Steady shear:

\[ S_{xy}(\dot{\gamma}) = \int_0^\infty \frac{dt}{\tau} e^{-t/\tau} Q_{xy}(\dot{\gamma}t) \quad \beta = D-E \text{ term} \]

\[ \frac{1}{\tau} = \frac{1}{\tau_d} + \beta \dot{\gamma} S_{xy} \quad \frac{\eta}{\dot{\gamma} \tau} \quad = \frac{\langle \lambda \rangle}{\dot{\gamma}} - \frac{1}{3} \frac{1}{\dot{\gamma}} \]

If \( \beta = 0 \) (no CCR) \( S_{xy} \rightarrow 0 \) as \( \dot{\gamma} \rightarrow \infty \)

For any \( \beta > 0 \) \( S_{xy} = S_{xy}^\infty \) and \( \dot{\gamma} \rightarrow \infty \)

\[ T_{xy} \rightarrow \alpha G_{\text{plateau}} \quad \alpha = \text{numerical} \quad \frac{1}{\langle \lambda \rangle} \]

\[ \eta \rightarrow \alpha G_{\text{plateau}} \frac{G}{\dot{\gamma}} \quad \text{(independent of } M) \]

\[ \eta = \frac{G \tau}{\dot{\gamma}} \quad \text{for large } \dot{\gamma} \]

**FIG. 13-9.** Non-Newtonian viscosity \( \eta \) plotted against shear rate, for narrow-distribution polystyrenes. Molecular weights from top to bottom, \( \times 10^6 \): 24.2, 21.7, 17.9, 11.7, 4.85.
What was certainly wrong with basic theory

\[ S_{xy}(\dot{\gamma}) = \int_0^\infty \frac{dt}{\tau} e^{-t/\tau} Q_{xy}(\dot{\gamma}t) \]

\[ \frac{1}{\tau} = \frac{1}{\tau_0} + \beta \dot{\gamma} S_{xy} \]

Maximum for all \( \beta < 3 \)

Mead, Larson, Doi (1998)

Include stretch fluctuation

\( \beta = 1 \) binary interaction model.
Additional physics (CCR2)


CCR

CCR2

We know that convection increases average distance between existing entanglements.

CCR2 postulates that (without stretch) the extended primitive chain "wanders" laterally.

and gets caught in new entanglements, partly renewing orientation.

CCR2 adds to CCR

A quantitative theory

1st part: forget CCR temporarily
only consider CCR2

Assumption: Elongated primitive chains only
keep their affine orientation for a length $a$

The rest goes random.

Then:

$$ S(t, t') = \int_{-\infty}^{t} \frac{df(x, t, t')}{dx} \cdot \frac{d\xi}{dt'} \cdot \frac{\xi}{t} $$

where $\xi$ is DE IAA tensor, and $f$ is fractional number of entanglements existing at $t'$, survived up to $t$ in the $x$-location along chain ($-\frac{1}{2} \leq x \leq \frac{1}{2}$)

$f$ obeys:

$$ \frac{df}{dt} = D \frac{df}{dx^2} - \frac{C}{A} (v f) $$

i.e. $t-t' \ f = 1$

B.C. $s = \pm \frac{1}{2} \ f = 0$

$$ V(s, t) = \frac{1}{2} (t') \int_{0}^{1} \langle \xi (x, \xi) \rangle \ d\xi $$
So far no CCR (only CCR2)

2nd part: To include CCR we write:

$$S_2 (s, t) = \int_0^t dt' \int_0^t dt'' \frac{P(s, t, t')}{P(t, t')} \frac{a E(t, t')}\Omega$$

where:

$$P(s, t, t') = f(s, t, t') \overline{f}(t, t')$$

$$\overline{f}(t, t') = \frac{1}{\sqrt{2}} \int_{-\sqrt{2}}^{\sqrt{2}} ds \ f(s, t, t')$$

Assumption of binary contacts ($\beta=1$) and of independence

Notice:

$$\overline{S}_2 (s) = \int_0^t dt' \int_0^t dt'' \frac{\overline{P}^2(t, t')}\Omega \frac{a E(t, t')}\Omega$$

similarly to double reptation.

Hence DCR model.
Dr. G. Marrucci (Naples) [ITP Complex Fluids Program 5-01-02] Convective Constraint Release - Approaches and Results

Polystyrene Melts, $\overline{M}_w / \overline{M}_n < 1.1$

\[
\frac{\tau_{yz}}{NnkT}
\]

<table>
<thead>
<tr>
<th>$\overline{M}_w \times 10^5$</th>
<th>$\lambda$(sec)</th>
<th>$T$(C)</th>
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Weissenberg number


Graphs showing:\n- $T_{xy}/G$ vs. $\dot{\gamma}$
- $\dot{\gamma}$ vs. $\tau_d$
- $T_{xy}/G$ vs. $\gamma T$

Graphs labeled: DCR model, Single relaxation time.