Chain Extension in Steady Shear Flow

Wolfgang Bruns and Wilfried Carl*

Iwan-N.-Stranski-Institut, Technische Universität Berlin, D-1000 Berlin 10, Germany

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Introduction

The stretching of a polymer chain in steady-state shear flow has been of minor importance in past research since rheological properties are easier to observe experimentally than conformational properties in nonequilibrium. Furthermore, it seems to us that there is a gap between theorists and experimentalists; to this end we calculated the deformation of a polymer chain in steady shear flow in different regimes (Θ, good solvent). The results are presented in a unique form which can directly be compared to experimental results.

Model and Equations

We make intensive use of the results and notation presented by Doi and Edwards in their book *The Theory of Polymer Dynamics* which will be referred to as TPD.[1] We start from the coupled Langevin equations of a polymer consisting of $N + 1$ beads with the vector $\mathbf{R}_n$ pointing from the (arbitrary) origin to the nth segment

$$\zeta \frac{d\mathbf{R}_0}{dt} = -k(\mathbf{R}_0 - \mathbf{R}_1) + \zeta\hat{\kappa}\cdot\mathbf{R}_0 + \mathbf{f}_0 \qquad (1)$$

$$\zeta \frac{d\mathbf{R}_n}{dt} = -k(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \zeta\hat{\kappa}\cdot\mathbf{R}_n + \mathbf{f}_n \qquad (2)$$

$$\zeta \frac{d\mathbf{R}_N}{dt} = -k(\mathbf{R}_N - \mathbf{R}_{N-1}) + \zeta\hat{\kappa}\cdot\mathbf{R}_N + \mathbf{f}_N \qquad (3)$$

Taking the continuous limit and introducing normal coordinates according to

$$\mathbf{X}_p(t) \equiv \frac{1}{N}\int_0^N dn \cos\frac{p\pi n}{N}\mathbf{R}_n(t) \qquad (4)$$

one arrives at

$$\dot{\mathbf{X}}_p + \frac{k_p}{\zeta_p}\mathbf{X}_p - \hat{\kappa}\cdot\mathbf{X}_p = \frac{1}{\zeta_p}\mathbf{f}_p \qquad (5)$$

For the Rouse model

$$\zeta_p = 2N\zeta \qquad (6)$$

with N the number of bonds, ζ the friction coefficient for a single bead, and

$$k_p = 2k\frac{\pi^2 p^2}{N}, \quad k = \frac{3k_B T}{l^2} \qquad (7)$$

l^2 being the mean-square bond length.

$$\hat{\kappa} = \dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (8)$$

is the velocity gradient tensor with the shear rate $\dot{\gamma}$ and $\mathbf{f}_n$ is a random force acting on the nth segment.

Results

Equation 5 can be solved by the method of harmonic analysis[2] with the steady-state result

$$\langle \mathbf{X}_p^2 \rangle = \frac{3k_B T}{k_p} + \frac{1}{2}\frac{k_B T}{k_p}\left(\frac{\zeta_p \dot{\gamma}}{k_p}\right)^2 \qquad (9)$$

The distribution of the random force is assumed Gaussian, satisfying the fluctuation–dissipation theorem (FDT)

$$\langle \mathbf{f}_p(t)\cdot\mathbf{f}_q(0) \rangle = 6\zeta_p k_B T \delta_{pq}\delta(t) \qquad (10)$$

The mean-square end-to-end distance can be shown to be

$$\langle R^2 \rangle = 16 \sum_{p=1,3,5,...} \langle \mathbf{X}_p^2 \rangle \qquad (11)$$

For the mean-square radius of gyration one obtains in a similar way

$$\langle S^2 \rangle = 2\sum_{p=1}^{\infty} \langle \mathbf{X}_p^2 \rangle \qquad (12)$$

Thus for the Rouse model one ends up with

$$\langle R^2 \rangle = Nl^2\left[1 + \frac{1}{6480}\left(\frac{N^2 l^2 \zeta \dot{\gamma}}{k_B T}\right)^2\right] \qquad (13)$$

and

$$\langle S^2 \rangle = \frac{Nl^2}{6}\left[1 + \frac{1}{8508}\left(\frac{N^2 l^2 \zeta \dot{\gamma}}{k_B T}\right)^2\right] \qquad (14)$$

Equations 13 and 14 are identical with those given by Bird et al.[3] and Frisch et al.,[4] respectively.

Preaveraged hydrodynamic interaction can be incorporated in ζ_p using the linearization approximation (see section 4.2 of TPD) with the result

$$\zeta_p = \eta_S(12\pi^3 N l^2 p)^{1/2} \qquad (15)$$

η_S being the solvent viscosity. It should be mentioned that one has to make the ad hoc assumption that the FDT remains unchanged; that is, eq 10 remains still valid with the above ζ_p. This assumption is necessary to obtain $\langle R^2 \rangle = Nl^2$ for $\gamma = 0$.

Inserting eq 15 and the unchanged k_p in eq 9 yields for the Zimm model

$$\langle R^2 \rangle = Nl^2\left[1 + \frac{(Nl^2)^3}{69.4}\left(\frac{\eta_S \dot{\gamma}}{k_B T}\right)^2\right] \qquad (16)$$

and

$$\langle S^2 \rangle = \frac{Nl^2}{6}\left[1 + \frac{(Nl^2)^3}{89.7}\left(\frac{\eta_S \dot{\gamma}}{k_B T}\right)^2\right] \qquad (17)$$

Up to now the results are valid for Θ solutions. In the good-solvent regime one may assume the segment–segment distance still be Gaussian distributed, but now with the variance

$$\langle R_{nm}^2 \rangle = |n - m|^{2\nu} l^2 \qquad (18)$$

Note that in this case l^2 is only a proportionality constant which is no longer related to the bond length. Equation 18 corresponds to the well-known uniform expansion approximation.[5] A calculation similar to that in section 4.2 of TPD yields

$$\zeta_p = \frac{(6\pi^3)^{1/2}\eta_S l \pi^{1-\nu} N^\nu p^{1-\nu}}{\Gamma(1-\nu)\cos\frac{(1-\nu)\pi}{2}} \qquad (19)$$

With $\nu = 1/2$ one gets eq 15 again; with $\nu = 3/5$ the result is

$$\zeta_p = 12.016\eta_S N^{3/5} l p^{2/5} \qquad (20)$$

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Since k_p is also affected by the excluded-volume interaction, one can estimate (eq 4.72 in TPD)

$$k_p = \frac{3k_BT}{\langle \mathbf{X}_p^2 \rangle_{eq}} \tag{21}$$

Now

$$\langle \mathbf{X}_p^2 \rangle_{eq} = \frac{1}{N^2}\int_0^N dn \int_0^N dm \cos\frac{p\pi n}{N} \cos\frac{p\pi m}{N} \langle \mathbf{R}_n \cdot \mathbf{R}_m \rangle \tag{22}$$

With

$$\langle (\mathbf{R}_n - \mathbf{R}_m)^2 \rangle = |n-m|^{2\nu} l^2 = \langle \mathbf{R}_n^2 \rangle + \langle \mathbf{R}_m^2 \rangle - 2\langle \mathbf{R}_n \cdot \mathbf{R}_m \rangle \tag{23}$$

one obtains

$$\langle \mathbf{X}_p^2 \rangle_{eq} = -\frac{1}{2N^2}\int_0^N dn \int_0^N dm\, |n-m|^{2\nu} l^2 \cos\frac{p\pi n}{N} \cos\frac{p\pi m}{N} \tag{24}$$

since $\langle \mathbf{R}_n^2 \rangle$ is independent of m and vice versa.

Putting $\alpha \equiv n/N$, $\beta \equiv m/N$, and $\nu = 3/5$ yields

$$\langle \mathbf{X}_p^2 \rangle_{eq} = -\frac{1}{2}N^{6/5} l^2 \int_0^1 d\alpha \int_0^1 d\beta\, |\alpha - \beta|^{6/5} \cos p\pi\alpha \cos p\pi\beta \tag{25}$$

$$\equiv -\frac{1}{2}N^{6/5} l^2 I(p) \tag{26}$$

The integral can easily be solved numerically. Inserting eqs 20, 21, and 26 into eq 9 and performing numerical integrations and summation over p yield finally for the Zimm-EV model

$$\langle R^2 \rangle = N^{6/5} l^2 \left[0.90 + \frac{(N^{6/5} l^2)^3}{191.8}\left(\frac{\eta_S \dot{\gamma}}{k_BT}\right)^2\right] \tag{27}$$

$$\langle S^2 \rangle = \frac{N^{6/5} l^2}{7}\left[0.99 + \frac{(N^{6/5} l^2)^3}{216.3}\left(\frac{\eta_S \dot{\gamma}}{k_BT}\right)^2\right] \tag{28}$$

The last equation takes into account that from

$$\langle R_{nm}^2 \rangle = |n-m|^{1+\epsilon} l^2 \tag{29}$$

it follows that[5]

$$\langle S^2 \rangle = N^{1+\epsilon} l^2 \frac{1}{6 + 5\epsilon + \epsilon^2} = \frac{N^{2\nu} l^2}{7} \tag{30}$$

for $\nu = 3/5$.

A similar calculation for the Rouse-EV model (with $\zeta_p = 2N\zeta$) yields

$$\langle R^2 \rangle = N^{6/5} l^2 \left[0.90 + \frac{1}{6928}\left(\frac{N^{11/5} l^2 \zeta \dot{\gamma}}{k_BT}\right)^2\right] \tag{31}$$

$$\langle S^2 \rangle = \frac{N^{6/5} l^2}{7}\left[0.99 + \frac{1}{7860}\left(\frac{N^{11/5} l^2 \zeta \dot{\gamma}}{k_BT}\right)^2\right] \tag{32}$$

To bring all the results in a unique form, one defines a reduced shear rate

$$\beta \equiv \frac{[\eta]\eta_S M \dot{\gamma}}{N_A k_B T} \tag{33}$$

where the intrinsic viscosity is given by

$$[\eta] = \frac{N_A k_B T}{2\eta_S M}\sum_{p=1}^{\infty}\frac{\zeta_p}{k_p} \tag{34}$$

(eq 4.147 in TPD). The validity of the above equation for each model is justified by the linearization approximation as was pointed out by Doi and Edwards. One gets

$$\text{Rouse} \qquad [\eta] = \frac{N_A N^2 l^2 \zeta}{36 M \eta_S} \tag{35}$$

$$\text{Rouse-EV} \qquad [\eta] = \frac{N_A N^{11/5} l^2 \zeta}{42.6 M \eta_S} \tag{36}$$

$$\text{Zimm} \qquad [\eta] = 0.425\frac{N_A}{M}(N^{1/2} l)^3 \tag{37}$$

$$\text{Zimm-EV} \qquad [\eta] = 0.170\frac{N_A}{M}(N^{3/5} l)^3 \tag{38}$$

In general one can write

$$\langle R^2 \rangle = \langle R^2 \rangle_0 (1 + C_1 \beta^2) \tag{39}$$

$$\langle S^2 \rangle = \langle S^2 \rangle_0 (1 + C_2 \beta^2) \tag{40}$$

with the coefficients C_1 and C_2 given in Table I.

Table I
Proportionality Constants for Different Models

model	C_1	C_2	model	C_1	C_2
Rouse	0.200	0.152	Zimm	0.080	0.062
Rouse-EV	0.262	0.231	Zimm-EV	0.180	0.160

It is interesting to note that the excluded volume tends to increase the value of the C_i's, while hydrodynamic interaction tends to decrease them. For the Zimm-EV model both effects nearly cancel.

In the recent literature one still finds the value $C_1 = 0.267$ for the Rouse model (see, e.g., ref 6); this results from an older work of Peterlin[7] which has already been corrected by Bird et al.[3] Obviously the corrected version did not enter the experimental literature yet.

Finally one can compare the results with a scaling prediction given by Oono[8] which reads

$$\langle R^2 \rangle = N^{2\nu} l^2 (1 + C\dot{\gamma}^2 N^{2\nu z}) \tag{41}$$

$z = 3$ with hydrodynamic interaction and $z = 2 + 1/\nu$ without it.

Insertion of the respective values for ν and comparison with eqs 13, 16, 27, and 31 show agreement which, in turn, justifies the approximations used. In addition, a similar scaling behavior of the mean-square radius of gyration for the Rouse-EV model (eq 32) has been predicted and confirmed by Frisch et al.[4] via dynamic Monte Carlo calculations.

References and Notes

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