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Dynamics of Stretched Polymer Chains. 2

Yitzhak Rabin*[†] and Jan W. Dash[‡]

La Jolla Institute, Center for Studies of Nonlinear Dynamics,[§]
La Jolla, California 92037. *Received July 12, 1984*

ABSTRACT: We study the internal modes of an ideal polymer chain that is being stretched by an external force. The effects of the force on the hydrodynamic interaction are investigated by using a preaveraged Oseen tensor approach, for both Gaussian and freely jointed polymer chains.

I. Introduction

Although there have been numerous theoretical investigations of the dynamics of isolated polymers in solution,[1] there were relatively few nonperturbative treatments of the dynamics of non-free-draining, stretched polymer chains.[2-4] In the pioneering work of Peterlin[2,3] polymers in realistic (shear and extensional) flow fields were considered. This has been done at the expense of neglecting the anisotropy of hydrodynamic interaction[2] and treating the dynamics of the lowest mode only[3] (dumbbell model). More recently, in a paper bearing the same title as ours (hereafter referred to as paper 1) Pincus[4] considered the dynamics of a chain stretched by an applied tensile force, focusing on the excluded-volume problem in the limit of high elongations (to which the tensile blob model[5] can be applied).

In view of recent experiments on dilute solutions of elongated chains[6-8] new theoretical investigations in this field are needed. In this work we attempt to study the dynamics of stretched polymer chains following the general approach of paper 1. However, since we do not use the tensile blob model, our results are not confined to the strong stretching limit and we can study the dynamics of ideal polymer coils in both the intermediate and the strong stretching regimes. In addition, we study the effect of the induced asymmetry of hydrodynamic interaction on the relaxation times of the internal modes of the chain. Finally, we investigate the dynamics of real (non-Gaussian) chains, using the $1/n$ expansion about the Gaussian distribution function for the chain[9] (the numerical coefficients in the expansion are taken to be those for a freely joined chain) and linearizing the equations of motion.

In section II, we present the derivation of the spectrum of relaxation times for the polymer modes, taking into acount hydrodynamic interaction via the Oseen tensor and preaveraging the tensor with respect to the distribution function appropriate for a polymer under traction. Closed-form analytic results for the preaveraged Oseen tensor elements are derived in the Appendix. Section III deals with the numerical results for the mode spectrum. The transition from the non-free-draining to the free-draining regimes as the applied tensile force is increased is investigated and is found to be nonmonotonic. The effects of the stretching on the various modes are compared and the stretching-induced asymmetry between longitudinal and transverse modes is studied. Non-Gaussian effects on the spectrum are investigated. In section IV, our main results are summarized and their relevance to some recent experiments is discussed.

II. Relaxation Spectrum

Consider a dilute solution of polymers of length Na where a is the segment size and N is the number of segments in a polymer chain. The viscosity coefficient of the solvent is η_0. This solvent is assumed ideal (ϑ solvent); i.e., we neglect excluded-volume effects.

Balancing the forces acting on the ith segment and neglecting inertial effects and Brownian motion,[1,10] we obtain the equation of motion for the position $\vec{R}_i$ of the ith segment

$$b(\mathrm{d}\vec{R}_i/\mathrm{d}t) = \vec{F}_i^{(\mathrm{e})} + \vec{F}_i^{(\mathrm{h})} \qquad (1)$$

[†] Permanent address: The Weizmann Institute, Rehovot, Israel.

[‡] On leave from CPT2, CNRS, Marseille, France. Present address: Bell Laboratories, Holmdel, NJ 07733.

[§] Affiliated with the University of California, San Diego.

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where $\vec{F}_i^{(e)}$ and $\vec{F}_i^{(h)}$ are respectively the entropic and hydrodynamic forces and b is the segment friction coefficient. The entropic restoring force on a segment can be derived from the distribution function for the unperturbed chain; for a Gaussian chain we obtain a linear restoring force[1]

$$\vec{F}_i^{(e)} = (3k_BT/a^2)(\vec{R}_{i+1,i} - \vec{R}_{i,i-1}) \tag{2}$$

where $\vec{R}_{i+1,i} = \vec{R}_{i+1} - \vec{R}_i$ is the vector connecting the ith and $(i + 1)$th neighboring segments. The hydrodynamic force $\vec{F}_i^{(h)}$ is due to the perturbation of solvent velocity at the ith segment by the frictional forces exerted on the solvent by the other segments of the polymer. It is given by the Oseen formula[1]

$$\vec{F}_i^{(h)} = \sum_{j(\neq i)} \mathbf{T}_{ij}\cdot\vec{F}_j^{(e)} \tag{3}$$

where $\mathbf{T}$ is the Oseen tensor

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta_0 R_{ij}}\left[\mathbf{I} + \frac{\vec{R}_{ij}\vec{R}_{ij}}{R_{ij}^2}\right], \quad i \neq j \tag{4}$$

with $\mathbf{I}$ being the unit tensor.

In order to proceed with a linear mode analysis of eq 1 we introduce the preaveraging approximation,[1] i.e., average the Oseen tensor with respect to the appropriate distribution function. Here, we consider a polymer chain stretched by an external tensile force $\vec{f}$. If we take the z axis as the direction of the force, the distribution function for a chain of length na is[9]

$$P_n(\vec{R}) = P_n^{(0)}(\vec{R})e^{R_z/\xi} \tag{5}$$

where $P_n^{(0)}(R)$ is the distribution function for the unperturbed chain (at zero force) and $\xi = k_BT/f$ is the "penetration" length of the force[5,11] (i.e., the force is strong (weak) on scales larger (smaller) than ξ). The cylindrical symmetry about the z axis implies that the preaveraged Oseen tensor is diagonal, i.e.

$$\langle T_{ij}^{\alpha\beta}\rangle_n = Z^{-1}\int \mathrm{d}^3R\, P_n(\vec{R})T_{ij}^{\alpha\beta} = \delta_{\alpha\beta}\langle T^{\alpha\alpha}\rangle_n, \tag{6}$$

$$\alpha, \beta = x, y, z$$

where $Z = \int \mathrm{d}^3R\, P_n(\vec{R})$ is the partition function and $n = |i - j|$ is the contour distance along the chain between the ith and jth segments. The only nonvanishing elements are $\langle T^{zz}\rangle_n$ and $\langle T^{xx}\rangle_n = \langle T^{yy}\rangle_n$.

Combining eq 1–6 and introducing the eigenmode expansion (with boundary conditions appropriate for a linear chain)

$$\vec{R}_n = \sum_{p,\omega} e^{-\omega t}\cos\,(pn\pi/N)\vec{Q}(p,\omega) \tag{7}$$

we obtain the relaxation spectrum for the internal modes

$$\tau_0/\tau_{p\alpha} = 4\sin^2\,(p\pi/2N)\Big[1 + 2b\sum_{n=1}^{N}\langle T^{\alpha\alpha}\rangle_n \cos\,(pn\pi/N)\Big] \tag{8}$$

with $\tau_{p\alpha} = \omega_{p\alpha}^{-1}$ being the relaxation time of the pth mode ($\alpha = z, x$ for longitudinal and transverse modes, respectively) and $\tau_0 = ba^2/3k_BT$.

The first term in the square brackets in eq 8 gives $\tau_{p\alpha} \sim N^2$ for the low-lying modes and is associated with the Rouse[12] (free-draining) contribution to the spectrum. The second term is responsible for hydrodynamic interaction and in the limit where it dominates over the Rouse term we obtain the Zimm[13] (non-free-draining) mode spectrum. Notice that in our approximation all the effects of the tensile force come only through the Zimm term.

In order to proceed we have to perform the appropriate averaging of the Oseen tensor. This involves computing the averages $\langle 1/R\rangle_n$, $\langle R_z^2/R^3\rangle_n$, and $\langle R_x^2/R^3\rangle_n$ with respect to the distribution function $P_n(R)$. In the following we examine two cases: (a) the Gaussian chain and (b) the non-Gaussian chain.

(a) With the Gaussian chain, the unperturbed distribution function is

$$P_n^{(0)}(\vec{R}) = \left(\frac{3}{2\pi na^2}\right)^{3/2} e^{-3R^2/2na^2} \tag{9}$$

(b) With the non-Gaussian chain, using the $1/n$ expansion about the Gaussian distribution function, we can proceed quite generally, expressing the distribution function in terms of its higher moments[9,14]

$$P_n^{(0)}(\vec{R}) = \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{3/2} e^{-3R^2/2na^2}\left[1 + g_4\left(15 - 30\frac{R^2}{\langle R^2\rangle} + 9\frac{R^4}{\langle R^2\rangle^2}\right) + \ldots\right] \tag{10}$$

where $g_4 = -(1/8)(1 - 3\langle R^4\rangle/5\langle R^2\rangle^2)$ can be shown to be of order $1/n$. The expansion can be truncated at the second term in the square brackets for elongations such that $R^2/\langle R^2\rangle \ll n$ (well below full extension). In this approximation, all the information about the local structure of the chain comes through the two moments $\langle R^2\rangle$ and $\langle R^4\rangle$ which can be computed in the framework of the various conformational models of polymer chains. Thus, one can systematically include corrections corresponding to more realistic description of the polymer—such as conformational barriers, etc.[9] Notice that in eq 8 the elements $\langle T^{\alpha\alpha}\rangle_n$ have to be computed for all values of n ($n = 1$, i, ..., N). Clearly, the $1/n$ expansion in eq 10 breaks down for small values of n. Nevertheless, we will proceed to use only the leading $1/n$ term in the expansion. This can be justified by a standard Fourier transform type of argument (n and p are conjugate variables), as long as we consider sufficiently long chains and do not investigate the highest internal modes for which the contribution from the small contour distance scales is significant.

For concreteness we consider the simplest non-Gaussian model of the polymer, i.e., the freely jointed chain. Neglecting the $O(1/n^2)$ terms, the distribution function is[9]

$$P_n^{(0)}(\vec{R}) = \left(\frac{3}{2\pi na^2}\right)^{3/2} e^{-3R^2/2na^2}\left[1 - \frac{3}{20n}\left(5 - \frac{10R^2}{na^2} + \frac{3R^4}{n^2a^4}\right)\right] \tag{11}$$

Using this distribution function, we can readily compute the partition function for a freely jointed chain under the action of a tensile force and obtain[15]

$$Z = \left[1 - \frac{1}{180n}\left(\frac{n^{1/2}a}{\xi}\right)^4\right] e^{(1/6)(n^{1/2}a/\xi)^2} \tag{12}$$

An outline of the straightforward, though quite tedious, calculation of the averaged Oseen tensor elements is presented in the Appendix. For the freely jointed chain we obtain

$$2b\langle T^{zz}\rangle_n = \frac{\gamma}{n^{1/2}}\left\{\left[1 + \frac{1}{5n}\left(x^2 - \frac{11}{4}\right)\right]F_1(x) - \frac{1}{5n}F_3(x)\right\} \tag{13}$$

$$2b\langle T^{xx}\rangle_n = \frac{\gamma}{2n^{1/2}}\left\{\left[1 + \frac{1}{5n}\left(x^2 - \frac{11}{4}\right)\right]F_2(x) - \frac{1}{5n}F_4(x)\right\} \tag{14}$$

where

$$x = na^2/6\xi^2 \tag{15}$$

and γ is the hydrodynamic coupling parameter

$$\gamma = (6/\pi^3)^{1/2}b/\eta_0 a \tag{16}$$

The functions $F_i(x)$ ($i = 1, ..., 4$) can be written as combinations of error functions and exponentials

$$F_1(x) = \tfrac{1}{4}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) - (1/4x)[\tfrac{1}{2}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) - e^{-x}] \tag{17}$$

$$F_2(x) = \tfrac{1}{4}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) + (1/4x)[\tfrac{1}{2}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) - e^{-x}] \tag{18}$$

$$F_3(x) = \tfrac{1}{2}(x^2 + \tfrac{3}{4})(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) + \tfrac{1}{4}(2x - 1)e^{-x} - (3/4x)[\tfrac{1}{2}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) - e^{-x}] \tag{19}$$

$$F_4(x) = \tfrac{1}{2}(x^2 + x - \tfrac{3}{4})(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) + \tfrac{1}{4}(2x + 1)e^{-x} + (3/4x)[\tfrac{1}{2}(\pi/x)^{1/2}\operatorname{erf}(x^{1/2}) - e^{-x}] \tag{20}$$

The above expressions for the preaveraged Oseen tensor elements are then substituted into eq 8. Notice, however, that eq 8 was derived by assuming a linear entropic restoring force. Strictly speaking, this assumption is not valid for non-Gaussian chains; in our approximation for the distribution function (keeping the $1/n$ terms in eq 10) we obtain cubic nonlinearities in the restoring force. Although we intend to investigate the fully nonlinear problem in the future, here we assume that the nonlinearity of the force can be treated in a mean-field fashion (in the spirit of the preaveraging approximation for the Oseen tensor), i.e., by replacing

$$\vec{F}^{(e)} = -K_1\vec{R} - K_2\vec{R}^3 \rightarrow -(K_1 + K_2\langle R^2\rangle)\vec{R} \tag{21}$$

This mean-field type approximation leads to renormalization of the elastic spring constant of the chain, which is then absorbed in the normalization constant τ_0 in eq 8. We expect this approximation to be reasonable as long as the nonlinearities can be considered as a small perturbation. It clearly breaks down when the applied force becomes strong on the scale of a single segment of the chain, i.e., as a/ξ becomes of order unity.

The Gaussian result is obtained by setting $F_3(x) = F_4(x) = 0$ and neglecting the $1/n$ terms in eq 13 and 14; this gives

$$2b\langle T^{zz}\rangle_n|_{\text{Gaussian}} = (\gamma/n^{1/2})F_1(x) \tag{22}$$

$$2b\langle T^{xx}\rangle_n|_{\text{Gaussian}} = (\gamma/2n^{1/2})F_2(x) \tag{23}$$

III. Results

The relaxation spectrum for the longitudinal and transverse modes is obtained by numerical evaluation of the Fourier sum in eq 8. We vary the external tensile force strength through the parameter

$$\lambda = \tfrac{2}{3}(a/\xi)^2 \tag{24}$$

The relative contribution of the hydrodynamic interaction is given by the reduced inverse relaxation time for the pth mode

$$\Delta\tau_p^{-1} = \{\tau_p^{-1} - \tau_p^{-1}(\text{Rouse})\}/\tau_p^{-1}(\text{Rouse}) \tag{25}$$

where $\tau_p^{-1}(\text{Rouse}) = 4\tau_0^{-1}\sin^2(p\pi/2N)$. Notice that $\Delta\tau_p^{-1}$ is independent of the hydrodynamic coupling parameter γ.

In Figure 1, $\Delta\tau_p^{-1}$ is plotted against the force parameter λ for the longitudinal modes $p = 1$, 2, and 10, for both Gaussian and freely jointed chains. We can distinguish between the (a) weak-, (b) intermediate-, and (c) strong-force regimes.

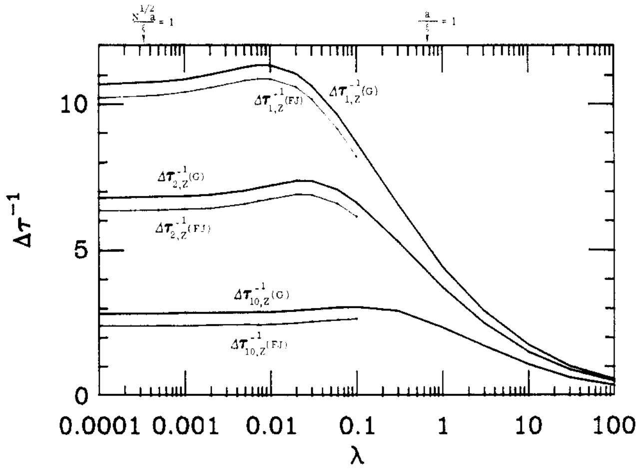

Figure 1. Reduced inverse relaxation times $\Delta\tau_{p,z}^{-1}$ for the first, second, and tenth longitudinal modes are plotted against the tensile force parameter λ. Results are presented for both Gaussian (G) and freely jointed (FJ) chains of $N = 2000$ segments. The weak force ($N^{1/2}a/\xi = 1$) and the very strong force limits ($a/\xi = 1$) are indicated by arrows.

(a) In the weak-force regime ($N^{1/2}a/\xi < 1$), the external force is weak on all intrapolymer scales and the spectrum is virtually unperturbed by it.

(b) In the intermediate-force regime ($N^{1/2}a/\xi > 1$ but for most scales n, $n^{1/2}a/\xi \ll 1$), the largest intrachain scales are strongly perturbed by the force and their contribution to the Fourier sum (eq 8) is sharply reduced; the shorter scales are not perturbed. As a result of the reduced cancellation between the corresponding terms in eq 8, the hydrodynamic interaction tends to increase with increasing force and the non-free-draining character of the chain is enhanced. (A similar effect has been predicted by Peterlin for Gaussian chains in shear and elongational flows.[3]) This effect is more pronounced for the lower modes (which are more sensitive to the large-scale dynamics). As the mode number p is increased, the maximum of hydrodynamic interaction is shifted toward higher values of the force parameter λ, since the higher modes are sensitive to smaller length scales that are "penetrated" at higher λ.

(c) In the strong-froce regime ($n^{1/2}a/\xi > 1$ for the majority of intrapolymer contour lengths), the external force "penetrates" most of the length scales in the chain. The hydrodynamic interaction decreases (logarithmically) with increasing λ. However, the Rouse spectrum is approached only asymptotically, for $a/\xi \gg 1$. This limit is unphysical for real (non-Gaussian) chains, for which the nonlinearity of the restoring force has to be taken into account already as $\xi \rightarrow a$. Thus, eq 1 becomes nonlinear and the linear mode analysis leading to the spectrum (eq 8) can no longer be applied. We hope to address the nonlinear problem in a future publication.

Notice that in our approximation the freely jointed chain results (Figure 1) are qualitatively similar to those for the Gaussian chain.[16] The deviation of $\Delta\tau_p^{-1}$ from the Gaussian value is almost independent of the mode number and the external tensile force. As one could expect for a stiffer chain, the free-jointed values are shifted toward their Rouse limit, i.e., hydrodynamic interaction is reduced. The effect is particularly important for the higher modes; for example, for $p = 100$ the hydrodynamic interaction of a freely jointed chain is less than 50% of that of a Gaussian chain.

Figure 2 illustrates the variation of $\Delta\tau_z^{-1}$ as a function of the longitudinal mode number p, at a fixed applied

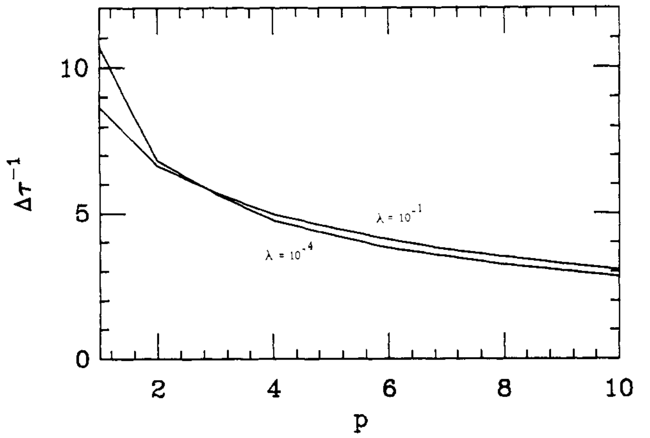

Figure 2. Reduced inverse relaxation times $\Delta\tau_{p,z}^{-1}$ are plotted against the longitudinal mode number p for weakly ($\lambda = 0.0001$) and strongly ($\lambda = 0.1$) perturbed Gaussian chains of $N = 2000$ segments.

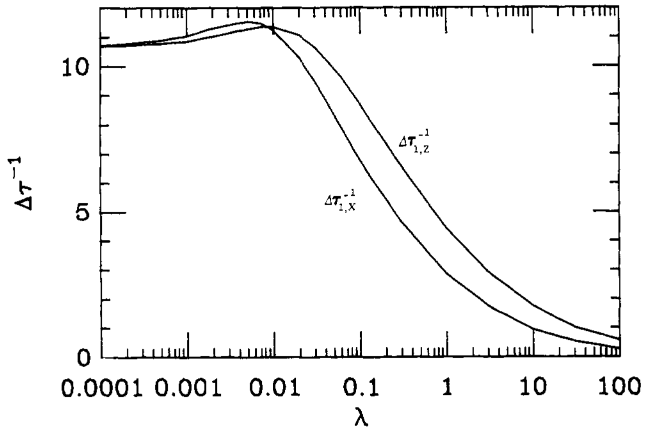

Figure 3. Reduced inverse relaxation times $\Delta\tau_{1,z}^{-1}$ and $\Delta\tau_{1,x}^{-1}$ for the lowest longitudinal and transverse modes, respectively, are plotted against the tensile force parameter λ, for a Gaussian chain of $N = 2000$ segments.

tensile force (on a Gaussian chain). The relative contribution of the hydrodynamic interaction is a rapidly decreasing function of p though the decrease is less pronounced at higher extensions. While in the zero force limit $\Delta\tau_{p=1}^{-1}$ is larger than in the strong-force regime, a crossover occurs around $p = 3$ and hydrodynamic effects on the higher modes are actually higher in the strong-force regime (the freely jointed chain results are quite similar).

In Figure 3 we compare the longitudinal and transverse spectra for the lowest mode. As expected, the degeneracy is lifted by the tensile force. In the intermediate-force regime the transverse modes exhibit slightly more pronounced hydrodynamic interaction effects than the longitudinal modes. As the force is increased, a crossover occurs and in the strong-force regime the transverse relaxation times increase much faster toward their limiting Rouse values. In fact, since asymptotically $F_1(x)/F_2(x) \rightarrow 1$ (eq 17 and 18, for $x \gg 1$) we obtain $\langle T^{zz}\rangle_n/\langle T^{xx}\rangle_n \rightarrow 2$ (eq 13 and 14) and hence $\Delta\tau_{pz}^{-1}/\Delta\tau_{px}^{-1} \rightarrow 2$ in the strong tensile force limit. The same qualitative behavior is observed for the higher modes and for freely jointed chains.

In Figure 4 we study the effect of different chain lengths on the relaxation time of the lowest mode, at various tensile force strengths. Hydrodynamic interaction increases with increasing chain length. This effect is particularly large in the intermediate-force regime in which the maximum of hydrodynamic interaction is much more pronounced for longer chains. Notice the shift of the maximum toward lower applied force strengths as the chain length is increased. This implies that for extremely long chains, the lowest modes will exhibit behavior characteristic of the intermediate-force regime, already at very low applied tensile force levels.

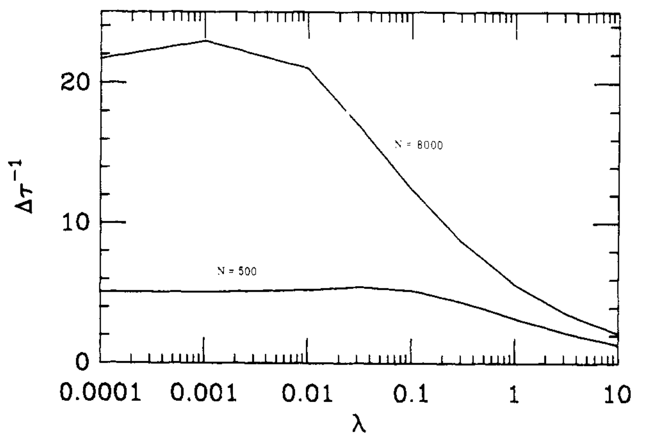

Figure 4. Reduced inverse relaxation times $\Delta\tau_{1,z}^{-1}$ are plotted against the tensile force parameter λ for chains of $N = 500$ and $N = 8000$ segments.

IV. Conclusion

We have derived and analyzed the relaxation spectrum for the modes of a stretched polymer chain. Non-Gaussian corrections have been shown to reduce the hydrodynamic interaction. This effect is found to be almost independent of the applied tensile force strength and thus can be estimated from the unperturbed coil results. The resulting shift from the Gaussian results can be significant even for the lowest modes and is probably much higher for real polymers that are, as a rule, stiffer than the freely jointed chain. Consideration of such dynamical real-chain effects can help us fill the gap between the scaling approach of polymer physics and the orientation toward molecular detail of polymer chemistry (in the same spirit as it has been done for the static properties[9]). It is also of paramount importance in practical applications such as turbulent drag reduction by polymer additives.[17]

We have confirmed the existence of an intermediate-force regime in which the longest intrapolymer scales are penetrated by the force but the shorter-distance scales are relatively unperturbed. In this regime, the hydrodynamic interaction actually *increases* with the applied force, resulting in an increasingly non-free-draining character of the polymer. At still higher applied tensile force levels the hydrodynamic interaction begins to decrease as the chain becomes stretched on all scales and the limit of Rouse dynamics is approached. The existence of the intermediate-force regime may help to explain the recent experimental results of the Bristol group[6-8] in which $\tau \sim N^{3/2}$ behavior was observed for elongated chains in all solvents, in disagreement with the theoretical predictions[11] of $\tau \sim N^{9/5}$ in good solvents (taking into account the excluded-volume effect). The explanation is that in this regime, which is the one appropriate for deformed polymer coils, the contribution of the largest distance scales (which dominate the excluded-volume effect) to the relaxation spectrum is drastically reduced by the tensile force and the remaining contributions from shorter scales are relatively insensitive to the excluded-volume effect.[18]

Finally, we would like to comment on the applicability of our results to realistic polymers in flow situations. Clearly, our model in which a polymer is stretched by an applied tensile force is a gross oversimplification as far as the flow is concerned. However, we believe that our results, which focus on the polymer side of the polymer–flow interaction problem, provide important insights to the more complicated problem of dynamics of polymers in extensional flow fields.

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Appendix

In order to compute the nonvanishing elements of the Oseen tensor we have to average $1/R$, R_z^2/R^3, and R_x^2/R^3 with respect to the distribution function appropriate for a chain under traction (eq 5). Upon performing the angular integrations we obtain

$$\left\langle \frac{1}{R} \right\rangle_n = \frac{2\pi\xi}{Z} \frac{\partial^2 M(\xi)}{\partial(1/\xi)^2} \tag{A.1}$$

$$\left\langle \frac{R_z^2}{R^3} \right\rangle_n = \frac{2\pi}{Z} \frac{\partial^2 [\xi M(\xi)]}{\partial(1/\xi)^2} \tag{A.2}$$

$$\left\langle \frac{R_x^2}{R^3} \right\rangle_n = \frac{\pi}{Z}\left\{ \xi \frac{\partial^2 M(\xi)}{\partial(1/\xi)^2} - \frac{\partial^2[\xi M(\xi)]}{\partial(1/\xi)^2} \right\} = \frac{1}{2}\left(\left\langle \frac{1}{R} \right\rangle - \left\langle \frac{R_z^2}{R^3} \right\rangle \right) \tag{A.3}$$

where Z is the partition function (eq 12) and

$$M(\xi) = \int_0^\infty \frac{\mathrm{d}R}{R^2} P_n^{(0)}(R)(e^{R/\xi} - e^{-R/\xi}) \tag{A.4}$$

Some care should be exercised in handling the integral in eq A.4 since the integrand diverges as $R \rightarrow 0$. However, as can be easily verified by isolating the singular contributions and substituting into eq A.1–A.3, the divergent terms cancel out in the final expressions and so they can be handled by introducing a cutoff on the lower limit of the integral in eq A.4. Using the expression for the distribution function of the freely joined chain, eq 11 (the Gaussian chain results can be easily obtained by neglecting the $1/n$ terms), we can write $M(\xi)$ as a linear combination of the integrals

$$L_m(\xi) = \int_0^\infty \frac{\mathrm{d}R}{R^2} R^m e^{-3R^2/2na^2}(e^{R/\xi} - e^{-R/\xi}) \tag{A.5}$$

with $m = 0, 2, 4$. Since $L_2(\xi) = \partial^2 L_0(\xi)/\partial(1/\xi)^2$ and $L_4(\xi) = \partial^4 L_0(\xi)/\partial(1/\xi)^4$, we need only to compute the integral $L_0(\xi)$. The divergence at $R \rightarrow 0$ is eliminated by replacing the lower limit by ϵ, integrating by parts, canceling the linearly divergent term, and isolating the logarithmically divergent term (it too will cancel in our final expressions). We obtain

$$L_0(\xi) = \frac{2}{\xi}(1 - \ln \epsilon) + \int_0^\infty \mathrm{d}R\, e^{-3R^2/2na^2}\left\{ -\left(\frac{3}{na^2} + \frac{\ln R}{\xi^2} \right)(e^{R/\xi} - e^{-R/\xi}) + \frac{3R \ln R}{na^2 \xi}(e^{R/\xi} + e^{-R/\xi}) \right\} \tag{A.6}$$

The above integrals can be evaluated by expanding the $e^{\pm R/\xi}$ exponentials and summing over terms of the form

$$I(2k+1) = \int_0^\infty \mathrm{d}R\, e^{-AR^2} R^{2k+1} \ln R, \quad k \text{ integer} \tag{A.7}$$

These integrals can be readily evaluated[19] giving

$$I(2k+1) = \frac{k!}{4A^{k+1}}\left[-\gamma_e + \sum_{m=1}^{k} \frac{1}{m} - \ln A \right] \tag{A.8}$$

where γ_e is the Euler constant.[19]

Combining all contributions we finally obtain

$$L_0(\xi) = \alpha/\xi + \frac{1}{\xi} \sum_{k=0}^{\infty} \frac{k!}{(2k+3)!}\left[\frac{2}{3} n (a/\xi)^2 \right]^{k+1} \tag{A.9}$$

where α is a constant (it cancels out in our subsequent manipulations and does not contribute to the elements of the Oseen tensor). Now we evaluate $L_2(\xi)$ and $L_4(\xi)$ and use them to compute $M(\xi)$ and its derivatives. After considerable algebra we arrive at the following expression for the elements of the preaveraged Oseen tensor:

$$\langle T^{zz} \rangle_n = \frac{4(6/\pi)^{1/2}}{n^{1/2}a} e^{-x} \times \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m+1}{(2m+1)(2m+3)} \times \left\{ 1 + \frac{1}{5n}\left[x^2 - \frac{11}{4} - m(2m+1) \right] \right\} \tag{A.10}$$

$$\langle T^{xx} \rangle_n = \frac{2(6/\pi)^{1/2}}{n^{1/2}a} e^{-x} \times \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m+2}{(2m+1)(2m+3)} \times \left\{ 1 + \frac{1}{5n}\left[x^2 - \frac{11}{4} - m(2m+1) \right] \right\} \tag{A.11}$$

where

$$x = na^2/6\xi^2$$

In order to obtain closed-form expressions for the elements $\langle T^{\alpha\alpha} \rangle_n$, we have to evaluate the four sums

$$F_1(x) = e^{-x} \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m+1}{(2m+1)(2m+3)} \tag{A.12}$$

$$F_2(x) = e^{-x} \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m+2}{(2m+1)(2m+3)} \tag{A.13}$$

$$F_3(x) = e^{-x} \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m(m+1)(2m+1)}{(2m+1)(2m+3)} \tag{A.14}$$

$$F_4(x) = e^{-x} \sum_{m=0}^{\infty} (4x)^m \frac{m!}{(2m)!} \frac{m(m+2)(2m+1)}{(2m+1)(2m+3)} \tag{A.15}$$

Using the doubling formula for the γ function[19] we recast $F_1(x)$ in the form

$$F_1(x) = \frac{\pi^{1/2}}{4} e^{-x} \sum_{m=0}^{\infty} x^m \frac{m+1}{\Gamma(m + 5/2)} \tag{A.16}$$

which, upon expanding the γ function and changing variables ($m \rightarrow m + 1$), can be written as

$$F_1(x) = {}^1\!/\!_4 e^{-x} \sum_{m=0}^{\infty} \frac{2^{m+1} x^{m-1}}{(2m+1)!!} m = {}^1\!/\!_4 e^{-x} \frac{\partial}{\partial x} \sum_{m=0}^{\infty} \frac{2^{m+1} x^m}{(2m+1)!!} \tag{A.17}$$

with $(2m + 1)!! = 1, 3, 5, ..., 2m + 1$. The above sum is related to an error function, since[19]

$$\operatorname{erf}(x^{1/2}) = \frac{2}{\pi^{1/2}} \sum_{m=0}^{\infty} \frac{2^m x^{m+1/2}}{(2m+1)!!} e^{-x} \tag{A.18}$$

Thus, we finally obtain

$$F_1(x) = \frac{\pi^{1/2}}{4} e^{-x} \frac{\partial}{\partial x}[x^{-1/2} e^x \operatorname{erf}(x^{1/2})] \tag{A.19}$$

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Equation 17 follows upon taking the derivative and using

$$\frac{\partial}{\partial x}\operatorname{erf}(x^{1/2}) = \frac{1}{(\pi x)^{1/2}}e^{-x}$$

Equation 18 for $F_2(x)$ is obtained in a similar manner.

Now we proceed to derive eq 19 for $F_3(x)$. First we rearrange the sum in eq A.14 in the form

$$F_3(x) = \frac{1}{4}e^{-x}\sum_{m=0}^{\infty}\frac{2^{m+1}x^{m-1}}{(2m+1)!!}(m-1)m(2m-1) \qquad \text{(A.20)}$$

Next we write $(m-1)m(2m-1) = 2(m-{}^3/_2)(m-{}^1/_2)(m+{}^1/_2)+{}^3/_2m-{}^3/_4$ and decompose $F_3(x)$ into three terms

$$F_3(x) = {}^1\!/_4e^{-x}(F_3^{(1)}(x)+F_3^{(2)}(x)+F_3^{(3)}(x)) \qquad \text{(A.21)}$$

where

$$F_3^{(1)}(x) = 2\sum_{m=0}^{\infty}\frac{2^{m+1}x^{m-1}}{(2m+1)!!}(m-{}^3\!/_2)(m-{}^1\!/_2)(m+{}^1\!/_2)$$

$$= 4x^{3/2}\frac{\partial^3}{\partial x^3}\sum_{m=0}^{\infty}\frac{2^m x^{m+1/2}}{(2m+1)!!} = 2\pi^{1/2}x^{3/2}\frac{\partial^3}{\partial x^3}[e^x\operatorname{erf}(x^{1/2})] \qquad \text{(A.22)}$$

$$F_3^{(2)}(x) = (2)\frac{3}{2}\sum_{m=0}^{\infty}\frac{2^m x^{m-1}}{(2m+1)!!}m = \frac{3}{2}\pi^{1/2}\frac{\partial}{\partial x}[x^{-1/2}e^x\operatorname{erf}(x^{1/2})] \qquad \text{(A.23)}$$

$$F_3^{(3)}(x) = -\frac{3}{2}\sum_{m=0}^{\infty}\frac{2^m x^{m-1}}{(2m+1)!!} = -\frac{3}{4}\pi^{1/2}x^{-3/2}e^x\operatorname{erf}(x^{1/2}) \qquad \text{(A.24)}$$

Taking the derivatives and combining the above expressions gives $F_3(x)$ (eq 19). The expression for $F_4(x)$ (eq 20) is derived by using the same method (however, in this case care must be taken to subtract the nonvanishing $m = 0$ term following the change of variables $m \rightarrow m + 1$ in the m sum).

References and Notes

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Molecular Dimensions in Poly(ethylene terephthalate) by Small-Angle Neutron Scattering

K. P. McAlea and J. M. Schultz*

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

K. H. Gardner

Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898

G. D. Wignall

National Center for Small Angle Scattering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

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ABSTRACT: Single-chain dimensions measured in bulk poly(ethylene terephthalate) (PET) samples by small-angle neutron scattering (SANS) have been found to be close to the unperturbed value. Thin films with labeled (deuterated) PET concentrations as high as 40% were cast from solution. Measurements were made with two molecular weight materials at three sample–detector distances. The SANS molecular weights obtained from both Zimm and Debye fits are within 25% of the GPC values in all cases. The average value of $R_g^{w}/M_w^{1/2}$ is 0.373 compared to the theoretical value for unperturbed dimensions of 0.394.

Introduction

The dimensions of chain molecules in amorphous polymers have been investigated by small-angle neutron scattering in a wide range of systems in the past decade and in general have been shown to be close to the unperturbed dimensions of chains in ideal Θ-solvents.[1–9] However, despite the importance of poly(ethylene terephthalate) (PET) from both scientific and technological viewpoints, to our knowledge no measurements of chain dimensions have been reported in either the amorphous or crystalline states. This is partly due to the difficulties encountered in preparing samples in which the background scattering arising from the polymer matrix and heterogeneities (voids, catalyst/solvent residues, etc.) is sufficiently low so as not to mask the scattering due to the contrast between the labeled (deuterated) and unlabeled (hydrogenous) molecules. Moreover, many of the earlier experiments[1–6] were performed with low relative concentra-

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