

Ch 07

Rheology of dilute polymer solutions

Dilute solution viscosity

- Relative viscosity

$$\eta_{rel} = \frac{\eta}{\eta_s}$$

- Specific viscosity

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s}$$

- Reduced viscosity

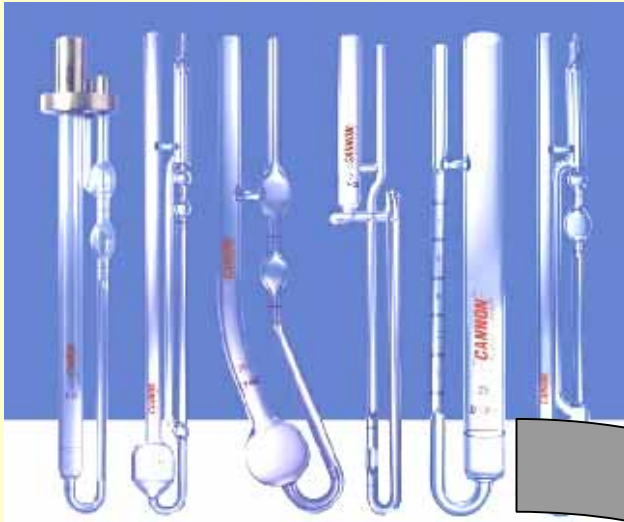
$$\eta_{red} = \frac{\eta_{sp}}{c}$$

- Inherent viscosity

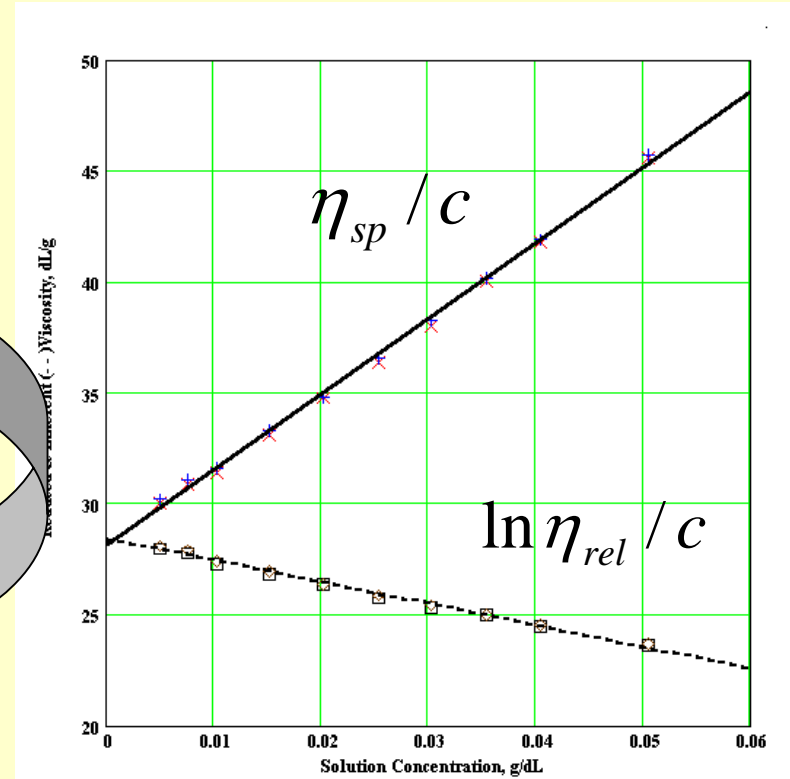
$$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

- Intrinsic viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\ln \eta_{rel}}{c}$$



$$[\eta] = KM^a$$



Molecular weight scaling

Rouse model: free draining, no hydrodynamic interaction

$$[\eta]_0 \propto \eta_0 - \eta_s \propto M \quad (\text{Rouse}) \quad [\eta]_0 = \mathbf{KM}^a, \quad a < 1 \quad (\text{experiment})$$

$$G' = G'' - \eta_s \omega \propto \omega^{1/2} \quad \text{at high frequencies}$$

Zimm model: hydrodynamic interaction (theta solvent)

$$[\eta]_0 = K_\theta M^{1/2} \quad K_\theta = \Phi \left[\langle R^2 \rangle_0 / M \right]^{3/2} = \Phi \left(\frac{C_\infty \ell^2}{m_0} \right)^{3/2}$$

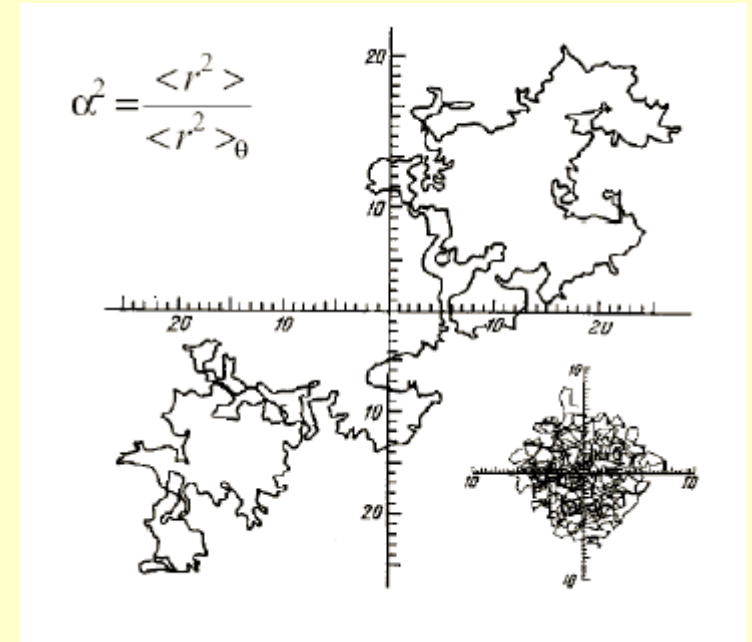
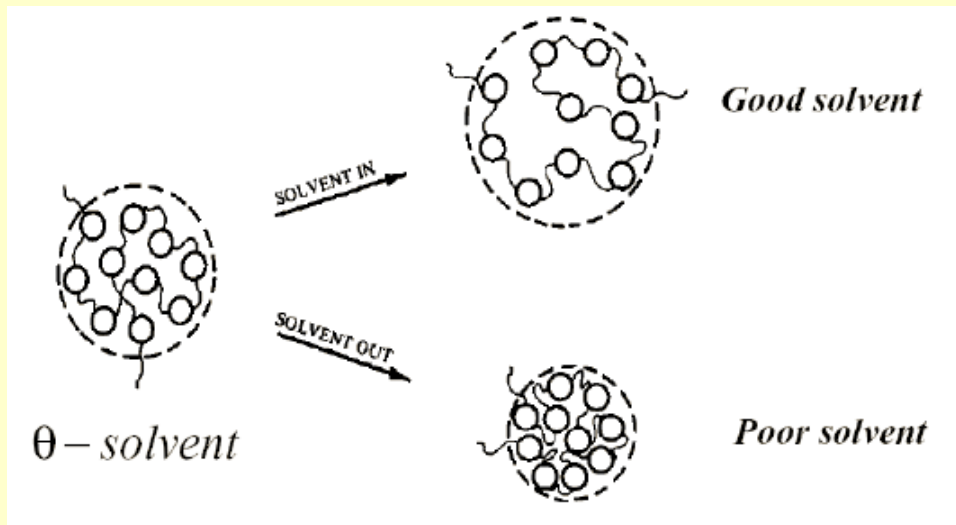
$$G'' - \eta_s \omega = \sqrt{3} G' \propto \omega^{2/3}$$

Hydrodynamic interaction parameter : 0 (Rouse) $< h^* < 0.25$ (Zimm)

$$h^* \equiv \zeta_b / (12\pi^3)^{1/2} R_s \eta_s$$

Solvent quality

related with hydrodynamic interaction, excluded volume effect



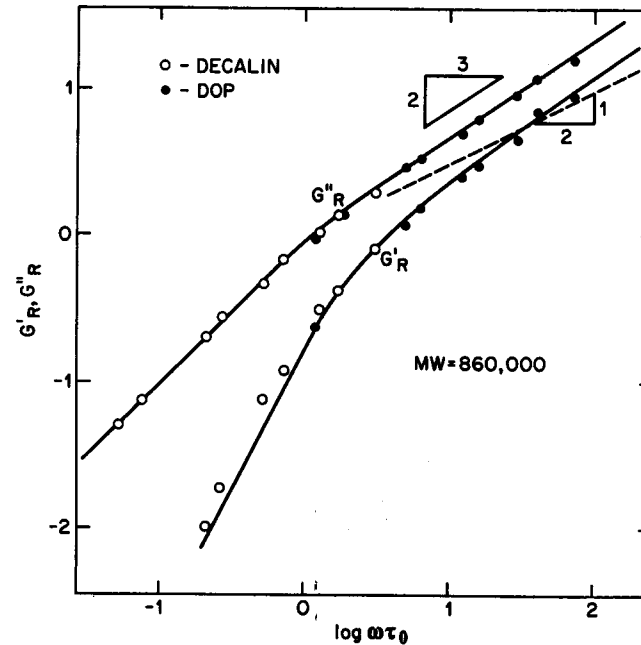


Figure 3.13 Linear viscoelastic data (symbols) for polystyrene in two theta solvents, decalin and dioctylphthalate, compared to the predictions (lines) of the Zimm theory with dominant hydrodynamic interaction, $h = \infty$. The reduced storage and loss moduli G'_R and G''_R are defined by $G'_R \equiv [G']M/N_Ak_B T$ and $G''_R \equiv [G'']M/N_Ak_B T$, where the brackets denote *intrinsic* values extrapolated to zero concentration, $[G'_R] \equiv \lim_{c \rightarrow 0}(G'/c)$ and $[G''_R] \equiv \lim_{c \rightarrow 0}[(G'' - \omega\eta_s)/c]$, and c is the mass of polymer per unit volume of solution. The characteristic relaxation time τ_0 is given by $\tau_0 = [\eta]_0 M \eta_s / N_A k_B T$. For frequencies $\tau_0 \omega$ greater than 10, G'_R and G''_R are proportional to $\omega^{2/3}$, in agreement with the Zimm theory, and not the Rouse theory, which predicts $G' = G'' - \eta_s \omega \propto \omega^{1/2}$. (From Johnson et al. 1970, with permission of the Society of Polymer Science, Japan.)

compare the slopes at high frequencies

Nonlinear rheology

Rouse and Zimm model predict constant shear viscosity and normal stress coefficients

Shear flow

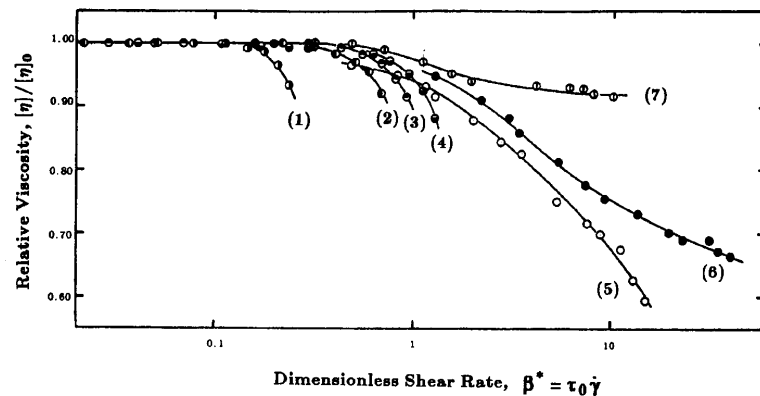


Figure 3.14 Curves of intrinsic relative shear viscosity versus dimensionless shear rate β^* for dilute solutions of poly(α -methylstyrene) with molecular weights of (1) 690,000, (2) 1,240,000, (3) 1,460,000, (4) 1,820,000, (5) 7,500,000, and (6) 13,600,000 in toluene (a good solvent), and (7) 13,600,000 in decalin (a theta solvent). (Reprinted with permission from Noda et al., *Journal of Physical Chemistry* 72:2890 Copyright 1968, American Chemical Society.)

Extensional flow

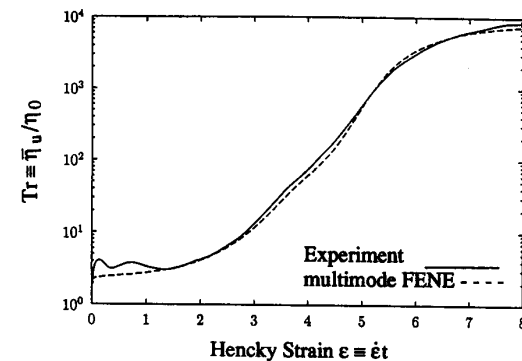


Figure 3.2 Trouton ratio, Tr , of uniaxial extensional viscosity $\bar{\eta}_u$ to zero-shear viscosity η_0 after start-up of steady uniaxial extension at a rate of $\dot{\epsilon} \approx 1 \text{ sec}^{-1}$ for a “Boger fluid” consisting of a 0.185 wt% solution of flexible polyisobutylene ($M_w = 2.11 \times 10^6$) in a solvent composed mostly of viscous polybutene with some added kerosene (solid line). The dashed line is a fit of a “multimode” FENE dumbbell model, where each mode is represented by a FENE dumbbell model, with a spring law given by Eq. (3-56), without preaveraging, as described in Section 3.6.2.2.1. The relaxation times were obtained by fitting the linear viscoelastic data, $G'(\omega)$ and $G''(\omega)$. The slowest mode, with $\tau_1 = 5$ sec, dominates the behavior at large strains; the best fit is obtained by choosing for it an extensibility parameter of $B = 40,000$. The value of $B = 3L^2 / \langle R^2 \rangle_0 = 3(0.82)^2 n / C_\infty$, predicted from the molecular characteristics, is around 20,000. This value is obtained using $n = M_w / 28 = 75,000$ backbone bonds and $C_\infty = 6.8$ (see Table 3-3). (From Verhoef et al. (1997), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

Mixed flow

$$\nabla \mathbf{v} = \frac{1}{2} G \begin{pmatrix} 1 + \alpha & 1 - \alpha \\ -(1 - \alpha) & -(1 + \alpha) \end{pmatrix}$$

$\alpha = 1$ for planar extension flow, $\alpha = 0$ for simple shear flow

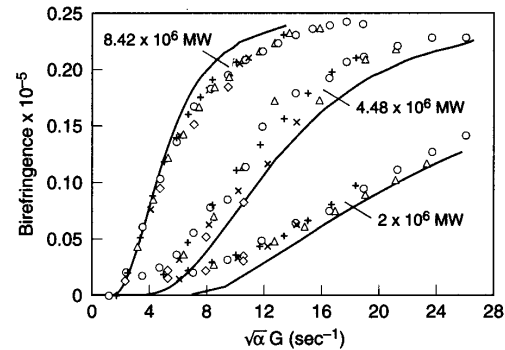
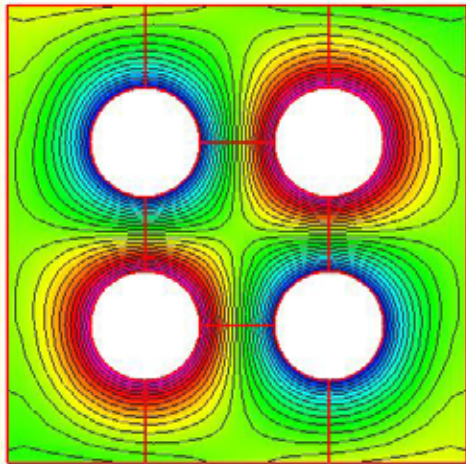


Figure 3.17 Birefringence as a function of the eigenvalue of the velocity gradient tensor, $\sqrt{\alpha}G$, for planar flows generated in a “four-roll mill,” for dilute solutions of polystyrenes of three different molecular weights in polychlorinated biphenyl solvent. Here G is the strain rate and α the “flow type” parameter. For planar extension, $\alpha = 1$ and $G = \dot{\epsilon}$ is the extension rate; for simple shear, $\alpha = 0$ and $G = \dot{\gamma}$ is the shear rate. The different symbols correspond to α values of 1.0 (\circ), 0.8 (Δ), 0.5 ($+$), and 0.25 (diamonds). The curves are theoretical predictions from the FENE dumbbell model, including conformation-dependent drag (discussed in Section 3.6.2.2.2). (From Fuller and Leal 1980, reprinted with permission from Steinkopff Publishers.)

$G\sqrt{\alpha}$

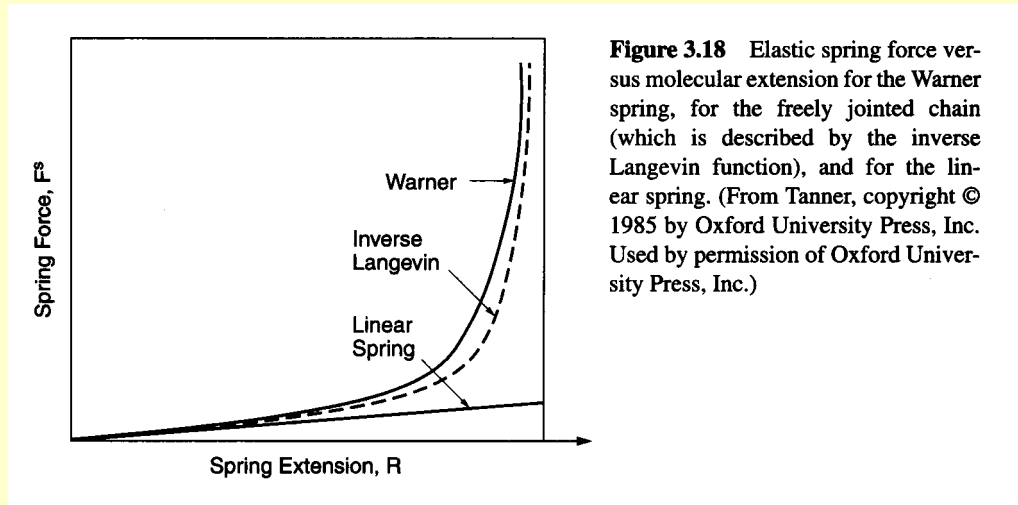
eigenvalue of the velocity gradient tensor equivalent to the extensional component of the flow

In a mixed flow, the stretching of a polymer is dominated by the extensional component of the flow

Finite extensibility

Finite extensible nonlinear elastic (FENE) model

$$\mathbf{F}^s = \frac{2\beta^2 k_B T}{1 - (R/L)^2} \mathbf{R} \equiv H(R^2) \mathbf{R}$$



$$\frac{\partial}{\partial t} \psi = - \frac{\partial}{\partial \mathbf{R}} \cdot \left[\mathbf{R} \cdot \nabla_{\mathbf{V}} \psi - \frac{2k_B T}{\zeta} \left(\frac{1}{k_B T} H(R^2) \mathbf{R} \psi + \frac{\partial \psi}{\partial \mathbf{R}} \right) \right]$$

$$\nabla \cdot \mathbf{S} + \frac{1}{\tau} \left(\frac{\mathbf{S}}{1 - (\text{tr} \mathbf{S}) / 2L^2} - \beta^{-2} \delta \right) = 0$$

$$\boldsymbol{\sigma} = \nu k_B T \beta^2 \left(1 - \frac{\text{tr} \mathbf{S}}{2L^2} \right)^{-1} \mathbf{S}$$

preaveraging
 $H(R^2) \rightarrow H(\langle R^2 \rangle)$

Prediction of FENE-P model

$$\frac{\eta_{\infty}^P}{\eta_0} = (\beta L)^{2/3} (\tau \dot{\gamma})^{-2/3}, \quad \frac{\Psi_{1,\infty}}{\Psi_{1,0}} = (\beta L)^{4/3} (\tau \dot{\gamma})^{-4/3}$$

$$\bar{\eta}_P \rightarrow \bar{\eta}_{p,\infty} = \frac{1}{2} \nu L^2 \zeta = 2 \nu L^2 H_0 \tau = 2 \nu k_B T B \tau = 2 B \eta_{p,0}$$

NS parameter

$$B = 3L^2 / \langle R^2 \rangle_0$$

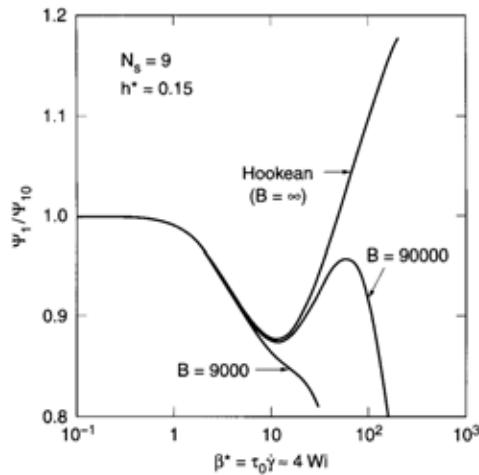


Figure 3.20 Dependence of the first normal stress coefficient on dimensionless shear rate β^* , as predicted by the bead-spring theory with conformation-dependent hydrodynamic interaction and finite extensibility with $N_s = 9$ springs, for various values of B . Here $Wi \equiv \dot{\gamma} \Psi_{1,0} / 2\eta_{p,0}$. (Adapted from J. Non-Newt. Fluid Mech., 34:181, Kishbaugh and McHugh, (1990), with kind permission from Elsevier Science - NL, Sara Burgerhartstraat 25, 1055 KV Amsterdam, The Netherlands.)

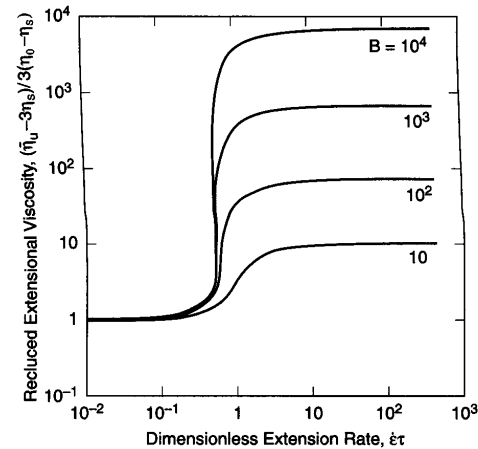


Figure 3.19 The polymer contribution to the steady-state uniaxial extensional viscosity $\bar{\eta}_u$ divided by the polymer contribution to the zero-shear viscosity $\eta_{p,0} = \eta_0 - \eta_s$ for the dumbbell model with a nonlinear "FENE" spring and various values of $B \equiv 2\beta L^2$. (From Bird et al. *Dynamics of Polymeric Liquids, Vol. 2*, Copyright © 1987. Reprinted by permission of John Wiley & Sons, Inc.)

Prediction of DNA motion

Worm-like chain model

$$\frac{F^s \lambda_p}{k_B T} = \frac{1}{4} \left(1 - \frac{R}{L}\right)^{-2} - \frac{1}{4} + \frac{R}{L}$$

Conformation dependent drag coef.

$$\zeta_{rod} = \frac{2\pi L \eta_s}{\ln(L/d)} = \frac{6.28L \eta_s}{\ln(L/d)}$$

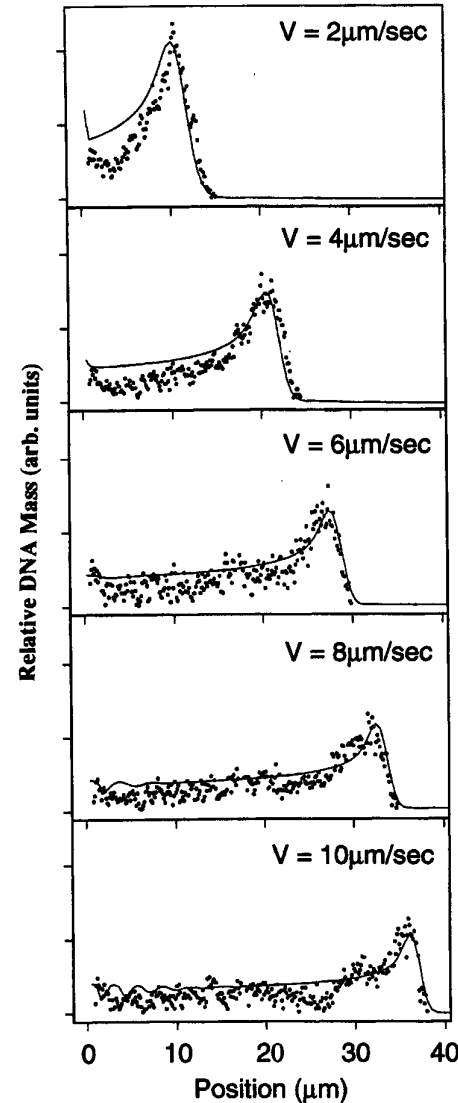


Figure 3.21 Distribution of bead mass as a function of position downstream of the tether point of a DNA molecule of length $L = 67.2 \mu\text{m}$ for various velocities measured in experiments similar to those described in the caption to Fig. 3-1. The lines are the predictions of Monte Carlo molecular simulations using the elastic force from the “worm-like chain” model, Eq. (3-57), and conformation-dependent drag, as described in the text. The value of the parameter $\zeta_{coil}/k_B T = 4.8 \text{ sec}(\mu\text{m})^{-2}$ is obtained from the diffusivity measurements of Smith et al. (1995); $\zeta_{rod}/k_B T = 9.1 \text{ sec}(\mu\text{m})^{-2}$ is obtained from Eq. (3-62) for a fully stretched filament. (From Larson et al. 1997, reprinted with permission from the American Physical Society.)