Excluded Volume Effects and Stretched Polymer Chains

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ABSTRACT: The renormalized elasticity theory for isolated flexible polymers developed recently by de Gennes is extended to the case of strong elongation ($Z/R_F$; $Z$ is the average end-to-end length in response to a uniform tension and $R_F$ is the excluded volume Flory radius of a free coil). It is shown that, in this regime, the elastic restoring force $f$ is nonlinear in the distortion and varies as $Z^{\nu_2}$ in three dimensions. The consequences of this behavior are discussed for: (1) the coil–stretch transition in strong shear flows and (2) elastic neutron scattering.

I. Introduction

There has been considerable recent success in the use of scaling theory to interpret elastic neutron scattering on dilute and semidilute polymer solutions in good solvents. The purpose of this paper is to extend these ideas to the study of some steady state properties of dilute but "strongly stretched" polymers in the presence of excluded volume interactions. By "strongly stretched", we mean that the chain experiences an external tension $\tau$ that the resulting end-to-end extension $Z$ exceeds the Flory radius of the unperturbed coil, but does not yet become comparable to the fully extended length $N\lambda$ ($N$ is the number of monomers, each of length $\lambda$), in which case strong nonlinearities and nonuniversal behavior associated with short range interactions between neighboring monomers come into play. Thus our strong stretching regime is delimited by the inequality

$$N^2 < Z/\alpha < N$$  \hfill (I.1)

where $\alpha$ is the Flory exponent ($\alpha = 5/3$ in three dimensions). de Gennes\(^1\) has shown that, in the presence of excluded volume interactions, the usual purely entropic elastic constant of a weakly distorted polymer coil is renormalized leading to a restoring force

$$f = 3(k_BTZ)/R_F^2$$  \hfill (I.2)

where the excluded volume renormalization is the substitution of the Flory radius $R_F$ by $R_F = N^{1/2}\lambda$ for the ideal chain radius $R_0 = N^{1/4}\lambda$. However, as the chain stretches, its average monomer density decreases leading to a weakening of the excluded volume effect. Thus for sufficiently large external forces, we expect to eventually recover ideal behavior with $Z \propto N$ rather than $Z \propto N^{1/2}$ as given by (I.2). This crossover will be described in terms of a competition between a "tensile screening length" $\xi_t = (\alpha Z)^{-1}$ and the Flory radius $R_F$. For weak stretching $R_F/\xi_t \ll 1$, the de Gennes results (eq I.2) should be valid, for stronger stretching with $R_F/\xi_t \gg 1$, we expect to find a modified elastic behavior with $Z \propto N$. To find the stress–strain relationship in this limit, we are tempted to employ a scaling argument. Let us assume that the average end-to-end separation may be written as

$$Z = R_F \Phi(R_F/\xi_t),$$  \hfill (I.3)

where $\Phi(x)$ is a yet unknown function. For $x \ll 1$, $\Phi(x) \propto x$, in order to recover (I.2). For $x \gg 1$ (but the inequality I.1 still satisfied), we assume $\Phi(x) \propto x^{\nu_2}$ where $\nu_2$ is determined by the condition, $Z \propto N$. This immediately leads to $p = \nu_2 - 1$ and

$$Z \propto f^{(1/\nu_2)-1}$$  \hfill (I.4)

which, for $\nu_2 = 5/3$, gives $Z \propto f^{2/3}$ instead of the usual linear Hooke's law. A more microscopic derivation of these results is based on self-avoiding walks on a lattice is given in section II.

The concept of the tensile screening length $\xi_t$ is also useful to describe elastic x-ray or neutron scattering, and is discussed in section III. For $\xi_t > 1$ [eq. (I.4)] is an effective scattering wavevector taking into account a change in metric due to stretching and $\xi$ is the angle between $\Phi(x)$, we expect to find the usual excluded scattering intensity\(^6\) $I \propto \xi^{-1/\nu_2}$. For strong screening $\xi_t < 1$, we recover the Benoit\(^6\) ideal chain result $I \propto \xi^{-2}$.

Finally in section IV, the nonlinearity already coming into play at moderate extensions described by (I.4) is shown to strongly reduce the shear rate separation between the "first order transition"\(^2\) and continuous transition\(^10\) regimes between coiled and highly stretched conformations in ultra-high velocity gradients.

II. Stress–Strain Relationship

This section is devoted to a microscopic derivation of the scaling arguments of (I.3) and (I.4) leading to the nonlinear ($f \propto Z^{\nu_2}$) restoring force in the strongly stretched limit ($R_F > \xi_t$). Consider the function $\Gamma_n(r)$ which is the number of independent self-avoiding walks of $n$ steps connecting the origin and the point $r$ on a three-dimensional lattice. This function is proportional to the end-to-end distribution function for the excluded volume problem.\(^7\) It has been shown\(^8,9\) for large $r$, that its Laplace transform

$$\Gamma_n(r) = \frac{\sum_{N=0}^\infty \Gamma_N(r)e^{-N\rho}}{\rho \Gamma(\nu_2)}$$  \hfill (II.1)

behaves similarly to the transverse spin correlations in the vicinity of a magnetic phase transition

$$\Gamma_n(r) \propto A(\alpha/r)e^{-Kr} \quad (Kr > 1)$$  \hfill (II.2)

where $A$ is a function of $\rho$ and the inverse correlation length $K = a^{-1}(\rho - \rho_c)^{1/3}$ where $\rho_c$ is the critical value of $\rho$ where $\int \Gamma_n(r) dr$ diverges. In the presence of an external tension, the appropriate normalized statistical weight $W_n(r)$ is then

$$W_n(r) = \Gamma_N(r)e^{Z/\xi_t} \int \Gamma_N(r)e^{Z/\xi_t} dr$$  \hfill (II.3)

leading to

$$Z = \int Z W_n(r) dr$$  \hfill (II.4)

Using (II.1)–(II.3) and performing the spatial integrations, we arrive at (I.3) with

$$\Phi(x) \propto x - \frac{d}{dx} \ln \left[ \sum_{N=0}^\infty \frac{e^{N\rho}}{(N\rho - N\rho_c)^{\nu_2} - x} \right]$$  \hfill (II.5)

Replacing the sum by an integral, we easily verify the scaling behavior in the previous section. Note that for an ideal chain $\nu_2 = 5/3$, $\Phi(x) \propto x$, independent of $\xi_t$, as expected (of course, always with the limitation $\xi_t < N$).

For the transverse size of the coil, it is easily verified by a similar calculation that the following scaling argument is justified. Let us write for the mean square extent
volume only grows as $f^{1/3}$ instead of linearly as in the absence of excluded volume effects. These results may be of some significance for rubber elasticity as well as modifying the coil–stretch transition as discussed in section IV.

### III. Static Structure Factor

Elastic neutron or X-ray scattering essentially measures the Fourier transform of the monomer density distribution, $\rho(r)$, 

$$I(q) = Re \left( \int \rho(r) e^{iq \cdot r} \, dr \right)$$

where $q$ is the scattering vector. In order to determine this quantity for stretched chains, we shall again make use of scaling arguments based on the tensile screening length concept.

For ideal chains, Benoit\(^6\) has shown that

$$I(q) \propto q^{-5/3}$$

As indicated in the Appendix, the structure factor is a function of an effective square scattering wave vector defined by

$$\tilde{q}^2 = q^2 + 4\xi^2 \cos^2 \theta$$

We expect that for weak stretching $\xi \gg 1$

$$I(q) \propto \tilde{q}^{-1}$$

while for strong elongations, $\xi \ll 1$, we recover ideal behavior

$$I(q) \propto q^{-2}$$

In other words, we have “tensile blobs”, similar to those in unstretched semidilute solutions\(^3\) of radius $\xi$, within which excluded volume effects are maintained; for distances exceeding $\xi$, the polymer behaves as an ideal coil of units of size $\xi$. Connecting (III.3) and (III.6) by a scaling function $S((\xi q)_c)^{-1}$, we write

$$I(q) = q^{-1/3} S((\xi q)_c^{-1})$$

where $S(0) = 1$ and $S(x) \rightarrow x^2$ for large $x$ such that (III.6) is recovered. The scaling exponent $r = 2 - \nu^{-1} = \frac{2}{3}$. Thus in the ideal regime we predict that $I(q) \propto f^{1/3}$ for fixed $q$. Note that this latter limit only obtains when $q$ is essentially perpendicular to $f$, and $\xi q < 1$. In the Appendix, we rederive these results with the aid of the self-avoiding walk distribution used in the previous section.

### IV. Coil–Stretch Transition

It has been recognized for some time\(^1\) that under the influence of ultra-high-velocity gradients there is a transformation from a coil to a nearly completely stretched conformation of polymer chains. This effect is the cause for the increase in viscosity of dilute polymer solutions under high-velocity gradients. Subsequently de Gennes\(^2\) pointed out that as the polymer distorts into a cigar-shaped conformation the shear is more effective in distorting the molecule because the screening by the hydrodynamic\(^1\) interactions is reduced. For ideal chains this leads to an onset of the coil–stretch transition at smaller shear rates and a sharp first-order type hysteretic transition. In this section we discuss the modifications of the de Gennes theory\(^2\) that occur when excluded volume interactions are included. There are basically two effects which came into play (both having the tendency to suppress the separation between first- and second-order transitions): (1) the Zimm relaxation time for ideal chains

$$\tau_0 \propto \eta R_0^3/6\pi \kappa T$$

where $\eta$ is the solvent viscosity and $R_0 \propto N^{1/6}$ becomes larger due to the excluded volume swelling of the molecules;\(^3\) i.e., $R_0$ is replaced by $R_F$; (2) the nonlinear stress–strain relationship of sections I and II forces the transition to higher shear rates.

We shall restrict our attention to the case of two-dimensional longitudinal gradients where the first-order transitional behavior is most pronounced. We shall follow closely the notation and methodology of ref 2. In the presence of a shear rate tensor $\mathbf{S}$, the current associated with the end-to-end distribution function $W(r)$ is

$$\mathbf{J} = \mathbf{S} \mathbf{W} + D(\mathbf{f} \cdot \mathbf{S}) \mathbf{W} - \nabla W$$

where $D$ is a diffusion constant which has a form for cigar-shaped molecules intermediate between the Zimm and Rouse\(^4\) values, $D_0$ and $D_s$, respectively,

$$D = D_s [1 + (D_0/D_s)(R_F/Z)]$$

where

$$D_s = k_B T B/N$$

is the Rouse diffusion constant valid in the free-draining limit where hydrodynamic effects are neglected ($B$ is the monomer mobility in the solvent) and is independent of excluded volume effects; the Zimm diffusion constant is

$$D_0 = R_F^2 \tau_0^{-1}$$

and is therefore proportional to $R_F^{-1}$ or $N^{-1/6}$. For $Z > R_F$, the form (IV.3) is a reasonable interpolation formula between the hydrodynamic regime for $Z \ll R_F$ and the free-draining limit for strongly stretched chains. The force $f$ in (IV.2) is essentially that discussed in sections I and II, i.e., $f = Z \ll R_F$ and $f = Z^{3/2}/Z > R_F$. For steady state longitudinal gradients, div $\mathbf{J} = 0$ is equivalent to $\mathbf{J} = 0$, which essentially gives a one-dimensional equation of the form

$$\partial W/\partial Z = -F(Z)W$$

where

$$F(Z) = -\beta f(Z) - (S/D)Z; \quad S = S_{zz}$$

The solution to (IV.6) is

$$W(Z) = W_0 \exp \left[ -\int_0^Z F(Z) \, dZ \right]$$

where $W_0$ is a normalization constant. Thus we may interpret

$$\beta V(Z) = \int_0^Z F(Z) \, dZ$$

as an effective potential energy. For $Z < R_F$, using (1.2) and $D \propto D_0$, we find

$$\beta V(Z) = (R_F^{-2} - S/D_0)(Z^2/2)$$

for

$$S > D_0 R_F^{-2} = \tau_0^{-1}$$

where $\tau_0$ is the renormalized Zimm relaxation time; we see clearly the instability toward a fully stretched configuration. For $Z > R_F$, we have
The effective potential energy then has a minimum at $Z^*$ in this region when $F(Z^*) = 0$, 

$$
Z^*/R_F = (S/\alpha)(Z_0)_{1/2} \approx (S/\alpha)^{-2}
$$

(IV.13)

Clearly the minimum is in the stretched regime only for $S_\alpha < 1$. This is to be compared with $(S/\alpha)^{-1}$ for ideal chains. The critical shear rate $S^*$ for a first-order transition occurs with $V(Z^*) = 0$. This leads to

$$
S^*/\alpha \approx (D_0/D_c)(1 - 2/3u - 1/5u)
$$

(IV.14)

For ideal chains ($\tau_0 = 1/2$), this gives the de Gennes' result\(^2\) that $S^* = (\theta_0/6)^{-1}$, which is the limit of interest for information on monomer distribution within the coil.

\(W_n(q) = \exp \left[ -n q^2 \left( 1 - 2i \cos \frac{\theta}{2} (q_\perp) - 1 \right) - \frac{1}{\xi^2} 1/2v + n \xi^{-1/3} \right] \) (A.5)

Summing over $n$, we obtain

$$
I(q) = \frac{1}{q^2[1 - 2i \cos \frac{\theta(q_\perp)}{2}] - \frac{1}{\xi^2} 1/2v - \xi^{-1/3}}
$$

(A.6)

Expanding the denominator using the binomial theorem we rediscover the results of section III.

References and Notes

(4) Actually $R_F \approx N/2a^{3/5}$, where $a$ is the excluded volume. For our purposes here, we assume $a \sim a^3$.
(7) Recall that we assume $v \sim a^3$ throughout.