Coil-Size Scaling and Reptation of Polymer Melts

2.341J Spring 2016
The complexity of the real problem
“Coarse Graining”

- Distill the essential physics describing the chain dynamics to simple(r) governing equations

- Chemical details and molecular specificity are collapsed into small number of chain-specific constants

- different analytic and simulation tools are appropriate to each scale


- FENE Dumbbell Const. Eqn.
  \[ \eta_p = (nk_B T) \lambda_z \]
  \[ D e = \lambda_z \dot{\varepsilon}_0 \]

- Bead-Spring Chain (Rouse/Zimm)
  \[ \lambda_i = \lambda_z / i^{3/2} \]
  \[ i = 1, 2, \ldots M = 225 \]

- Kramers' (Freely-Jointed) Bead-Rod Chain
  \[ N = (n/15) = 2885 \]
  \[ a = 12.3 \; l \]
  \[ L = R_{max} / \sqrt{\langle R^2 \rangle_{eq}} \approx 93 \]

- Freely-Rotating Bead-Rod Chain (Kuhn & Kuhn, Flory R.I.S.)
  \[ \langle R^2 \rangle_{eq} = C_{\infty} n l^2 \]
  \[ C_{\infty} = 10 \]

- Primary Chemical Structure
  \[ n = (2M_w / m_0) = 43,300 \]
  \[ l = 1.54 \; \text{Å} \]

data for Polystyrene: \( M_w = 2.25 \times 10^6 \; \text{g/mol} \)
**Fig. 8-1** Linear viscoelastic data for polystyrene in two theta solvents. For frequencies $\lambda \omega$ greater than 10, $G'$ and $G''$ scale as $\omega^{2/3}$, in disagreement with the Rouse theory, which predicts a proportionality to $\omega^{1/2}$ in this regime. Here $G'_R \equiv G'/n\kappa T$ and $G''_R \equiv (G'' - \eta_s \omega)/n\kappa T$; $\lambda \equiv [\eta]_0 \eta_s M/N_A kT$ (from Johnson et al., reproduced with permission from Polym. J.).

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Monodisperse Polystyrene in a viscous oligomeric styrene oil ("resin"). M. Verani, MS Thesis (2004); fit one parameter: $\zeta$ (friction coefficient).
Extensional Flows: (Doyle, Spiegelberg, McKinley, Shaqfeh, JNNFM 1997)

Kramers Bead-Rod Chain in Extensional Flow
N = 200, Wi = 20
Summary (from last Class)

<table>
<thead>
<tr>
<th></th>
<th>Rouse</th>
<th></th>
<th>Zimm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((\eta = \frac{1}{2}))</td>
<td>Theta Solvent ((\eta = \frac{1}{2}))</td>
<td>Good Solvent ((\eta = \frac{3}{5}))</td>
</tr>
<tr>
<td>Friction Coeff</td>
<td>(\bar{\gamma}) [N s/m]</td>
<td>(M_w)</td>
<td>(M_w^{1/2})</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>(D_{\text{trans}}) [m²/s]</td>
<td>(M_w^{-1})</td>
<td>(M_w^{-1/2})</td>
</tr>
<tr>
<td>Relaxation Time</td>
<td>(\tau_{\text{rel}}) [s]</td>
<td>(M_w^2)</td>
<td>(M_w^{3/2})</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>([\eta]) [cP]</td>
<td>(M_w)</td>
<td>(M_w^{1/2})</td>
</tr>
</tbody>
</table>

⇒ These are predictions that can be probed experimentally (rheometry, light scattering, viscometry)
The behavior of $\eta_0$ as a function of $c$ and $M$ is fairly well understood. At low concentrations an expression of the form $\eta_0 = \eta_0(c[\eta]_0)$ may be used to consolidate data for a given polymer-solvent system over a wide range of both concentration and molecular weight of the polymer. An example is the Martin equation:

$$\eta_0 - \eta_s = \eta_0 c[\eta]_0 e^{k'-d\eta_0} \tag{3.6-15}$$

in which $k'$ is an arbitrary constant. Actually, a slightly better fit with data is obtained by replacing $[\eta]_0$ with $M^m$ and choosing $d'$ to fit data. It is found that $d'$ is close to the Mark–Houwink exponent.

At high concentrations $\eta_0$ is governed by the product $cM$. The most striking feature of $\eta_0(cM)$ is illustrated in Fig. 3.6-4 for a variety of undiluted polymers. It is seen that $\eta_0$ goes from a linear to a 3.4 power dependence on $M$ at some critical molecular weight $M_c$

$$\eta_0 \propto M \quad (M < M_c)$$

$$\eta_0 \propto M^{3.4} \quad (M > M_c) \tag{3.6-16}$$

DPL, Chapter §3.6

See Equations 3.6-15 and 3.6-16, and Fig. 3.6-4 in R. Byron Bird et al, *Dynamics of Polymeric Liquids*, John Wiley and Sons, Inc. removed due to copyright restrictions.
Linear Viscoelasticity from the Maxwell Model

- **Input:**
  \[ \gamma = \gamma_0 \sin \omega t \]
  \[ \dot{\gamma} = (\gamma_0 \omega) \cos \omega t \]

- **Output:**
  \[ \tau = \gamma_0 \left[ G''(\omega) \cos(\omega t) + G'(\omega) \sin(\omega t) \right] \]

**Maxwell Model**

\[ G''(\omega) = G_0 \frac{(\lambda \omega)}{1 + (\lambda \omega)^2} \]
\[ G'(\omega) = G_0 \frac{(\lambda \omega)^2}{1 + (\lambda \omega)^2} \]

**De =**\[\lambda \omega \sim \frac{G'(\omega)}{G''(\omega)} \sim \frac{\text{storage}}{\text{dissipation}}\]

\[ \lambda \approx 1/\omega^* \approx 1.5 \text{s} \]

\[ \lambda \approx 1/\omega^* \approx 1000 \text{s} \]

\[ \eta'' \sim \omega^{-1/4} \]

\[ \eta'' \sim \omega^{-1/4} \]
Entangled Polymer Melts: *Reptation*

P.G. DeGennes


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 out 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.

Fig. 9.1
Reptation steps: (a) formation of a loop at the tail of the snake and elimination of the tail segment of the confining tube; (b) propagation of the loop along the contour of the tube; (c) release of the loop at the head of the snake and formation of a new section of the confining tube.

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Pierre-Gilles de Gennes (1932-2007)
Nobel Prize 1991
“The Founding Father of Soft Matter”

[https://web.archive.org/web/20130621152528/](https://web.archive.org/web/20130621152528/)

Reptare: to wriggle like a snake
Entangled Polymers

P.G. DeGennes  M. Doi & S.F. Edwards

Molecular Dynamics

[https://www.youtube.com/watch?v=Y7XAroFgVQs]

LAMMPS (Open Source)

[https://www.youtube.com/watch?v=oB79II_63rM]
Direct Observation

Perkins, Smith, Chu, Science 1994
Indirect Observation: “Polymer Welding”

Polymer–polymer welding. One can weld a pair of polymer blocks by bringing them into close contact and maintaining them slightly above the glass transition temperature for a certain time $t$. Interdiffusion takes place, and the junction develops mechanical strength. The essential difference with the preceding case is that for the purposes of welding, the interesting time interval $t$ is smaller than the reptation time $\tau$. In other words, the thickness of the mixing layer is smaller than the size of a coil.

In some experiments$^{15}$ carried out in Lausanne, Switzerland, researchers monitored the state of the mixing layer by fracturing the junction and measuring the fracture energy per unit area, $G$, as a function of the welding time. Experimentally $G(t)$ saturates after one reptation time $\tau$, and increases at earlier times according to

$$G \approx G_{\text{max}} \left(\frac{t}{\tau}\right)^{1/2} \quad (t < \tau)$$

The following sketch suggests a microscopic picture of the welding process.

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Reptation Model Fit

- Monodisperse Polyisoprene (Baumgaertel & H. Winter, U.Mass, 1992)

Rubbery Modulus ($G_N$) almost unchanged

$M_e \sim 4,800$ g/mol

$M_w = 20,000$ to $300,000$

$\tau_d \propto M_w^{3.4}$

(data from Baumgaertel et al. 1992)
Recent Developments

- Contour Length Fluctuations (CLF); reptation (curvilinear diffusion) along a tube of fluctuating length

  - Kuzu & Doi, 1983

Reptation and Contour-Length Fluctuations in Melts of Linear Polymers

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(Received 14 January 1998)

We present an analytical theory of stress relaxation in monodisperse linear polymer melts that contains contributions from both reptation and contour-length fluctuations, modeled as in our previous work on arm retraction in star polymers. Our approach resolves two long-standing problems with reptation theory: it predicts a zero-shear viscosity \( \eta \) scaling as \( \eta \sim N^{3.4} \) over a broad range in chain length \( N \) before reaching an asymptotic \( N^3 \) dependence, and a power law \( \omega^{-\alpha} \) in the dynamic loss modulus \( G''(\omega) \) with \( 0 < \alpha < 1/4 \) depending on chain length, in agreement with experiment. [S0031-9007(98)06599-5]

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CLF Results

FIG. 1. Predicted viscosity $\eta$ as a function of chain length $N/N_e$ shows without adjustable parameters an effective exponent of 3.4. Plotted as $\eta/N^3$ versus $N/N_e$, crossover occurs at around $N/N_e = 200$, as in experiment [15].

$$\eta \sim N^{3.4} \text{ or } \eta \sim \left(\frac{N}{N_e}\right)^{3.4} = Z^{3.4}$$

FIG. 2. Computed loss modulus $G''(\omega)$ compared to data of Ref. [16] for narrow-MWD polystyrene melts. A common value of $\tau_e$ and $G$ has been taken for the three curves. The variation in slope above $\omega \tau_d = 1$ results from “contamination” of the $-1/4$ behavior by Rouse modes inside the tube. Arrows mark $\omega \tau_d = 1$. (Lines are guides to the eye of slope 1/8, 1/5.5, 1/4.5).

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“Fully Loaded Model”

- Reptation + Contour Length Fluctuations + Convective Constraint Release + Finite Extensibility (+ Anisotropic Tube Deformation!)
- Marrucci & coworkers; McLeish & coworkers “Rolie-Poly” Model;

Stretching CCR model

\[ R(s, t + \Delta t) = \Delta t \left( D \frac{R'' R'}{R' R'} R' + k \frac{R'}{R'} R' + \frac{3}{2} \frac{1}{|R'|} \frac{\partial^2 R}{\partial s^2} + g(s, t) \right) + R(s + \Delta \xi(t), t) \]

R(s,t) = Space curve equation of chain contour parameterised by s.
W. Graessley, *Polymer*, 21 (1980); pp.258-262

- All polymeric fluids can be characterized by their location on a diagram representing effects of \((c, M_w)\).

- Solvent quality exponent, \(\nu\)

- Ideal Gaussian chain (random walk) \(\nu = 1/2\)

- \(c^* \sim M_w^{1-3\nu} \Leftrightarrow M_w \sim (c^*)^{-1/(1-3\nu)}\)

- \(c^\infty \sim M_w^{-2} \Leftrightarrow M_w \sim (c^\infty)^{-1/2}\)