Fluctuating Tubes:
A New Reptation Model for Entangled Polymer Systems

E. Donth

Technische Hochschule „Carl Schorlemmer" Leuna-Merseburg, Sektion Physik,
DDR-4200 Merseburg, German Democratic Republic

Summary
    Using some features of the fluctuation dissipation theorem
and a simple method for the description of Brownian motion of
chain segments it is shown that two different reptation times
exist (for shearing and diffusion, respectively) if the entang-
lement points have a sufficient fast and large scale motion that
does not destroy the network topology. Viscosity and diffusion
coefficient are compatibly obtained as $\eta \sim N^{3.5}$ and $D \sim N^{-2}$ in
polymer melts and concentrated systems of long chain molecules.

Introduction
    Reptation times T_R for tube models in entangled systems (DE
GENNES 1971, EDWARDS 1967, DAOUD and DE GENNES 1979) are very
long for long polymer chains. We must therefore check if the
viscosity η or the (self) diffusion coefficient D are influenced
by other slow mobilities in the rubber plateau zone.
    Entanglement points (shortly E-points) are considered as re-
presentatives for topological constraints due to the entangle-
ment network. Its topology can only be varied by the movement
of the chain ends (tube renewal). But invariant topology does
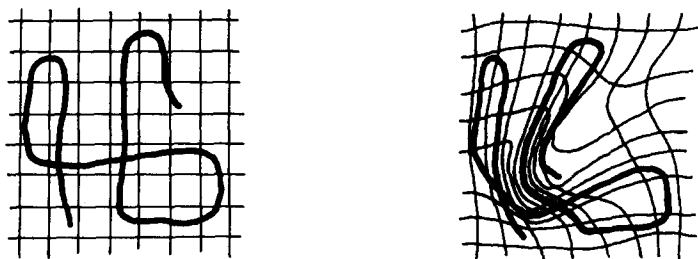not mean that the E-points are fixed in space, see Fig. 1.

Figure 1. Coiling mobility of a chain in an entanglement network

RICHTER et al. (1981) suggested, discussing neutron scattering
experiments (RICHTER et al. 1981, HIGGINS et al. 1981), that
E-points should have a certain mobility as the chains showed a
Rouse like mobility at least up to the range of 4 nm. We assume
that such a mobility does not vary the topology and corresponds
therefore to Fig.1. As suggested by this Figure, imagined in

3 dimensions, such a mobility would be increased if the E-points can slip along the chains. Large scale rearrangements of chains or their parts are possible as can be seen from pictures of larger regions as compared to Fig.1.

Let us define a "coiling time" T_E as the time necessary for a new "geometric" arrangement of a chain due to the E-point mobility in dimensions of the radius of the chain, R_o. (By the way, T_E has only a simple meaning if $T_E < T_R$, otherwise the identification of E-points would be difficult.)

This note is to show that the viscosity is influenced by the mobility of E-points if such a coiling time $T_E < T_R$ exists. A full paper will be published elsewhere (DONTH 1982).

Two different reptation times, $T_R^D \neq T_R^\eta$, are possible for $T_E < T_R$

According to the fluctuation dissipation theorem, the linear response to a spatial gradient of a variable is determined by homogeneous fluctuations of the conjugated variable in small subsystems. Fluctuation of the chemical potential is responsible for D, and fluctuation of the shear angle is responsible for η. These fluctuations are very similar in a system of small spherical particles or in the reptation model for chains in fixed tubes. Therefore Einstein's relation between D and η is applicable there. (In fixed tubes, for instances: $D_t = D_1/N = kT\mu_t$, D_t and μ_t are the diffusion coefficient and the mobility of the chain along the tube, respectively, N is a measure for the chain length proportional to the mass of a macromolecule, k is Boltzmann's constant and T temperature.)

But these two fluctuations are not equivalent in all cases. Consider the total movement of the chains, coiling and reptation simultaneously, in entangled systems for $T_E < T_R$ (model of "fluctuating tubes"). Tube renewal means that a given chain has obtained a new environment consisting of other chain segments as before. This corresponds one-to-one to the fluctuation of the chemical potential as geometric coiling does not alter this "chemical" environment.

But rearranging relevant for shear angles has topological and geometric aspects. Therefore, the viscosity is influenced by coiling and we have to estimate the effect of the E-point mobility on η. If this effect is considerable then Einstein's relation is violated and two different reptation times are obtained, $T_R^D \neq T_R^\eta$, T_R^D for diffusion and T_R^η for viscosity.

By the way, differences between relaxation times for different variables are common for the dynamics in the glass transition zone (see, e.g. DONTH 1981). Such a behavior seems to be typical for cooperative movements in the scale of 1 to some 10 nanometers.

A Rouse diffusion model for the mobility of E-points

Fig. 2 shows a model that gives $T_E < T_R$ for $N > N_c$, N_c being a measure for the entanglement spacing. The E-point is symbolically represented by a ring. A similar picture is shown by BALL et al.(1981). Assume two things, (i) the ring can slip along
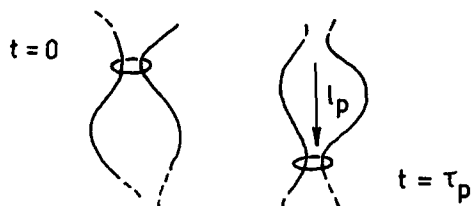
Figure 2. E-point mobility due to Rouse modes of temporary
parallel chains

both chains provided that they are temporary parallel, and (ii)
the touch of the two chains moves according to the Rouse model.
This results in $\tau_p \approx \tau_0(l_p/a)^4$ if the Rouse modes of both chains
are similar ($p \approx p_1 \approx p_2$; τ_p and l_p are explained in Fig.2, a is
the length of a statistical segment, τ_0 is an elementary jump
time, so that $D_1 = a^2/\tau_0$). Summing up over the Rouse mode in-
dices p from 1 to N_c we obtain the diffusion coefficient of an
E-point, D_E, as

$$D_E \approx \overline{(\Delta x^E)^2}/\tau \approx D_1(\ln N_c/N_c) , \qquad (1)$$

where $\overline{(\Delta x^E)^2} = \Sigma l_p^2$ and $\tau = \Sigma \tau_p$.

The continuity of the chains and the mean (averaging large
regions) distance between the E-points during their diffusion
are preserved in the following model: Consider a chain as a
bead-spring model but identify a bead with an E-point having
the diffusion coefficient D_E instead of kT/ξ_0 for a segment of
the original Rouse model. Then the characteristic time for the
longest mode of the chain, consisting of N/N_c new beads and
having a "segment length" $\sqrt{a^2 N_c}$, is precisely T_E. Thus

$$T_E \approx \tau_0 N^2/\ln N_c \sim N^2 . \qquad (2)$$

This means $T_{E_{\eta}} < T_R^D$ for long chains as $T_R^D \sim N^3$. Therefore, modifi-
cations for T_R are to be expected in comparison to the model of
fixed tubes.

Estimation of the viscosity exponent in entangled melts and concentrated systems

A simple phenomenological description of Brownian motion is
used for estimating the viscosity. Details of the movement of
E-points are not necessary for the calculations.

Taking an elementary motion step of a chain segment, Δx, as
a sum of two parts, $\Delta x = \Delta x^E + \Delta x^T$, where E stands for the dif-
fusion of E-points and T for the in-tube reptation. Consider
time steps (labelled as i and j) in which the movements of the
chain segments are mutually statistical independent, $\overline{\Delta x_i \Delta x_j} = 0$
for $i \neq j$. Then the mobility is split into three parts as

$$\overline{(\Sigma \Delta x_i)^2} = \Sigma \overline{(\Delta x_i^T)^2} + \Sigma \overline{(\Delta x_i^E)^2} + \Sigma \overline{\Delta x_i^T \Delta x_i^E} \quad . \tag{3}$$

The first term on the r.h.s. describes a pure in-tube motion and is interpreted as the reptation corresponding to the response of a diffusion experiment, $D_t = D_1/N$.

The second term describes the pure diffusion of the E-points that does not alter the topology of the network. Neither D nor η is influenced by this term because mingling or flow of chains in entangled systems is only possible if the topology of the network is altered.

The third term is interpreted as the mobility responsible for shear in entangled systems. Using $\overline{\Delta x_i \Delta x_j} = 0$ again, multiplication by $1 = (\Sigma \Delta x_i^T)/(\Sigma \Delta x_i^T)$ gives $\overline{(\Sigma (\Delta (x_i^T)^2) \cdot (\Sigma \Delta x_i^E)/(\Sigma \Delta x_i^T)}$. Assuming statistical independence of (i) reptation mobility inside the tube and (ii) shift of E-points we can factorize and obtain

$$D_t \cdot \overline{(\Sigma \Delta x_i^E)/(\Sigma \Delta x_i^T)} \quad .$$

The bared quotient stands for the average of: the shift due to E-point diffusion, if the shift due to reptation has a certain value (remember $\overline{\Sigma \Delta x_i^T} = \overline{\Sigma \Delta x_i^E} = 0$). If $T_E < T_R^D$, this quotient is a pure geometry-to-topology ratio of chains for long averaging times and should be of order R_0/L_t, L_t being the curvilinear length (contour length) of the tube. Therefore, the total mobility as relevant for mingling and flow, expressed in the form of a "diffusion coefficient" $\widetilde{D}^{total} \sim \overline{(\Sigma \Delta x_i)^2}$, is obtained from eq.(3) as

$$\widetilde{D}^{total} = D_t + 0 + \widetilde{D}_\eta \, , \quad \widetilde{D}_\eta \approx D_t R_0/L_t \quad . \tag{4}$$

We obtain actually two different reptation times,

$$T_R^D = L_t^2/D_t \quad \text{and} \quad T_R^\eta = L_t^2/\widetilde{D}_\eta = L_t^3/D_t R_0 \quad . \tag{5}$$

In entangled polymer melts and concentrated systems $R_0 \sim N^{1/2}$ and $L_t \sim N$, therefore $T_R^D \sim N^3$, $T_R^\eta \sim N^{3.5}$, $T_R^\eta > T_R^D$,

$$D \sim R_0^2/T_R^D \sim N^{-2} \quad \text{and} \quad \eta \sim G_0 T_R^\eta \sim N^{3.5} \quad . \tag{6}$$

The shear elastic modulus in the plateau zone, G_0, does not depend on N in such systems.

If the macromolecules are branched having long mobile side chains, then the branches can coil itself and we expect similar factors that influence the viscosity (as compared to the reptation in fixed tubes). For starlike polymers having arms of similar lengths, this factor would be approximately the same for all arms as well as for the whole star, namely $D_t/\widetilde{D}^\eta \approx L_t/R_0$ as above ($\sim N^{+1/2}$ in concentrated systems and $\sim (N/g)^{+1/2}$ in semidiluted systems, see below). A computer simulation of three-arm stars in fixed tubes (EVANS 1981) results in $T_R \sim N^4$ for

polymer melts, corresponding to $\eta \sim N^4$ and $D \sim N^{-3}$. Using the factor for fluctuation tubes, we obtain $T_R^\eta \sim N^{4.5}$ and $\eta \sim N^{4.5}$, whereas $T_R^D \sim N^4$ and $D \sim N^{-3}$ are not affected by the coiling mobility.

Semidilute solutions

Let g be the number of monomers in one subunit of size ξ and c the mass of monomeric units per unit volume, then for an ideal chain of these subunits

$$L_t \sim (N/g)\xi \quad , \quad R_o \sim (N/g)^{1/2}\xi \quad , \quad D_t \sim g/N\xi \; . \qquad (7)$$

From eq.(5) follows

$$T_R^D \sim (N/g)^3 \xi^3 \qquad \text{and} \qquad T_R^\eta \sim (N/g)^{3.5}\xi^3 \; . \qquad (8)$$

From $D \sim R_o^2/T_R^D$ and $\eta \sim G_o T_R^\eta$, using $G_o \sim (1/\xi)^3$, we obtain

$$D \sim (g/N)^2/\xi \qquad \text{and} \qquad \eta \sim (N/g)^{3.5} \; . \qquad (9)$$

Scaling arguments (DE GENNES 1976) such as $g \sim c^{-5/4}$ and $\xi \sim g^{3/5}$ give then

$$D \sim N^{-2}c^{-1.75} \qquad \text{and} \qquad \eta \sim N^{3.5}c^{4.375} \; . \qquad (10)$$

This corresponds well to the experimental exponents as quoted by LEGER et al. (1981)

$$-2.0 \pm 0.1 \; , \quad -1.7 \pm 0.1 \quad \text{and} \quad 3.4 \pm 0.1 \; , \quad 4.5 \pm 0.5 \; . \qquad (11)$$

Conclusions

I think that the last two experimental exponents eq.(11), the experimental exponent 3.4 ± 0.1 for concentrated systems or polymer melts, and an experimental exponent near 4.5 in three-arm starlike polymers are an indication for the (topology conserving) mobility of entanglement points in large scales (R_o). By the way, such a mobility could be of some importance for explaining lamellar crystallization structures in polymers. Fixed tubes enhance the topological difficulties of pulling an entangled chain into a regularly folded array. But fluctuating tubes (that means such a mobility equivalent to a sufficient high diffusion of E-points) diminish these difficulties to a reasonable degree without to sacrifice the idea of reptation. During crystallization, the E-points can be relegated to the amorphous interlayers between crystal lamellae until this process is stopped by a too high density of E-points there or by too long diffusion paths of E-points necessary for some thickness of the lamellae.

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