Dynamics of Semidilute Polyelectrolyte Solutions

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We apply dynamic scaling to both unentangled and entangled semidilute polyelectrolyte solutions. The unentangled semidilute regime can span three to four decades of polymer concentration in low-salt solutions. In this range we predict such phenomena as a concentration independent self-diffusion coefficient, relaxation time that is a decreasing function of concentration c, and explain the empirical Fuoss law for the viscosity $\eta \sim c^{1/2}$. In the low-salt entangled regime we predict the concentration independent relaxation time and the viscosity $\eta \sim c^{3/2}$ that are observed experimentally.

The solution properties of charged polymers are dramatically different from those of uncharged ones [1]. For example, the viscosity η of polyelectrolyte solutions at low concentrations c follows the Fuoss law $\eta \sim c^{1/2}$ [2], while the concentration dependence of solution viscosity of uncharged polymers is never weaker than linear. Despite significant interest in polyelectrolyte solutions, this example and many of their other unique properties have not been satisfactorily explained, because of an incomplete picture of the static configuration and entanglement of polyelectrolyte chains in semidilute solutions.

A significant fraction of recent theoretical work was based on the ideas of electrostatic persistence length proposed by Odijk [3] and by Skolnick and Fixman [4]. However, Barrat and Joanny [5] have shown that the electrostatic persistence length of an intrinsically flexible chain is proportional to the Debye screening length. Thus, the newly emerging picture for the static configuration of a polyelectrolyte chain is very reminiscent of the scaling picture of de Gennes *et al.* [6]. Below, we outline this static picture (more details will be given in a future publication [7]) and develop a dynamic scaling theory based on it.

Consider a polyelectrolyte solution of flexible chains with degree of polymerization N, monomer size b, and total charge N/A (A is the number of monomers between charges) in a solvent with Bjerrum length $l_B = e^2/\varepsilon kT$. Charges on the chain repel each other, and this electrostatic repulsion can collectively lead to chain stretching on length scales larger than the electrostatic blob size D [6,7]. The size of the electrostatic blob D and the number of monomers in it g_e are functions of A, b, l_B, and solvent quality for the uncharged backbone, but are independent of N, c, and the presence of the salt. In the absence of screening (for example, in a dilute salt-free solution) the polyelectrolyte configuration is that of a fully extended chain of N/g_e electrostatic blobs of length

$$L \approx DN/g_e \approx Nb/B. \tag{1}$$

The parameter $B \equiv Nb/L$ is a function of $A^2 b/l_B$ that depends on solvent quality [7]. The polyelectrolyte is a stretched chain of electrostatic blobs as long as the Coulomb repulsion between them is not screened, i.e., as long as the chain is shorter than the electrostatic screening length r_D. Here, we focus on salt-free solutions [for which Eq. (1) gives the dilute chain size] and comment on the effects of added salt at the end of this Letter. The overlap concentration is

$$c^* \approx N/L^3 \approx (B/b)^3/N^2. \tag{2}$$

In semidilute solution ($c > c^*$) there are two different types of chain behavior on smaller and larger length scales separated by the correlation length ξ. The configuration of chain sections on length scales shorter than ξ is similar to that in dilute solutions (extended). On length scales longer than the correlation length ξ, the chain has random walk statistics. The correlation length in semidilute solution starts at $\xi \approx L$ at overlap ($c = c^*$) and follows a power law in concentration

$$\xi \approx L(c^*/c)^{1/2} \approx (B/cb)^{1/2}. \tag{3}$$

The value $\frac{1}{2}$ of the scaling exponent makes the correlation length ξ independent of degree of polymerization N. Note that the correlation length ξ is proportional to the Debye screening length $r_D = (4\pi l_B c)^{-1/2}$. The correlation volumes ξ^3 are space filling, each with g monomers in them,

$$g \approx c\xi^3 \approx (B/b)^{3/2}c^{-1/2}. \tag{4}$$

Since both electrostatic and excluded volume interactions are screened on length scales longer than the correlation length ξ, the polyelectrolyte chain is a random walk of size

$$R \approx \xi(N/g)^{1/2} \approx (b/cB)^{1/4}N^{1/2}, \tag{5}$$

with a stronger concentration dependence ($R \sim c^{-1/4}$) than uncharged polymers ($R \sim c^{-1/8}$). The above static picture is similar to the one described in the work of

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de Gennes *et al.* [6]. Next, we develop a dynamic scaling model based on the simple static picture outlined above.

The hydrodynamic interaction between different parts of the chain subsection controls its dynamics on length scales shorter than the correlation length ξ. The motion of this subsection is therefore Zimm-like (nondraining) [8]. The relaxation time τ_ξ of the subsection of size ξ is proportional to its volume ξ^3

$$\tau_\xi \approx (\eta_s/kT)\xi^3, \tag{6}$$

where η_s is the solvent viscosity [9].

The hydrodynamic interaction is screened on distance scales longer than the correlation length ξ. The polyelectrolyte behaves as a Rouse chain of N/g beads with longest relaxation time [8]

$$\tau \approx \tau_\xi(N/g)^2 \approx (\eta_s/kT)(b/B)^{3/2}N^2c^{-1/2},$$
$$c^* < c < c_e, \tag{7}$$

where c_e is the entanglement concentration. Note that this *relaxation time decreases with increasing concentration*—a highly unexpected property for a polymer solution. The relaxation time of uncharged polymers always increases with concentration.

This unique concentration dependence of relaxation time τ leads to another unexpected result for unentangled polyelectrolyte solutions. The self-diffusion coefficient D is proportional to the ratio of the mean square size of a chain and its relaxation time

$$D \approx R^2/\tau \approx (kT/\eta_s)B/bN, \quad c < c_e. \tag{8}$$

Polyelectrolyte chains in semidilute solution have a *concentration independent self-diffusion coefficient* that is equal to its value in dilute solution ($D_0 \approx kT/\eta_s L$).

The modulus of an unentangled solution is of the order of the thermal energy kT per chain

$$G \approx ckT/N, \quad c < c_e. \tag{9}$$

The viscosity of an unentangled semidilute polyelectrolyte solution

$$\eta \approx G\tau \approx \eta_s(b/B)^{3/2}Nc^{1/2}, \quad c^* < c < c_e, \tag{10}$$

is proportional to the square root of concentration in agreement with the empirical Fuoss law.

The Rouse-like behavior of semidilute solutions continues up to the concentration at which chains begin to entangle. Significant overlap of neighboring chains is required in order for them to constrain each other's motion. One of the simplest conjectures on the nature of entanglement is that a "universal" number n of overlapping chains is required for entanglement [10]. Thus, entanglement effects begin at concentration $c_e \approx nN/R^3 \approx n(c^*c_e^3)^{1/4}$. The universal number n was estimated [10] to be $5 \le n \le 10$, and the entanglement concentration is 3 to 4 orders of magnitude above the overlap concentration

$$c_e \approx n^4c^*. \tag{11}$$

Above the entanglement concentration (at $c > c_e$), the topological interactions dominate at distance scales larger

than the tube diameter a. This distance scale is defined so that there are always n strands of different chains (of N_e monomers each) inside a volume a^3. It is easy to see that the tube diameter $a \approx n\xi$ and the degree of polymerization between entanglements is

$$N_e \approx n^2g, \tag{12}$$

where g is the number of monomers in a correlation volume ξ^3 [Eq. (4)].

The longest relaxation time in the entangled regime can be estimated from the reptation model. We assume dynamics to be Zimm-like up to the correlation length ξ, Rouse-like for the strand of $N_e/g \approx n^2$ beads of size ξ, and reptationlike for N/N_e entanglement strands. The relaxation time of entangled polyelectrolyte solutions

$$\tau \approx \tau_\xi(N_e/g)^2 (N/N_e)^3 \approx (\eta_s/kT)(b/B)^3N^3/n^2,$$
$$c > c_e \tag{13}$$

is *concentration independent*. This is a highly unusual behavior since the relaxation time in solutions of entangled uncharged polymers is concentration dependent ($\tau \sim c^{3/2}$ in good solvents and $\tau \sim c^{7/3}$ in θ solvents).

The self-diffusion coefficient in entangled solutions can be estimated from chain size [Eq. (6)] and relaxation time τ [Eq. (13)]:

$$D \approx R^2/\tau \approx (kT/\eta_s)(B/b)^{5/2}n^2/N^2c^{1/2} \approx D_0(c_e/c)^{1/2},$$
$$c > c_e. \tag{14}$$

The modulus of entangled polymers is the thermal energy kT per entanglement strand

$$G \approx kTc/N_e \approx (kT/n^2)(bc/B)^{3/2}, \quad c > c_e, \tag{15}$$

and the viscosity is

$$\eta \approx G\tau \approx \eta_s(b/B)^{9/2}c^{3/2}N^3/n^4, \quad c > c_e. \tag{16}$$

The crossover between unentangled and entangled behavior occurs at viscosity $\eta(c_e) \approx n^2\eta_s$, up to 2 orders of magnitude above the solvent viscosity η_s, as it does in uncharged polymers in good solvents. The concentration dependence of viscosity of entangled polyelectrolytes ($\eta \sim c^{3/2}$) is much weaker than that of entangled uncharged polymers ($\eta \sim c^{15/4}$ in good solvents and $\eta \sim c^{14/3}$ in θ solvents).

At a higher concentration c_D, electrostatic blobs begin to overlap, and we expect the solution dynamics to crossover to that of uncharged polymers. This crossover concentration is $c_D \approx g_e/D^3$, where D is the size of the electrostatic blob.

We summarize our dynamic scaling predictions in Fig. 1. These are in very good agreement with a number of experiments.

(i) Viscosity was one of the first experimentally observed anomalous properties of polyelectrolyte solutions [2]. The reduced viscosity $\eta_R \approx (\eta - \eta_s)/c\eta_s$ decreases with concentration c over a wide concentration range.
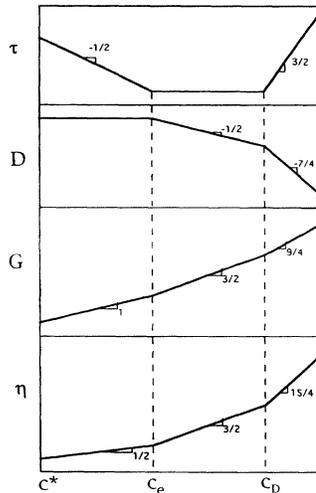
FIG. 1. Concentration dependence of relaxation time τ, self-diffusion coefficient D, terminal modulus G, and viscosity η for polyelectrolyte in semidilute solutions in good solvent (logarithmic scales).

The reduced viscosity η_R of uncharged polymers is always an increasing function of concentration. A phenomenological law

$$\eta_R \sim \left[1 + (c/c_0)^{1/2} \right]^{-1}, \qquad (17)$$

where c_0 is a constant, was proposed by Fuoss [2] to describe this anomaly of polyelectrolyte viscosity. Numerous experiments reconfirmed the validity of this unusual concentration dependence. The Fuoss law [Eq. (17)] has the same scaling (for $c > c_0$) as our prediction for the unentangled semidilute regime [Eq. (10)], $\eta \sim c^{1/2}$.

(ii) Self-diffusion coefficient of a series of sodium polystyrenesulfonate in molecular weight range from 16 000 to 354 000 was measured recently in aqueous salt-free solutions by pulsed field gradient NMR [11]. Up to quite high concentrations (0.1M), they find the self-diffusion coefficient $D \sim c^0 N^{-1.0 \pm 0.5}$ in perfect agreement with our prediction for unentangled polyelectrolytes [Eq. (8)].

(iii) The frequency dependence of storage G' and loss G'' moduli of high molecular weight poly(2-vinyl pyridine) at concentration 0.02M in acidic ethylene glycol solutions was observed [12] to be in agreement with the Rouse model ($G' \sim G'' \sim \omega^{1/2}$ at high frequency). This observation confirms our assumption that dynamics of semidilute polyelectrolyte solutions is Rouse-like.

(iv) We predict that a crossover between unentangled and entangled regimes should correspond to a minimum in reduced viscosity $\eta_R = (\eta - \eta_s)/\eta_s c$ (because $\eta_R \sim c^{-1/2}$ for $c < c_e$ and $\eta_R \sim c^{1/2}$ for $c > c_e$). This minimum has been observed in a number of experiments [13].

The rheology of narrow molecular weight distribution entangled poly (N-methyl-2-vinylpyridinium chloride) in water was recently studied in great detail [14,15]. The main results of these experiments are as follows:

(i) Both the measured molecular weight and the concentration dependences of viscosity in salt-free solution $\eta \sim M^3 c^{1.5}$ are in perfect agreement with our predictions [Eq. (13)] for the entangled regime.

(ii) The experimentally observed concentration dependence of the plateau modulus $G \sim c^{1.3}$ is in good agreement with our prediction [Eq. (15)] for the entangled regime. The measured concentration dependence of the recoverable compliance $J_e \sim c^{-1.3}$ is also in good agreement with our model (we predict $J_e \sim 1/G \sim c^{-1.5}$ in entangled regime).

(iii) The relaxation time has very weak concentration dependence $\tau \sim c^{0.2}$ that substantially increases upon addition of salt. This observation is consistent with our prediction of a concentration independent relaxation time in salt-free entangled polyelectrolyte solutions.

(iv) A relatively sharp crossover was observed at concentration $c \approx 0.2$ g/cm^3 from the concentration dependence of the rheological properties unique for the entangled polyelectrolyte solutions ($\eta \sim c^{1.5}$, $G \sim c^{1.3}$, $J_e \sim c^{-1.3}$) to those of uncharged polymers ($\eta \sim c^5$, $G \sim c^2$, $J_e \sim c^{-2}$). Our model predicts this crossover at concentration c_D, where electrostatic blobs begin to overlap because charge effects are fully screened.

(v) Another crossover was observed in all rheological properties upon addition of salt in agreement with our predictions outlined below.

For simplicity and due to lack of space, we do not discuss the effects of salt in the present Letter. It will be described in detail in a future publication [7]. But for completeness, we list the predictions of our model for polyelectrolyte solutions with added salt, both in semidilute unentangled and in entangled regimes. We can express some property X for a polyelectrolyte solution with added monovalent salt of (concentration c_s) in terms of the same property X_0 in the salt-free solution as

$$X \approx X_0 (1 + 2A c_s/c)^\alpha, \qquad (18)$$

where $2A c_s/c$ is the salt ion to counterion ratio. We list the values of exponent α for various properties in Table I. For low-salt solutions ($c_s \ll c/2A$) we recover the salt-free behavior discussed in detail in the present Letter. For solutions with high-salt concentration, the electrostatic interaction is screened and our predictions reduce to those for uncharged polymer solutions.

In the present Letter we introduce the dynamic scaling model of semidilute polyelectrolyte solutions. Our description is based on a simple static scaling picture. In this picture, the electrostatic interactions are irrelevant on length scales smaller than the electrostatic blob size D and are screened (at low-salt concentrations) on length scales larger than correlation length $\xi \sim r_D \sim c^{-1/2}$. Between these two length scales, the polyelectrolyte is a stretched chain of electrostatic blobs. The main result

TABLE I. Predicted exponents α for various quantities X as defined in Eq. (18).

X	Statics			Unentangled				Entangled			
	ξ	g	R	τ	G	D	η	τ	G	D	η
α	$\frac{1}{4}$	$\frac{3}{4}$	$-\frac{1}{8}$	$-\frac{3}{4}$	0	$\frac{1}{2}$	$-\frac{3}{4}$	$-\frac{3}{2}$	$-\frac{3}{4}$	$\frac{5}{4}$	$-\frac{9}{4}$

of our dynamic scaling model is that there is a wide range of concentrations (up to four decades) of unentangled Rouse-like behavior. In this regime (for $c^* < c < c_e$) (a) relaxation time decreases with concentration $\tau \sim c^{-1/2}N^2$, (b) self-diffusion coefficient is independent of concentration $D \sim c^0N^{-1}$, and (c) viscosity follows the Fuoss law $\eta \sim c^{1/2}N$. At higher concentrations ($c > c_e$) chains entangle, and we predict (a) concentration independent relaxation time $\tau \sim c^0N^3$, (b) plateau modulus and recoverable compliance $G \sim 1/J_e \sim c^{3/2}N^0$, (c) viscosity $\eta \sim c^{3/2}N^3$, and (d) self-diffusion coefficient $D \sim c^{-1/2}N^{-2}$. At higher concentration $c > c_D$, the dynamic properties cross over to those of uncharged polymers. The predictions of our model are in excellent agreement with our experiments.

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