is especially appropriate because it encompasses the concepts of Brownian motion with overall stress relaxation ("snake-like" motion).
- The latter sections of the article (which were not handed out) go into more detail on the development of the theory and the predictions for a number of practical problems. Somewhat too much detail for beginning students, but an excellent introduction for the interested polymer researcher.

Tangle of long earthworms. The motion of these "Red Wigglers" through the snail 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

Pierre-Gilles de Gennes, professor of the Collège de France, is director of the École Supérieure de Physique et de Chimie Industrielles, in Paris.

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 out⁴ 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.

reptation



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.)



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

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

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 confirmed⁵ the general picture and the transition from local wiggling motions to an overall Brownian motion along the tube.



tube renewal

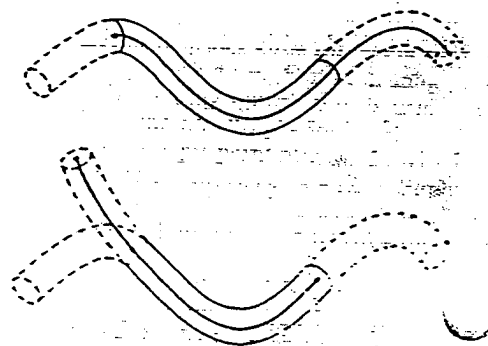
Now we can use the Einstein diffusivity relation to calculate the chain's Brownian motion along the tube

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

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

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

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



These ideas led Masao Doi and Edwards to develop⁶ a precise theory of