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# Dynamics of Polymers in Concentrated Solutions in the Random Phase Approximation: Stiffness Effect

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The dynamics of ideally flexible polymers in concentrated nonentangled solutions are well described by the Doi–Edwards theory.[1] At very high concentrations, these dynamics are expected to depend somewhat on the conformational details of the chain.

To take into account these features, the Doi–Edwards theory is extended here in two main aspects, in the spirit of the optimized Rouse–Zimm approximation to the polymer dynamics.[2] First, the unperturbed single chain static structure factor is calculated exactly for a discrete chain of known non-Gaussian statistics and by avoiding large wave vector approximations. Results are presented only for the freely rotating chain model to describe the stiffness effect. Second, in the Langevin dynamics of the collective coordinates the full hydrodynamic interaction is considered by adding the free draining contribution to the nondraining counterpart.

In the polymer concentrated solutions, where density fluctuations are small, and in the short time regime (shorter than the reptation time), the time evolution of the dynamical structure factor is found to be single exponential[1]

$$g(k,t) = g(k)\exp(-\Gamma(k)t) \tag{1}$$

Here $g(k,t)$ and $g(k)$ are the dynamical and static structure factors and $\Gamma(k)$ is the characteristic rate constant.

Dealing with a discrete bead description of the polymer, it is better to introduce the exact Oseen mobility tensor,

$$\mathbf{H}_{ai,bj} = \frac{1}{\zeta}\delta_{ai,bj} + \int d\mathbf{q}\,\frac{1}{(2\pi)^3\,\eta_0 q^2}\times (\mathbf{1} - \hat{\mathbf{q}}\hat{\mathbf{q}}^{\mathrm{T}})e^{i\mathbf{q}\cdot\mathbf{R}_{ai,bj}}(1-\delta_{ai,bj}) \tag{2}$$

which includes the free draining contribution (first term in the right-hand side of eq 2) disregarded in the Doi–Edwards approach. Here $\boldsymbol{R}_{ai,bj}$ are the distances between beads $i$ and $j$ belonging to polymer $a$ and $b$, respectively. Following the Doi–Edwards procedure,[1] $\Gamma(k)$ is obtained as

$$\Gamma(k) = \frac{k_BT}{\zeta}\frac{k^2}{g(k)} + \frac{k_BT}{4\pi^2\eta_0}\frac{1}{g(k)}\int_0^\infty dq\, q^2[g(q)-g(\infty)]\times\left[\frac{q^2+k^2}{2qk}\log\left|\frac{k+q}{k-q}\right| - 1\right] \tag{3}$$

with $\zeta$ the segment friction coefficient and $\eta_0$ the solvent viscosity. In the right part of eq 3, the first term is the free draining counterpart, and the second term takes into account the exact Oseen interaction. The subtraction in the first square parentheses of eq 3 of the constant large $k$ limit of the static structure factor, $g(\infty)$, takes into account that the hydrodynamic interaction is effective only between different segments, a condition ignored in the nondraining approximation, and ensures the convergence of the $q$ integral. When the free draining contribution is ignored and in the rough large wave vector approximation, which implies that $g(\infty)$ becomes zero, the well-known Doi–Edwards expression[1] is recovered.

In the random phase approximation and for a $\delta$ function excluded volume, the static structure factor may be written in the general form

$$g^{-1}(k) = g_0^{-1}(k) + c\mathrm{v} \tag{4}$$

with v the excluded volume parameter, $c$ the average segment density and $g_0(k)$ the unperturbed static structure factor for a single chain of $n$ beads of coordinates $\boldsymbol{R}_i$:

$$g_0(k) = n^{-1}\sum_{i,j=1}^{n}\exp\left[-\frac{k^2}{6}\langle|\mathbf{R}_i - \mathbf{R}_j|^2\rangle\right] = 1 + 2n^{-1}\sum_{j=1}^{n-1}(n-j)\exp\left[-\frac{k^2}{6}\langle|\mathbf{R}_{j0}|^2\rangle\right] \tag{5}$$

The stiffness effect is now introduced in $\Gamma(k)$ of eq 3 by a proper choice of the equilibrium mean square distances $\langle|\boldsymbol{R}_i - \boldsymbol{R}_j|^2\rangle$. In the case of a freely rotating chain model the latter distances are given exactly[3] by

$$\langle|\mathbf{R}_i - \mathbf{R}_j|^2\rangle = l^2|i-j|\left\{\frac{1+p}{1-p} - \frac{2p}{|i-j|}\frac{1-p^{|i-j|}}{(1-p)^2}\right\} \tag{6}$$

with $l$ the segment length,

$$p = -\cos\theta \tag{7}$$

the stiffness parameter, and $\theta$ the valence angle. In the limit $p \to 0$ and $p \to 1$ the Gaussian expression $l^2|i-j|$ and the rod expression $l^2|i-j|^2$ are respectively recovered. Using the proper form for the unperturbed interbead distances, a hierarchy of dynamical models, generally referred to as optimized Rouse–Zimm (ORZ) models,[2] can be easily generated. Another interesting case is the rotational isomeric state (RIS) chain model, not considered here.

The rate constant $\Gamma$ can be rewritten in the useful form

$$\Gamma = k^2 D_{\mathrm{G}}F(p) \tag{8}$$

with

$$D_{\mathrm{G}} = \frac{k_{\mathrm{b}}T}{6\pi\eta_0\xi_{\mathrm{G}}} \tag{9}$$

the cooperative diffusion coefficient for a Gaussian chain with a correlation length of the concentration fluctuations given as

$$\xi_{\mathrm{G}} = \frac{l}{(12c\mathrm{v})^{1/2}} \tag{10}$$

Here $F(p)$ is a corrective factor which is a function of the adimensional wave vector $kl$, of the adimensional Gaussian correlation length $\xi_{\mathrm{G}}/l$, of the stiffness of the chain and of the number of beads $n$. It is easy to show that in the case of a semiflexible polymer the correlation

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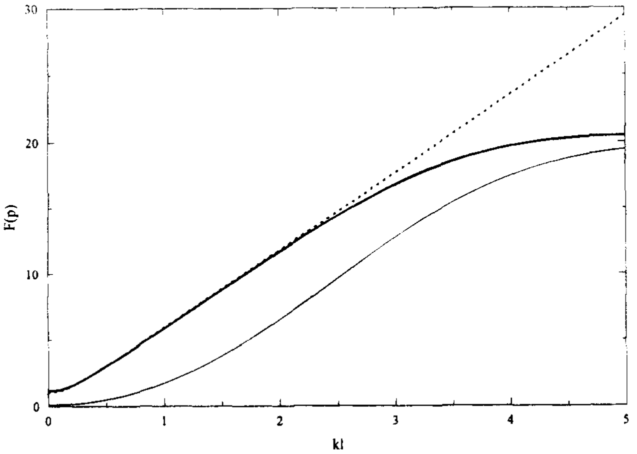

**Figure 1.** Corrective factor $F(p)$ as a function of $kl$ for $p = 0$ and $n = 1000$. Dotted curve: Doi–Edwards solution. Full curve: eq 7. Light curve: free draining contribution.

length becomes wave vector dependent. For this reason, the rate constant $\Gamma$ is described here in terms of the Gaussian correlation length, which has the constant value given in eq 10, while the remaining $kl$ effects are included in the $F(p)$ factor. For a Gaussian chain ($p = 0$) and using the large $k$ expression for the unperturbed static structure factor $g_0(k) = 12/(kl)^2$, $F(p)$ becomes the Doi–Edwards function $F(k\xi_G)$.[1]

In Figure 1 the corrective factor $F(p)$ is reported against $kl$ for $p = 0$ and $n = 1000$. In the small $kl$ range $F(0)$ becomes a constant, and $\Gamma(k)$ displays a diffusion-like $k^2$ dependence. The small difference between our limiting value and the Doi–Edwards limit 1.0, is due to our choice of the discrete "exact" definition of $g_0(k)$, given by eq 5, instead of the large $kl$ expression.

In the important intermediate $kl$ range ($0 \ll kl < 2$) our partial draining result of eq 3, with $\zeta_r = \zeta/6\pi\eta_0 l = 0.25$, is practically coincident with the Doi–Edwards result, obtained for Gaussian chains in the nondraining limit. This is clear evidence that the nondraining limit and the "exact" partial draining with $\zeta_r = 0.25$ are almost equivalent, a well-known result for the viscoelastic properties.[4,5] In this intermediate range, $\Gamma(k)$ shows the well-known $(kl)^3$ behavior. Note that at very large $kl$ ($kl > 2.5$) $F(0)$ becomes constant due both to the decreasing to zero of the hydrodynamic interaction contribution and to the asymptotically constant behavior of the free draining contribution.

In Figure 2 it is shown that in the interesting range, $0 \ll kl < 2.0$, by increasing the stiffness, not only $F(p)$ increases but also the curvature of the function changes. For larger $kl$ values all the curves at different stiffnesses converge to the same asymptotic limit, displayed in Figure 1, due to the vanishing of the effect of the hydrodynamic interaction. As a consequence a $k^2$ dependence for $\Gamma(k)$ is ultimately obtained.

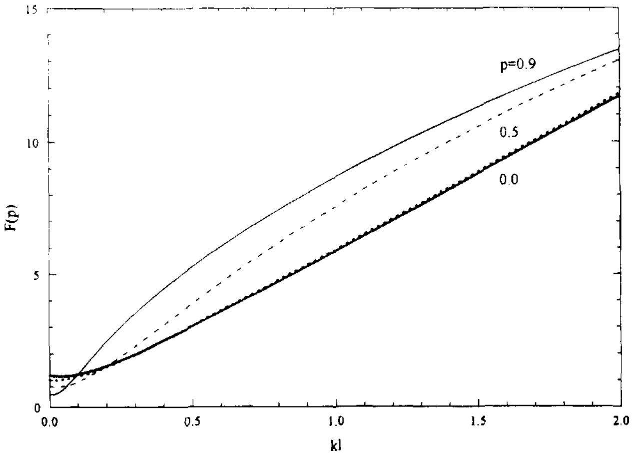

**Figure 2.** Corrective factor $F(p)$ for $n = 1000$ and $p = 0, 0.5, 0.9$. Dotted curve: Doi–Edwards solution.

In both figures a value of $\xi_G/l = 5$ has been used. This low value corresponds to a high concentration and excluded volume parameter (see eq 10). Similar stiffness effects are obtained at larger $\xi_G$ values.

These results indicate that the dynamic structure factor of concentrated nonentangled polymer solutions should be dependent on the persistence length, and in general on the conformational details of the polymer chain.

Important effects are expected in the case of concentrated solutions of semiflexible polymers such as polyelectrolytes.[6]

## References and Notes

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