Summary for the reptation theory

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1. Parameters

Length scales

b :	Average distance between consecutive beads
d :	Diameter of tube
$\sqrt{Nb^2}$:	End-to-end length of chan
$L = \dfrac{Nb^2}{d}$:	Contour length of tube

Diffusion constants

$D_b = \dfrac{k_B T}{\zeta}$:	Bead
$D_R = \dfrac{k_B T}{(N+1)\zeta}$:	Center of mass of chain (Rouse model)

Time scales

$$\tau_b = \frac{\zeta b^2}{k_B T}: \quad \text{The diffusion time of beads}$$

$$\tau_e = \frac{\pi d^4 \zeta}{12 k_B T b^2}: \quad \text{The entanglement time defined as } \phi_n(\tau_e) = d^2$$

$$\tau_R = \tau_{p=1} = \frac{b^2 \zeta (N+1)^2}{3\pi^2 k_B T} \quad \frac{b^2 \zeta}{3\pi^2 k_B T} N^2: \quad \text{The Rouse relaxation time}$$

$$\tau_d = \frac{L^2}{\pi^2 D_R} = \frac{1}{\pi^2}\left(\frac{Nb^2}{d}\right)^2 \frac{(N+1)\zeta}{k_B T} \quad \frac{b^4 \zeta}{\pi^2 d^2 k_B T} N^3:$$

The reputation time / Disentanglement time

Other parameters

$$Z = \frac{L}{d} = \frac{Nb^2}{d^2}: \quad \text{Number of steps in a primitive chain / Entanglement umber}$$

2. Beads (segments) motions

1) $t < \tau_e$ -> Rouse in 3D

$$\phi_n(t) = \left(\frac{12 k_B T b^2}{\pi \zeta}\right)^{1/2} t^{1/2} \qquad (1)$$

2) $\tau_e < t < \tau_R$ -> Rouse in tube constraint

$$\phi_n(t) = d\left(\frac{4k_B T b^2}{3\pi\zeta}\right)^{1/4} t^{1/4} \tag{2}$$

3) $\tau_R < t < \tau_d$ -> free diffusion in tube constraint

$$\phi_n(t) = d\left(\frac{2k_B T b^2}{(N+1)\zeta}\right)^{1/2} t^{1/2} \tag{3}$$

4) $\tau_d < t$ -> free diffusion in 3D

$$\phi_n(t) = 6Dt = \frac{2d^2 k_B T}{b^2\zeta}\frac{1}{N^2}t \tag{4}$$

<u>**3. Stress relaxation function**</u>

1) $t < \tau_e$ -> Rouse

$$G(t) \approx \frac{ck_B T}{\sqrt{24\pi}}\sqrt{\frac{\tau_b}{t}} \tag{5}$$

2) $t > \tau_e$ -> reptation

The reputation theory predicts the stress relaxation function of the from

$$G(t) = G_N^0 \frac{8}{\pi^2}\sum_{p=1,3,5,}^{\infty}\frac{1}{p^2}\exp\left[-\frac{p^2}{\tau_d}t\right]. \tag{6}$$

$$G_N^0 \approx G_R(t=\tau_e) = \frac{ck_B T}{\sqrt{24\pi}}\sqrt{\frac{\tau_b}{\tau_e}} = \frac{ck_B T}{\sqrt{2\pi}}\frac{b^2}{d^2} \tag{7}$$

The shear viscosity is thus calculated as

$$\begin{aligned}
\eta &= \int_0^\infty G(t)dt = \int_0^\infty dt G_N^0 \frac{8}{\pi^2}\sum_{p=1,3,5,}^{\infty}\frac{1}{p^2}\exp\left[-\frac{p^2}{\tau_d}t\right] \\
&= G_N^0\frac{8}{\pi^2}\sum_{p=1,3,5,}^{\infty}\frac{1}{p^2}\int_0^\infty dt\exp\left[-\frac{p^2}{\tau_d}t\right] \\
&= G_N^0\frac{8}{\pi^2}\tau_d\sum_{p=1,3,5,}^{\infty}\frac{1}{p^4} = G_N^0\frac{8}{\pi^2}\tau_d\frac{\pi^4}{96} = \frac{\pi^2}{12}G_N^0\tau_d \\
&\propto N^3
\end{aligned} \tag{8}$$