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 ($\bar{Z}/R_F \gg 1$, $\bar{Z}$ 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 $\bar{Z}^{3/2}$ 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[3] 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 if the chain experiences an external tension $\mathbf{f}$, that the resulting end-to-end extension $\bar{Z}$ exceeds the Flory radius of the unperturbed coil, but does not yet become comparable to the fully extended length Na (N is the number of monomers, each of length a), 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

$$N^\nu < \bar{Z}/a \ll N \qquad (I.1)$$

where ν is the Flory exponent ($\nu = \frac{3}{5}$ 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

$$f = 3(k_B T \bar{Z})/R_F^2 \qquad (I.2)$$

where the excluded volume renormalization is the substitution of the Flory radius[4] $R_F \simeq N^\nu a$ for the ideal chain radius $R_0 = N^{1/2}a$. 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 $\bar{Z} \propto N$ rather than $\bar{Z} \propto N^{2\nu}$ as given by (I.2). This crossover will be described in terms of a competition between a "tensile screening length" $\xi_t = (\beta f)^{-1}$ and the Flory radius R_F. For weak stretching $R_F/\xi \ll 1$, the de Gennes result (eq I.2) should be correct; for stronger stretching with $R_F/\xi_t \gg 1$, we expect to find a modified elastic behavior with $\bar{Z} \propto N$. 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

$$\bar{Z} = R_F \Phi(R_F/\xi_t), \qquad (I.3)$$

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

$$\bar{Z} \propto f^{(1/\nu)-1} \qquad (I.4)$$

which, for $\nu = \frac{3}{5}$, gives $\bar{Z} \propto f^{2/3}$ instead of the usual linear Hooke's law. A more microscopic derivation of these results

based on self-avoiding walks on a lattice is given in section II.

The concept of the tensile screening length ξ_t is also useful to describe elastic x-ray or neutron scattering, and is discussed in section III. For $\bar{q}\xi_t > 1$ [$\bar{q} = (q^2 + 4\cos^2\theta\xi_t^{-2})^{1/2}$ is an effective scattering wavevector taking into account a change in metric due to stretching and θ is the angle between $\mathbf{q}$ and $\mathbf{f}$], we expect to find the usual excluded scattering intensity[5] $I \propto \bar{q}^{-1/\nu}$. For strong screening $\bar{q}\xi_t < 1$, we recover the Benoit[6] ideal chain result $I \propto \bar{q}^{-2}$.

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 ($f \propto \bar{Z}^{3/2}$) restoring force in the strongly stretched limit ($R_F > \xi_t$). Consider the function $\Gamma_n(\mathbf{r})$ which is the number of independent self-avoiding walks of n steps connecting the origin and the point $\mathbf{r}$ 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

$$\Gamma\rho(\mathbf{r}) = \sum_{N=0}^{\infty} \Gamma_N(\mathbf{r})e^{-N\rho} \qquad (II.1)$$

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

$$\Gamma\rho(\mathbf{r}) \simeq A(a/r)e^{-Kr} \qquad (Kr > 1) \qquad (II.2)$$

where A is a function of ρ and the inverse correlation length $K = a^{-1}(\rho - \rho_c)^\nu$ where ρ_c is the critical value of ρ where $\int \Gamma\rho(\mathbf{r})\,d\mathbf{r}$ diverges. In the presence of an external tension, the appropriate normalized statistical weight $W_N(\mathbf{r})$ is then

$$W_N(\mathbf{r}) = \Gamma_N(\mathbf{r})e^{Z/\xi_t}/\int \Gamma_N(\mathbf{r})e^{Z/\xi_t}\,d\mathbf{r} \qquad (II.3)$$

leading to

$$\bar{Z} = \int Z W_N(\mathbf{r})\,d\mathbf{r} \qquad (II.4)$$

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

$$\Phi(x) \simeq x\frac{d}{d(x^2)}\left\{\ln\sum_\rho \frac{e^{N\rho}}{(N\rho - N\rho_c)^{2\nu} - x^2}\right\} \qquad (II.5)$$

Replacing the sum by an integral, we easily verify the scaling behavior in the previous section. Note that for an ideal chain $\nu = \frac{1}{2}$, $\Phi(x) \propto x$, independent of ξ_t, as expected (of course, always with the limitation $\bar{Z} < Na$).

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

$$\bar{r}_\perp{}^2 = R_F{}^2 \Theta(R_F/\xi_t) \tag{II.6}$$

where $\Theta(x)$ is a function of the scaling variable R_F/ξ_t such that $\Theta(0) = 1$; for $R_F/\xi_t \gg 1$ we expect to recover ideal behavior with $r_\perp{}^2 \propto N$. Assuming $\Theta(x) \sim x^r$ $(x \gg 1)$, we are then led to $r = \nu^{-1} - 2$. Thus, in the strongly stretched regime, the cross section diminishes as

$$\bar{r}_\perp{}^2 \propto f^{-1/3}. \tag{II.7}$$

In this regime, combining (I.4) with (II.7), we see that the 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, $\rho(\mathbf{r})$,

$$I(\mathbf{q}) = Re \left\{ \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \, d\mathbf{r} \right\} \tag{III.1}$$

where $\mathbf{q}$ 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

$$I(\mathbf{q}) \propto (q^2 + 4\xi_t{}^{-2} \cos^2\theta)^{-1} \tag{III.2}$$

where θ is the angle between $\mathbf{q}$ and $\mathbf{f}$. For $\mathbf{f} = 0$ but in the presence of excluded volume,[5]

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

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

$$\bar{q}^2 = q^2 + 4\xi_t{}^{-2} \cos^2\theta \tag{III.4}$$

We expect that for weak stretching $\bar{q}\xi_t \gg 1$

$$I(\mathbf{q}) \propto \bar{q}^{-1/\nu} \tag{III.5}$$

while for strong elongations, $\bar{q}\xi_t \ll 1$, we recover ideal behavior

$$I(\mathbf{q}) \propto \bar{q}^{-2} \tag{III.6}$$

In other words, we have "tensile blobs", similar to those in unstretched semidilute solutions,[3] of radius ξ_t within which excluded volume effects are maintained; for distances exceeding ξ_t, the polymer behaves as an ideal coil of units of size ξ_t. Connecting (III.5) and (III.6) by a scaling function $S((q\xi_t)^{-1})$, we write

$$I(\mathbf{q}) = \bar{q}^{-1/\nu} S[(\bar{q}\xi_t)^{-1}] \tag{III.7}$$

where $S(0) = 1$ and $S(x) \to x^r$ for large x such that (III.6) is recovered. The scaling exponent $r = 2 - \nu^{-1} = \frac{1}{3}$. Thus in the ideal regime we predict that $I(\mathbf{q}) \propto f^{1/3}$ for fixed $\mathbf{q}$. Note that this latter limit only obtains when $\mathbf{q}$ is essentially perpendicular to $\mathbf{f}$, and $q\xi_t < 1$. 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[10] that under the influence of ultra-high-velocity gradients there is a transformation from a coil to a nearly completely stretched conformatin 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[11] 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

$$\tau_0 \cong \eta R_0{}^3/6\pi kT \tag{IV.1}$$

where η is the solvent viscosity and $R_0 \simeq N^{1/2}a$ becomes larger due to the excluded volume swelling of the molecules;[1] 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 $W(\mathbf{r})$ is

$$\mathbf{J} = \mathbf{Sr}W + D[(\mathbf{f}/kT)W - \nabla W] \tag{IV.2}$$

where D is a diffusion constant which has a form for cigar-shaped molecules intermediate between the Zimm and Rouse[12] values, D_0 and D_r respectively,

$$D \cong D_r[1 + (D_0/D_r)(R_F/\bar{Z})] \tag{IV.3}$$

where

$$D_r = k_B TB/N \tag{IV.4}$$

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

$$D_0 = R_F{}^2 \tau_0{}^{-1} \tag{IV.5}$$

and is therefore proportional to $R_F{}^{-1}$ or $N^{-\nu}$. For $\bar{Z} > R_F$, the form (IV.3) is a reasonable interpolation formula between the hydrodynamic regime for $\bar{Z} \sim R_F$ and the free-draining limit for strongly stretched chains. The force $\mathbf{f}$ in (IV.2) is essentially that discussed in sections I and II, i.e., $f \propto \bar{Z}$ for $\bar{Z} < R_F$ and $\mathbf{f} \propto \bar{Z}^{3/2}$ for $\bar{Z} > R_F$. 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

$$\partial W/\partial Z = -F(Z)W \tag{IV.6}$$

where

$$F(Z) = -\beta f(Z) - (S/D)Z; \qquad S = S_{ZZ} \tag{IV.7}$$

The solution to (IV.6) is

$$W(Z) = W_0 \exp\left[-\int_0^Z F(Z) \, dZ \right] \tag{IV.8}$$

where W_0 is a normalization constant. Thus we may interpret

$$\beta V(Z) \equiv \int_0^Z F(Z) \, dZ \tag{IV.9}$$

as an effective potential energy. For $Z < R_F$, using (I.2) and $D \simeq D_0$, we find

$$\beta V(Z) = (R_F{}^{-2} - S/D_0)(Z^2/2) \tag{IV.10}$$

for

$$S > D_0 R_F{}^{-2} = \tilde{\tau}_0{}^{-1} \tag{IV.11}$$

where $\tilde{\tau}_0$ is the renormalized Zimm relaxation time; we see clearly the instability toward a fully stretched configuration. For $Z > R_F$, we have

$$F(Z) \cong (R_F^{-1}Z^\nu)^{1/1-\nu} - (S/D_0)(Z^2/R_F) \qquad \text{(IV.12)}$$

The effective potential energy then has a minimum at Z^* in this region when $F(Z^*) = 0$,

$$Z^*/R_F \cong (S\tilde{\tau}_0)^{(1-\nu)/(3\nu-2)} \cong (S\tilde{\tau}_0)^{-2} \qquad \text{(IV.13)}$$

Clearly the minimum is in the stretched regime only for $S\tilde{\tau}_0 < 1$. This is to be compared with $(S\tau_0)^{-1}$ for ideal chains. The critical shear rate S^* for a first-order transition occurs with $V(Z^*) = 0$. This leads to

$$S^*\tilde{\tau}_0 \cong (D_0/D_r)^{(3\nu-2)/(1-\nu)} \qquad \text{(IV.14)}$$

For ideal chains ($\tilde{\tau}_0 = \tau_0$, $\nu = \frac{1}{2}$), this gives the de Gennes' result[2] that $S^* \geq \tau_R^{-1} = D_r/R_0^2 \ll \tau_0^{-1}$. In fact $\tau_0 S^* \sim N^{-1/2}$. For excluded volume chains, $S^* \geq (\tilde{\tau}_0 \tau_R)^{-1/2}$, and $\tilde{\tau}_0 S^* \sim (\tilde{\tau}_0/\tau_R)^{1/2} \sim N^{-1/5}$. Note that in both the ideal and excluded volume cases $S^* \propto N^{-2}$, but with excluded volume swelling of the molecule, the second- and first-order transitions occur much closer together.

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Appendix

This Appendix is concerned with an alternate derivation of the static structure factor results of section III. The essential assumption here is that $\rho(\mathbf{r})$ is given by the sum of end-to-end distribution functions $W_n(\mathbf{r})$, (II.3),

$$\rho(\mathbf{r}) \cong \sum_{n=0}^{N} W_n(\mathbf{r}) \qquad \text{(A.1)}$$

This is not exact because the space filling character of a distribution of various length chains is not identical with the correct $\rho(\mathbf{r})$. However, we believe that (A.1) should reproduce the appropriate scaling behavior. The scattering intensity may then be written as

$$I(\mathbf{q}) \cong Re \sum_{n=0}^{N} W_n(\mathbf{q})$$

$$W_n(\mathbf{q}) = \gamma_n(\mathbf{q})/\gamma_n(0) \qquad \text{(A.2)}$$

where $W_n(\mathbf{q})$ is the Fourier transform of $W_n(\mathbf{r})$ and

$$\gamma_n(\mathbf{q}) = \int \Gamma_n(\mathbf{r}) e^{(i\mathbf{q}+\beta\mathbf{f})\cdot\mathbf{r}} \, d\mathbf{r} \qquad \text{(A.3)}$$

Using (II.1) and (II.2), we find

$$\gamma_n(\mathbf{q}) \cong 2a \sum_\rho \frac{e^{n\rho}}{a^{-2}(\rho - \rho_c)^{2\nu} + q_\perp^2 + (q_\| - 2\xi_t^{-1})^2} \qquad \text{(A.4)}$$

where $(q_\perp, q_\|)$ are respectively the components of $\mathbf{q}$ perpendicular and parallel to $\mathbf{f}$. From the structure of $I(q)$, (A.1–A.3), we note that, quite generally, the dependence of the structure factor on the applied force only appears through $(\beta\mathbf{q}\cdot\mathbf{f})^2$ and thus $I(\mathbf{q})$ is only a function of $\tilde{q}^2$, eq III.11. For $qR_F \gg 1$, which is the limit of interest for information on monomer distribution within the coil,

$$W_n(\mathbf{q}) \approx \exp\left\{-n\left|q^2\left[1 - \frac{2i\cos\theta}{\xi_t^2}(q\xi_t)^{-1}\right] - \frac{1}{\xi_t^2}\right|^{1/2\nu} + n\xi_t^{-1/\nu}\right\} \qquad \text{(A.5)}$$

Summing over n, we obtain

$$I(\mathbf{q}) = Re\left\{\frac{1}{\left|q^2[1 - 2i\cos\theta(q\xi_t)^{-1}] - \dfrac{1}{\xi_t^2}\right|^{1/2\nu} - \xi_t^{-1/\nu}}\right\} \qquad \text{(A.6)}$$

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

References and Notes

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