POLYELECTROLYTE DYNAMICS

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I. INTRODUCTION

Considerable progress has been made during the last five decades in a molecular understanding of the behavior of solutions of uncharged polymers. In general, the polymer dynamics can be classified into the Kirkwood–Riseman–Zimm–Rouse dynamics, entropic barrier model, and reptation dynamics as the polymer concentration is progressively increased [1–6]. However, such an understanding is lacking for solutions of polyelectrolytes. The general features of the dynamical properties of polyelectrolyte solutions are qualitatively different from those of neutral polymers. Experimental observations of these differences as manifest in the occurrence of electrophoretic mobility, diffusion of polyelectrolytes, and viscosity of polyelectrolyte solutions are richly documented in the literature [7–35], although a systematic experimental investigation on a given system does not yet exist. An example of an apparently surprising behavior is that the velocity of a polyelectrolyte molecule in a dilute solution under an electric field is the same for two chemically identical polymers, differing in molecular weight by several orders of magnitude. The wisdom, with support by extensive experimental measurements on uncharged polymers, that bigger molecules move slower than smaller molecules does not hold for polyelectrolytes. Another surprising result is that in polyelectrolyte solutions without any added salt, measured diffusion coefficients using dynamic light scattering are independent of both molar mass and polymer concentration over three decades in each variable. These results and other experimental data are amply documented in the literature [7–35]. For each of the dynamical quantities, there are many theoretical attempts [36–49]. A successful attempt to provide a conceptual framework to explain all of the major features of dynamics of polyelectrolyte solutions was recently presented by the author [50]. The present review is strongly influenced by the author’s theory on polyelectrolyte dynamics. There are still several questions to be answered, which are remarked at the end of the review. Before we outline the ingredients of the theory, we first review three key dynamical properties unique to polyelectrolytes.
A. Electrophoretic Mobility in an Infinitely Dilute Solution

The electrophoretic mobility $\mu$ of a polyelectrolyte chain in an infinitely dilute solution containing an added salt at concentration $c_s$ under a constant external electric field $E$, as defined through

$$v_p = \mu E$$  \hspace{1cm} (1)

where $v_p$ is the velocity of the polyelectrolyte, is independent [35] of molecular weight $M$ at all salt concentrations:

$$\mu \sim M^0$$  \hspace{1cm} (2)

This is a surprising result in view of the following argument [51], due to Hückel. Defining $Q$ and $D$ to be respectively the net charge and the translational diffusion coefficient of the polyelectrolyte, the balance of frictional force ($k_BT/D)v_p$, and electrical force $QE$ gives

$$\frac{k_BT}{D}v_p = QE$$  \hspace{1cm} (3)

so that

$$\mu \sim QD$$  \hspace{1cm} (4)

where $k_BT$ is Boltzmann’s constant times the absolute temperature. $Q$ is proportional to $M$. In infinitely dilute solutions, full hydrodynamic interactions are present so that $D$ is inversely proportional to the radius of gyration $R_g$ of the polyelectrolyte so that

$$\mu \sim \frac{M}{R_g}$$  \hspace{1cm} (5)

Since $R_g$ scales with $M$ with an effective exponent $\nu$, $R_g \sim M^\nu$, we have

$$\mu \sim M^{1-\nu}$$  \hspace{1cm} (6)

In the limit of low salt concentrations, the conformation of polyelectrolytes is expected to be rod-like so that $\nu = 1$. In this limit, Eq. (2) is recovered. However, as the concentration of the added salt increases, the effective exponent $\nu$ decreases toward $3/5$. Therefore we expect from Eq. (6) that $\mu$ will increase with $M$ at higher salt concentrations, in contradiction with the experimentally observed result of Eq. (2). There are several erroneous claims in the literature
that $D$ is given by the Rouse law, proportional to $\frac{1}{M}$ in infinitely dilute solutions at all salt concentrations. This conjecture is produced to agree with experimental observations but without any derivation.

**B. Diffusion Coefficients**

The light scattering data [24–34] of polyelectrolyte solutions are characteristic of two diffusion coefficients $D_f$ (fast) and $D_s$ (slow). $D_f$ for a solution with a given $c_s$ increases with monomer concentration $c$ and above a certain concentration $c_1$, $D_f$ is independent [31, 33, 34] of both $c$ and $M$.

$$D_f \sim c^0 M^0, \quad c \geq c_1$$

(7)

The slow diffusion coefficient is measurable only at high enough polyelectrolyte concentrations. The value of $c$ at which the slow mode appears is higher if $c_s$ is higher. When the ratio $\lambda \equiv c/c_s$ is about 1, the onset of the slow mode and the crossover between the smaller $D_f$ for $\lambda < 1$ and higher $D_f$ for $\lambda > 1$ occur. $D_s$ depends [33] on $c$ strongly,

$$D_s \sim c^{-\beta(M)}$$

(8)

where $\beta$ is an apparent exponent depending on molecular weight. The absolute scattering intensity associated with the slow mode increases [34] upon decreasing $c_s$.

**C. Viscosity**

The reduced viscosity $\eta_r$ of a polyelectrolyte solution at the monomer concentration $c$ is defined by

$$\eta_r = \frac{\eta - \eta_0}{\eta_0 c}$$

(9)

where $\eta$ and $\eta_0$ are the viscosities of the solution and the solvent, respectively. $\eta_r$ depends on $c$ monotonically for polyelectrolyte solutions at sufficiently high salt concentrations, as in the case of neutral polymers, and at low polyelectrolyte concentrations it can be expanded as a virial series,

$$\eta_r = [\eta][1 + k_H[\eta]c + \cdots]$$

(10)

where $[\eta]$ is the intrinsic viscosity and $k_H$ is the Huggins coefficient. On the other hand, at low salt concentrations, $\eta_r$ is nonmonotonic [11–23] in the dependence on $c$. At very low concentrations, $\eta_r$ increases rapidly with $c$ and then decreases with $c$ at low but higher concentrations after reaching a maximum $\eta_{r\text{max}}$ at $c_{\text{max}}$. 
At much higher concentrations ($c$ greater than say $c_e$) $\eta_r$ increases again with $c$. In the intermediate concentration region where $\eta_r$ decreases with $c$, the experimental data at low salt concentrations are fitted empirically to the Fuoss law,

$$\eta_r \sim \frac{1}{\sqrt{c}}$$

(11)

$\eta_{r_{\text{max}}}$ increases [19] linearly with $M$. An increase in the salt concentration moves $c_{\text{max}}$ toward higher $c$ so that $c_{\text{max}} \sim c_e$, and it drastically lowers the value of $\eta_{r_{\text{max}}}$. Analogous to the viscosity behavior, the dynamic storage and loss moduli also show [22] a peak with $c$. The unusual behavior at low $c_e$ where the reduced viscosity increases with dilution in the polyelectrolyte concentration range between $c_{\text{max}}$ and $c_e$, along with the occurrence of a peak in the reduced viscosity versus $c$, has remained as one of the most perplexing properties of polyelectrolytes over many decades.

In order to resolve these challenges, it is essential to account for chain connectivity, hydrodynamic interactions, electrostatic interactions, and distribution of counterions and their dynamics. It is possible to identify three distinct scenarios: (a) polyelectrolyte solutions with high concentrations of added salt, (b) dilute polyelectrolyte solutions without added salt, and (c) polyelectrolyte solutions above overlap concentration and without added salt. If the salt concentration is high and if there is no macrophase separation, the polyelectrolyte solution behaves as a solution of neutral polymers in a good solvent, due to the screening of electrostatic interaction. Therefore for scenario (a), all concepts developed for solutions of uncharged polymers can be implemented, except for the additional role played by counterions. In scenario (b), chains place themselves as far away as possible from each other due to the repulsive interactions between them. Under these conditions, the average distance $\Lambda$ between the chains scales with polyelectrolyte concentration $c$ according to

$$\Lambda \sim c^{-1/3}$$

(12)

as expected from the geometrical consideration. In this dilute regime, different segments in the same chain interact with screened Coulomb interaction where the electrostatic screening arises from the counterions and salt ions if present. There can also be condensation of counterions on the polyelectrolyte chain. For the salt-free solutions, the electrostatic screening length $\kappa^{-1}$ is very large. In scenario (b), chain dynamics, hydrodynamics, intersegment electrostatics, and counterion dynamics describe the dynamical properties.
In scenario (c) corresponding to semidilute solutions, polyelectrolyte chains interpenetrate. Under these circumstances, there are three kinds of screening. The electrostatic interaction, excluded volume interaction, and the hydrodynamic interaction between any two segments of a labeled polyelectrolyte chain are all screened by interpenetrating chains. Each of these three interactions is associated with a screening length, namely, $\kappa^{-1}$, $\xi$, and $\xi_H$. These screening lengths are coupled to each other. By considering a thermodynamic description of the double screening of electrostatic and excluded volume interactions, it has recently been shown [48] that for semidilute conditions we have

$$
\xi \sim \begin{cases} 
  c^{-1/2}, & \text{low salt} \\
  c^{-3/4}, & \text{high salt} 
\end{cases}
$$

At the same time $R_g$ of a labeled polyelectrolyte chain is derived to be

$$
R_g \sim \begin{cases} 
  \sqrt{N} c^{-1/4}, & \text{low salt} \\
  \sqrt{N} c^{-1/8}, & \text{high salt} 
\end{cases}
$$

These calculated results have been quantitatively verified by experiments [52–54].

The nature of screening of hydrodynamics, its coupling with the screening of electrostatic and excluded volume interactions, and its role in various dynamical properties are discussed in the following sections. In addition to the above-mentioned contributing factors, entanglements between chains play a role in high polyelectrolyte solutions. Only scaling considerations are given for this effect. Except for this effect, formulas for crossover functions in terms of chain length, salt concentration, and polymer concentration are presented. After presenting the theoretical model, along with the theory for dilute and semidilute solutions, we conclude by comparing with the qualitative features of experiments.

II. THEORETICAL MODEL

We consider a system of $n$ polyelectrolyte chains each of $N$ segments, $n_c$ counterions, $n_\gamma$ ions of species $\gamma$ from dissolved salt, and $n_s$ solvent molecules in volume $\Omega$. The total charge on each polyelectrolyte is $Q$ assumed to be proportional to $N$.

A. Solvent

Provided that the polyelectrolyte chains are much larger than the solvent molecules, the solvent can be treated as a homogeneous isothermal viscous
continuum obeying the linearized Navier–Stokes equation (in the steady state limit)

\[-\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{F}(\mathbf{r})\]  

(15)

Here \(\mathbf{v}(\mathbf{r})\) is the velocity field at any space point \(\mathbf{r}\), \(p\) is the pressure, \(\eta_0\) is the shear viscosity of the solvent containing salt ions and counterions, and \(\mathbf{F}(\mathbf{r})\) is the force arising from any potential field in the solution. As an example, if electrical charges are present in the solution under an externally imposed uniform electrical field \(\mathbf{E}\), \(\mathbf{F}(\mathbf{r})\) is given by

\[\mathbf{F}(\mathbf{r}) = \mathbf{F}_s(\mathbf{r}) + \mathbf{r}(\mathbf{r}) \mathbf{E}\]  

(16)

Here \(\mathbf{F}_s(\mathbf{r})\) is any force imposed by an external boundary condition such as a shear flow and \(\mathbf{r}(\mathbf{r})\) is the electrical charge density at \(\mathbf{r}\).

The hydrodynamic property of the solvent follows from Eq. (15) as

\[\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}')\]  

(17)

with \(\mathbf{G}(\mathbf{r})\) being the Oseen tensor,

\[\mathbf{G}(\mathbf{r}) = \frac{1}{8\pi\eta_0|\mathbf{r}|} \left( 1 + \frac{\mathbf{r}\mathbf{r}}{|\mathbf{r}|^2} \right)\]  

(18)

Upon Fourier transform, \(\mathbf{G}\) becomes

\[\mathbf{G}(\mathbf{k}) = \frac{1}{\eta_0 k^2} \left( 1 - \frac{\mathbf{k}\mathbf{k}}{k^2} \right)\]  

(19)

with \(k\) being the modulus of \(\mathbf{k}\).

**B. Polymer**

The equation of motion for the position vector \(\mathbf{R}_{ai}\) of the \(i\)th segment of the chain \(\alpha\) at time \(t\) is given by the Langevin equation,

\[m\ddot{\mathbf{R}}_{ai} = \mathbf{F}_{\text{connectivity}} + \mathbf{F}_{\text{interactions}} + \mathbf{F}_{\text{friction}} + \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{ran}}\]  

(20)

where the various terms on the right-hand side of the equation are described as follows.
The force arising from the chain connectivity is related to the probability of realizing particular configurations. The probability for the $i$th Kuhn step connecting $\mathbf{R}_i$ and $\mathbf{R}_{i-1}$ is

$$P_{ai}(\mathbf{R}_{x,i} - \mathbf{R}_{x,i-1}) = \left( \frac{3}{2\pi \ell^2} \right)^{3/2} \exp \left[ -\frac{3}{2} \left( \frac{\mathbf{R}_{x,i} - \mathbf{R}_{x,i-1}}{\ell^2} \right)^2 \right]$$ (21)

where $\ell$ is the Kuhn length. The free energy of the chain due solely to chain connectivity is

$$-k_B T \sum_{i=1}^{N} \ln P_i = \text{constant} + \sum_{i=1}^{N} \frac{3k_B T}{\ell^2} (\mathbf{R}_i - \mathbf{R}_{i-1})$$ (22)

The connectivity force on $i$th segment of $\alpha$th chain is

$$\mathbf{F}_{\text{connectivity}} = -\frac{\partial}{\partial \mathbf{R}_{\alpha,i}} \left[ \left( k_B T \sum_{i=1}^{N} \ln P_{\alpha,i} \right) \right]$$

$$= -\frac{3k_B T}{2\ell^2} \frac{\partial}{\partial \mathbf{R}_{\alpha,i}} \left[ (\mathbf{R}_{\alpha,i+1} - \mathbf{R}_{\alpha,i})^2 + (\mathbf{R}_{\alpha,i} - \mathbf{R}_{\alpha,i-1})^2 \right]$$

$$= -\frac{3k_B T}{\ell^2} \left[ -\mathbf{R}_{\alpha,i+1} + 2\mathbf{R}_{\alpha,i} - \mathbf{R}_{\alpha,i-1} \right]$$

$$= -\frac{3k_B T}{\ell^2} \sum_{i=1}^{N} (2\delta_{i,j} - \delta_{i,j+1} + \delta_{i,j-1}) \mathbf{R}_{\lambda,j}$$ (23)

where $(2\delta_{i,j} - \delta_{i,j+1} + \delta_{i,j-1})$ is the Rouse matrix. We do not concern ourselves with the end effects, although these effects can be rigorously treated [3–4].

Assuming that the total charge $Q$ of a polyelectrolyte chain is uniformly distributed on the chain backbone so that each segment carries a charge of $e\varepsilon_p$ where $e$ is the electronic charge and by integrating over the positions of counterions, salt ions, and solvent molecules, the potential interaction $V$ between any two segments $i$ and $j$ separated by a distance $\mathbf{R}_{ij}$ is taken to be [48]

$$\frac{V(\mathbf{R}_{ij})}{k_B T} = w\delta(\mathbf{R}_{ij}) + \frac{e^2 l_B}{|\mathbf{R}_{ij}|} \exp(-\kappa|\mathbf{R}_{ij}|)$$ (24)

where $w$ is the short-ranged “excluded volume” denoting the solvent quality, and $l_B \equiv e^2/k_B T\epsilon$ is the Bjerrum length with $\epsilon$ being the effective dielectric constant of the solution. The Debye length $\kappa^{-1}$, within the approximations behind
Eq. (24), arises from only the counterions and the dissociated salt ions,

\[
\kappa^2 = \frac{4\pi e^2}{\epsilon k_B T} \left( z_e^2 \rho_e + \sum_\gamma Z_\gamma^2 \rho_\gamma \right)
\]

(25)

where \( \rho_e \) and \( \rho_\gamma \) are the number densities of counterions and the \( \gamma \)th salt ion. Therefore the force arising from intersegment potential interactions is

\[
\mathbf{F}_{\text{interactions}} = -\nabla_{\mathbf{R}_{\alpha,i}} \sum_{\beta=1}^n \sum_{j=1}^N V(\mathbf{R}_{\alpha,i} - \mathbf{R}_{\beta,j})
\]

(26)

The frictional force is given as

\[
\mathbf{F}_{\text{friction}} = -\zeta \dot{\mathbf{R}}_{\alpha,i}
\]

(27)

where \( \dot{\mathbf{R}}_{\alpha,i} \) is the velocity of the \( i \)th segment of \( \alpha \)th chain and \( \zeta \) is a phenomenological parameter, called bead friction coefficient, representing the microscopic details of friction of a segment against the background solvent. \( \mathbf{F}_{\text{ext}} \) is any externally imposed force, such as electrical or gravitational, acting at \( \mathbf{R}_{\alpha,i} \). \( \mathbf{F}_{\text{ran}} \) is the fluctuating noisy force arising from the solvent, acting at \( \mathbf{R}_{\alpha,i} \). The correlation of this noise is stipulated by the fluctuation–dissipation theorem in terms of the temperature and \( \zeta \). Combining Eqs. (20–27), we get the equation of motion for the \( i \)th segment of \( \alpha \)th chain as

\[
\zeta \dot{\mathbf{R}}_{\alpha,i} + \Delta_{\alpha} \mathbf{R}_{\alpha,i} = \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{ran}}
\]

(28)

where \( \Delta_{\alpha} \) denotes the terms from connectivity and interactions,

\[
\Delta_{\alpha} = \frac{3k_B T}{\ell^2} \sum_{i=1}^N (2\delta_{i,j-1} - \delta_{i,j} - \delta_{i,j+1}) \mathbf{R}_{\alpha,i} + \nabla_{\mathbf{R}_{\alpha,i}} \sum_{\beta=1}^n \sum_{j=0}^N V(\mathbf{R}_{\alpha,i} - \mathbf{R}_{\beta,j})
\]

(29)

\textbf{C. Polymer and Solvent}

The dynamics of the solvent and polymer are coupled in a polymer solution. Although this coupling is expressed partly through the friction and noise terms in Eq. (28), a complete description requires a boundary condition. The most common choice of this boundary condition is the no-slip condition

\[
\dot{\mathbf{R}}_{\alpha i} = \mathbf{v}(\mathbf{R}_{\alpha i})
\]

(30)
Using this boundary condition as a constraint, the equations of motion for the combined system of polymer and solvent can be derived to be [55–59]

\[-\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla p(\mathbf{r}) = \mathbf{F}(\mathbf{r}) + \sum_{a=1}^{n} \sum_{j=0}^{N} \delta(\mathbf{r} - \mathbf{R}_{aj})\sigma_{aj} \tag{31}\]

\[\Delta_{z} \mathbf{R}_{aj} = -\sigma_{aj} + \mathbf{F}_{\text{ext}} + \mathbf{F}_{\text{ran}} \tag{32}\]

Here \(\sigma_{aj}\) is a Lagrange multiplier and is to be eliminated by using the boundary condition of Eq. (30). The coupled equations are solved using the multiple scattering formalism, the details of which are provided in Refs. 55–59. The objective is to determine \(\sigma_{aj}\) using Eq. (30) and then calculate the microscopic velocity field from Eq. (31), which upon averaging over the distributions of polyelectrolyte chain configurations gives the viscosity of the solution and the self diffusion coefficient of the polyelectrolyte. Within the multiple scattering formalism, the effective equation of motion for the polyelectrolyte solution becomes [55–59]

\[-\eta_0 \nabla^2 \langle \mathbf{v}(\mathbf{r}) \rangle + \nabla \langle p(\mathbf{r}) \rangle + \int d\mathbf{r}' \Sigma(\mathbf{r} - \mathbf{r}') \cdot \langle \mathbf{v}(\mathbf{r}') \rangle = \mathbf{F}(\mathbf{r}) \tag{33}\]

where the angular brackets indicate the above-mentioned average and the kernel \(\Sigma\) contains information about the modified viscosity and the extent of hydrodynamic screening. For the polyelectrolyte solution, the average velocity field is given by

\[\langle \mathbf{v}(\mathbf{r}) \rangle = \int d\mathbf{r}' \mathcal{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') \tag{34}\]

whereas the hydrodynamic property of the solvent follows from Eq. (17). In the presence of polyelectrolyte chains, \(\mathbf{G}(k)\) is replaced by \(\mathcal{G}(k)\), where

\[\mathcal{G}^{-1}(k) = \mathbf{G}^{-1}(k) + \Sigma(k) \tag{35}\]

with \(\Sigma(k)\) being the Fourier transform of \(\Sigma(\mathbf{r})\),

\[\Sigma(k) = \int d\mathbf{r} \Sigma(\mathbf{r}) \exp(ik \cdot \mathbf{r}) \tag{36}\]

and \(\mathcal{G}^{-1}(k)\) being the Fourier transform of \(\mathcal{G}^{-1}(\mathbf{r})\) defined by

\[\int d\mathbf{r}' \mathcal{G}^{-1}(\mathbf{r} - \mathbf{r}') \cdot \mathcal{G}(\mathbf{r}' - \mathbf{r}'') = \mathbf{1}\delta(\mathbf{r} - \mathbf{r}'') \tag{37}\]
The change $\eta - \eta_0$ in shear viscosity of the solvent due to the polyelectrolyte chains is given by

$$\eta - \eta_0 = k \lim_{\delta \to 0} \delta^{-2} (1 - k \delta) \cdot \Sigma(k)$$  \hspace{1cm} (38)$$

where $\eta$ is the shear viscosity of the solution. As will be shown below, $\Sigma(k)$ becomes independent of $k$ for length scales shorter than average radius of gyration of the polyelectrolyte chains at higher concentrations. We write the transverse component of the $k$-independent $\Sigma(k)$ as $\eta_0 \xi^{-2}_H$, where $\xi_H$ is the hydrodynamic screening length. This will be determined explicitly in the next section.

### III. DILUTE SOLUTIONS

In this section, we ignore all interchain interactions and address the situation of polyelectrolyte solutions at infinitely dilute conditions. Since isolated chains are now being considered, the chain label is dropped in this section.

#### A. Effective Chain Dynamics

Combining Eqs. (17) and (31), the velocity field at space location $r$ follows as

$$v(r) = \int dr' G(r - r') \cdot \left[ F(r') + \sum_{j=0}^{N} \delta(r' - R_j) \sigma_j \right]$$  \hspace{1cm} (39)$$

Using the boundary condition of Eq. (30), the velocity of the $i$th segment is given by

$$\dot{R}_i = v(R_i) = \int dr' G(R_i - r') \cdot \left[ F(r') + \sum_{j=0}^{N} \delta(r' - R_j) \sigma_j \right]$$  \hspace{1cm} (40)$$

$$= \int dr' G(R_i - r') \cdot F(r') + \sum_{j=0}^{N} G(R_i - R_j) \sigma_j$$  \hspace{1cm} (41)$$

For $i = j$, $G(R_i - R_j)$ given by Eq. (18) is not valid and it is simply the reciprocal of the bead friction coefficient. Hence

$$\dot{R}_i = \int dr' G(R_i - r') \cdot F(r') + \frac{1}{\zeta} \sigma_i + \sum_{j\neq i} G(R_i - R_j) \cdot \sigma_j$$  \hspace{1cm} (42)$$
so that
\[
\sigma_i = \zeta \left[ \dot{\mathbf{R}}_i - \int d\mathbf{r}' G(\mathbf{R}_i - \mathbf{r}') \cdot \mathbf{F} (\mathbf{r}') - \sum_{j \neq i} G(\mathbf{R}_i - \mathbf{R}_j) \cdot \sigma_j \right] \tag{43}
\]

The physical interpretation of this equation is readily apparent. \(\sigma_i\) is the force exerted on the fluid by the \(i\)th segment given by
\[
\sigma_i = \zeta (\mathbf{R}_i - \mathbf{v}_i) \tag{44}
\]
where \(\mathbf{v}_i\) is the velocity the fluid would possess at the location of the \(i\)th segment if that segment were absent. \(\mathbf{v}_i\) is the sum of velocity in the absence of the polymer chain
\[
\mathbf{v}_i^0 = \int d\mathbf{r}' G(\mathbf{R}_i - \mathbf{r}') \cdot \mathbf{F} (\mathbf{r}') \tag{45}
\]
and the sum of velocities arising from hydrodynamic coupling with forces of all other segments of the same chain,
\[
\sum_{j \neq i} G(\mathbf{R}_i - \mathbf{R}_j) \cdot \sigma_j \tag{46}
\]
Returning to Eq. (43), it can be rewritten as
\[
\sum_{j=0}^{N} \mathbf{D}_{ij} \cdot \sigma_j = \dot{\mathbf{R}}_i - \int d\mathbf{r}' G(\mathbf{R}_i - \mathbf{r}') \cdot \mathbf{F} (\mathbf{r}') \tag{47}
\]
where the diffusion tensor is defined by
\[
\mathbf{D}_{ij} = \left[ \frac{1}{\zeta} \mathbf{1}_{ij} + (1 - \delta_{ij}) G(\mathbf{R}_i - \mathbf{R}_j) \right] \tag{48}
\]
with \(\mathbf{1}\) being the unit tensor. By multiplying Eq. (32) by \(\mathbf{D}_{ij}\) and summing over \(j\), it follows from Eqs. (29) and (47) that
\[
\dot{\mathbf{R}}_i + \sum_j \left[ \frac{1}{\zeta} \mathbf{1}_{ij} + (1 - \delta_{ij}) G(\mathbf{R}_i - \mathbf{R}_j) \right] \cdot \left[ \frac{3k_B T}{\ell^2} \sum_p (2\delta_{j,p} - \delta_{j,p+1} + \delta_{j,p-1}) \mathbf{R}_p + \nabla_{\mathbf{R}_j} \sum_p V(\mathbf{R}_j - \mathbf{R}_p) \right] = \mathbf{v}_{\text{ran}}(i) \tag{49}
\]
where $F$ is now taken to be zero and $v_{\text{ran}}(i)$ is a noise from the background velocity proportional to $F_{\text{ran}}(i)$, acting on the $i$th segment. Since we are interested in relatively long polymer chains, summations over segment indices can be replaced by integrals over arclength variables. Letting $s' = j\ell$,

$$
\frac{1}{\ell^2} \sum_p (2\delta_{j,p} - \delta_{j,p+1} + \delta_{j,p-1}) R_p = -\frac{\partial^2 R(s')}{\partial s'^2}
$$

(50)

so that Eq. (49) becomes

$$
\dot{R}(s) +\int_0^L ds' D[R(s) - R(s')] \cdot \left[ -\frac{3k_B T \partial^2 R(s')}{\ell^2} \right. \\
+ \nabla R(s') \int_0^L ds'' V[R(s) - R(s')] \\
\left. = v_{\text{ran}}(s) \right]
$$

(51)

where

$$
D[R(s) - R(s')] = \frac{1}{\zeta} \delta(s - s') + (1 - \ell \delta(s - s')) G[R(s) - R(s')]
$$

(52)

Equation (51) is highly nonlinear. One of the key approximations made to enable analytical calculations is the preaveraging approximation, whereby the diffusion tensor $D[R(s) - R(s')]$ is replaced by its average over chain configurations,

$$
D[R(s) - R(s')] \approx \langle D[R(s) - R(s')] \rangle
$$

(53)

$$
= \frac{1}{\zeta} \delta(s - s') \\
+ [1 - \delta(s - s')] \left\langle \frac{1}{6\pi n_0} \frac{1}{|R(s) - R(s')|} \right\rangle
$$

(54)

$$
\equiv 1D(s - s')
$$

(55)

which depends only on $s - s'$. We now introduce the Rouse modes by defining the Fourier transform,

$$
\dot{R}(q) = \int_0^L ds \ R(s) \exp(iqs)
$$

(56)

The variable $q$, which is conjugate to the arc length variable $s$, labels the normal mode. If we work with the discretized chain model ($i$ variable, instead of $s$
variable), \( q \) is actually \( 2\pi p/L \), where \( p = 0, 1, 2, \ldots, N \). The integer variable \( p \) is called the Rouse mode variable. \( q \) is proportional to \( L^{-1} \) and \( p = 0 \) represents the motion of the center of mass of the chain. Writing Eq. (51) in terms of its Fourier transform, we obtain

\[
\dot{\mathbf{R}}(q) + \hat{D}(q) \left[ \frac{3k_B T}{\ell} q^2 \hat{\mathbf{R}}(q) + \int_0^L ds e^{-isq} \mathbf{F}_{\text{interaction}}[\mathbf{R}(s')] \right] = \hat{\mathbf{v}}_{\text{ran}}(q) \quad (57)
\]

where \( \hat{D}(q) \) is the Fourier transform of \( D(s-s') \). The second term inside the square brackets in Eq. (57) depicting potential interactions can be expressed in terms of Rouse modes. In general \( q \)th mode is coupled to all other modes. As shown in Ref. 58, the assumption of full decoupling among the Rouse modes is equivalent to replacing the factor \( \ell \) (in the first term of square brackets) by an effective Kuhn length \( \ell_1 \) which is \( q \)-dependent. For \( q \to 0 \), \( \ell_1/\ell \) is exactly the expansion factor of the mean square end-to-end distance \( \langle R^2 \rangle \) of a chain due to excluded volume interactions (both short-ranged and electrostatic),

\[
\langle R^2 \rangle = L\ell_1 (q \to 0) \quad (58)
\]

The mode–mode decoupling calculation for an isolated uncharged chain in a good solution shows that [50, 58]

\[
\left( \frac{\ell_1}{\ell} \right)^{5/2} - \left( \frac{\ell_1}{\ell} \right)^{3/2} = \frac{2\sqrt{3}}{\pi} \frac{w}{\sqrt{q\ell}} \quad (59)
\]

where \( w \) is the excluded volume parameter defined in Eq. (24). For small \( q \) and large \( w \) (i.e., for large values of the Fixman parameter \( w\sqrt{L} \)), \( \ell_1 \) approaches

\[
\ell_1 \sim q^{-1/5} \quad (60)
\]

which is consistent with

\[
\ell_1 \sim q^{1-2\nu} \quad (61)
\]

where \( \nu \) is the size exponent.

By making the above approximations (preaveraging and uniform expansion), the Langevin equation for the polymer segment can be written as

\[
\dot{\mathbf{R}}(q) + \frac{3k_B T}{\ell_1} \hat{D}(q)\dot{\mathbf{R}}(q) = \hat{\mathbf{v}}_{\text{ran}}(q) \quad (62)
\]
The \( q \)-dependent diffusion coefficient is obtained as follows:

\[
\hat{D}(q) = \int_0^L d(s - s') e^{iq(s - s')} D(s - s')
\]

\[
= \frac{\ell}{\zeta} + \frac{1}{6\pi\eta_0} \int_0^\infty d(s - s') e^{iq(s - s')} \left\langle \frac{1}{|R(s) - R(s')|} \right\rangle
\]

For Gaussian chains,

\[
\left\langle \frac{1}{|R(s) - R(s')|} \right\rangle = \left( \frac{6}{\pi \ell |s - s'|} \right)^{1/2}
\]

With the approximation of uniform expansion by potential interactions, we can assume that

\[
\left\langle \frac{1}{|R(s) - R(s')|} \right\rangle = \left( \frac{6}{\pi \ell_1 |s - s'|} \right)^{1/2}
\]

where \( \ell_1 / \ell \) is the expansion factor for the mean-square end-to-end distance and is proportional to \( (L/\ell)^{2\nu - 1} \). Inserting Eq. (66) into Eq. (64), we obtain

\[
\hat{D}(q) = \frac{\ell}{\zeta} + \frac{1}{\eta_0 \sqrt{\ell_1 q}}
\]

Since \( \ell_1 \) is proportional to \( L^{2\nu - 1} \) and \( q \) is proportional to \( 1/L \), \( \ell_1 \) is proportional to \( q^{1-2\nu} \). Substitution of Eq. (67) into Eq. (62) gives the Langevin equation for the Rouse modes of the chain within the approximations of preaveraging for hydrodynamic interactions and mode–mode decoupling for intersegment potential interactions. Equation (62) yields the following results for relaxation times and various dynamical correlation functions.

1. **Relaxation Times**

An inspection of Eq. (62) on dimensional grounds gives the characteristic time \( \tau_q \) as

\[
\tau_q = \frac{\ell_1}{3k_B T \hat{D}(q)^2}
\]

Substituting Eq. (67) into Eq. (68), we get

\[
\tau_q = \frac{\ell_1}{3k_B T q^2 \left[ \frac{\ell}{\zeta} + \frac{1}{\eta_0 \sqrt{\ell_1 q}} \right]}
\]
a. Free-Draining Limit. If hydrodynamic interaction is absent \((\eta_0 \to \infty)\),
called the free-draining limit, \(\tau_q\) becomes

\[
\tau_{q,\text{Rouse}} = \frac{\zeta \ell_1}{3k_B T \ell q^2}
\]  

(70)

These are the Rouse relaxation times. For Gaussian chains \((\ell_1 = \ell)\), they become

\[
\tau_{q,\text{Rouse}} = \frac{\zeta}{3k_B T q^2}
\]  

(71)

\[
= \zeta \frac{L^2}{12\pi^2 k_B T p^2}
\]  

(72)

where \(p\) is the Rouse mode index. For a chain with size exponent \(\nu\), Rouse relaxation times are

\[
\tau_{q,\text{Rouse}} \sim \frac{\zeta}{T} \left( \frac{L}{p} \right)^{2\nu+1}
\]  

(73)

and the longest relaxation time, called the Rouse time \(\tau_{\text{Rouse}}\) is proportional to \(L^{2\nu+1}\),

\[
\tau_{\text{Rouse}} \sim L^{2\nu+1}
\]  

(74)

b. Non-Free-Draining Limit. In dilute solutions, the hydrodynamic interactions dominate. Under this condition, \(\tau_q\) becomes from Eq. (69)

\[
\tau_q \sim \frac{\eta_0}{3k_B T} \left( \frac{\ell_1}{q} \right)^{3/2}
\]  

(75)

These are the Zimm relaxation times and are proportional to \(L^{3\nu}\),

\[
\tau_{q,\text{Zimm}} \sim \frac{\eta_0}{T} q^{-3\nu}
\]  

(76)

For Gaussian chains,

\[
\tau_{q,\text{Zimm}} = \frac{\eta_0}{3(2\pi)^{3/2} k_B T} \left( \frac{L}{p} \right)^{3/2}
\]  

(77)
In general, the longest relaxation time is

$$\tau_{q,Zimm} \sim \frac{n_0}{T} R_g^3$$  \hspace{1cm} (78)$$

Therefore we expect

$$\tau_{Zimm} \sim \begin{cases} L^3, & \text{low salt} \\ L^{9/5}, & \text{high salt.} \end{cases}$$  \hspace{1cm} (79)$$

2. Segment-to-Segment Correlation Function

In this section, we present derivation of the correlation function, \(\langle [R(s,t) - R(s',t')]^2 \rangle\). By defining the Fourier transform

$$\tilde{R}(q, \omega) = \int_{-\infty}^{\infty} dt \hat{R}(q,t) \exp(i\omega t)$$  \hspace{1cm} (80)$$

Eq. (62) becomes

$$i\omega \tilde{R}(q, \omega) + \frac{3k_BT \tilde{D}}{\ell_1} \tilde{R}(q, \omega) = \tilde{v}_{\text{ran}}(q, \omega)$$  \hspace{1cm} (81)$$

By formally solving this equation, we obtain

$$\tilde{R}(q, \omega) = \frac{\tilde{v}_{\text{ran}}(q, \omega)}{(i\omega + \frac{3k_BT \tilde{D}}{\ell_1} q^2)}$$  \hspace{1cm} (82)$$

Since the stochastic term \(\tilde{v}_{\text{ran}}\) is defined only in terms of its correlation function, we construct the correlation function,

$$\langle \tilde{R}(q, \omega) \cdot \tilde{R}^*(q', \omega') \rangle = \frac{\langle \tilde{v}_{\text{ran}}(q, \omega) \cdot \tilde{v}_{\text{ran}}^*(q', \omega') \rangle}{(i\omega + \frac{3k_BT \tilde{D}}{\ell_1(q)} q^2)} \left( -i\omega' + \frac{3k_BT \tilde{D}(q')}{\ell_1(q')} q'^2 \right)$$  \hspace{1cm} (83)$$

where the angular brackets indicate the average over the thermal Brownian forces, and the superscript * indicates the complex conjugate. For simplicity we assume, as in the case of the Brownian motion of a particle, that \(\tilde{v}_{\text{ran}}(q, \omega)\) is a white noise. Now \(\langle \tilde{v}_{\text{ran}}(q, \omega) \cdot \tilde{v}_{\text{ran}}^*(q', \omega') \rangle\) is proportional to \(\delta(q - q')\delta(\omega - \omega')\),

$$\langle \tilde{v}_{\text{ran}}(q, \omega) \cdot \tilde{v}_{\text{ran}}^*(q', \omega') \rangle = \Theta \delta(q - q')\delta(\omega - \omega')$$  \hspace{1cm} (84)$$
where the proportionality factor $\Theta$ is to be determined below from a consideration of equilibrium.

The correlation function $\langle [R(s, t) - R(s', t')]^2 \rangle$ follows from its Fourier transform as

$$
\langle [R(s, t) - R(s', t')]^2 \rangle = 2 \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} dq' \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' [e^{-i(q-q')s-i(\omega-\omega')t} - 2e^{-iqs-i\omega t + iq's + i\omega't'} + e^{-i(q-q')s'-i(\omega-\omega')t}] \langle \tilde{R}(q, \omega) \cdot \tilde{R}'(q', \omega') \rangle
$$

(85)

Substituting Eq. (83) in Eq. (85) and by performing $q'$ and $\omega'$ integrals, we obtain

$$
\langle [R(s, t) - R(s', t')]^2 \rangle = 2 \int_{-\infty}^{\infty} dq \int_{-\infty}^{\infty} d\omega \frac{\Theta[1 - \cos(q(s-s'))e^{i\omega(t-t')}}{(i\omega + \frac{3k_BT\ell(q)}{\ell_1(q)})(-i\omega + \frac{3k_BT\ell(q)}{\ell_1(q)})}
$$

$$
= \int_{-\infty}^{\infty} dq \frac{\Theta\ell_1(q)}{2\pi 3k_BT\ell(q)} [1 - \cos(q(s-s'))e^{-\frac{\omega(t-t')}{q}}]
$$

(86)

The equal time correlation function,

$$
\langle [R(L, t) - R(0, t)]^2 \rangle = \int_{0}^{\infty} dq \frac{\Theta\ell_1(q)}{\pi 3k_BT\ell(q)} [1 - \cos(qL)]
$$

(87)

is the equilibrium result

$$
\langle [R(L, t) - R(0, t)]^2 \rangle = L\ell_1
$$

(88)

By comparing Eqs. (87) and (88), we get the following expression for $\Theta$:

$$
\Theta = 6k_BT\ell(q)
$$

(89)

Therefore, $\langle [R(s, t) - R(s', t')]^2 \rangle$ follows as

$$
\langle [R(s, t) - R(s', t')]^2 \rangle = 2 \int_{0}^{\infty} dq \frac{\ell_1(q)}{\pi q^2} [1 - \cos(q(s-s'))e^{-\frac{\omega(t-t')}{q}}]
$$

(90)
The mean-square displacement of a labeled monomer is

$$\langle [\mathbf{R}(s, t) - \mathbf{R}(s, t')]^2 \rangle = 2 \int_0^\infty \frac{dq \ell_1(q)}{q^2} \left(1 - e^{-\frac{|t-t'|}{q}}\right)$$  \hspace{1cm} (91)

When hydrodynamic interaction dominates, \( \tau_q \sim q^{-3v} \), so that

$$\langle [\mathbf{R}(s, t) - \mathbf{R}(s, t')]^2 \rangle \sim \int_0^\infty dq \ q^{-(2v+1)}(1 - e^{-q^3|t-t'|})$$
$$\sim |t-t'|^{2/3}$$  \hspace{1cm} (92) \hspace{1cm} (93)

The incoherent dynamical structure factor is given by

$$S_{inc}(\mathbf{k}, t) = \exp(-k^2 \langle [\mathbf{R}(s, t) - \mathbf{R}(s, t')]^2 \rangle /6)$$
$$\sim \exp(-k^2 |t-t'|^{2/3})$$  \hspace{1cm} (94)

where \( \mathbf{k} \) is the scattering wave vector. \( S_{inc}(\mathbf{k}, t) \) is therefore of the form

$$\exp[-(k^3 |t-t'|)^{2/3}]$$  \hspace{1cm} (95)

so that the decay rate is proportional to \( k^3 \). On the other hand, if the hydrodynamic interaction is absent, \( \tau_q \sim q^{-(1+2v)} \), so that

$$\langle [\mathbf{R}(s, t) - \mathbf{R}(s', t')]^2 \rangle \sim \int_0^\infty dq \ q^{-(1+2v)}(1 - e^{-q^{1+2v}|t-t'|})$$
$$\sim |t-t'|^{2v/(1+2v)}$$  \hspace{1cm} (96) \hspace{1cm} (97)

Now, the decay rate of the incoherent dynamic structure factor is proportional to \( k^{(1+2v)/v} \). Therefore, the \( k \)-dependence of the decay rate for salt-free solutions is independent of whether the hydrodynamic interaction is present or not.

B. Translational Friction Coefficient

The translational friction coefficient \( f_i \) of the polymer chain at infinitely dilute solutions is calculated by equating the net force acting on the chain, \(- \sum_i \langle \sigma_i \rangle \), and \(-f_i \mathbf{R}^0 \), where \( \mathbf{R}^0 \) is the net drift velocity of the center of mass of the chain

$$\sum_i \langle \sigma_i \rangle = f_i \mathbf{R}^0$$  \hspace{1cm} (98)
If there is no velocity field in the absence of polymer \(\mathbf{F} = 0\), \(\sigma_i\) follows from Eq. (43) as

\[
\langle \sigma_i \rangle = \zeta \langle \dot{R}_i \rangle - \zeta \sum_{j \neq i} \langle \mathbf{G}(\mathbf{R}_i - \mathbf{R}_j) \cdot \sigma_j \rangle
\]  

(99)

Assuming that \(\dot{R}_i\) is the same as the center-of-mass velocity \(\mathbf{R}^0\) for all \(i\) and invoking the preaveraging approximation, we get

\[
\langle \sigma_i \rangle = \zeta \mathbf{R}^0 - \zeta \sum_{j \neq i} \langle \mathbf{G}(\mathbf{R}_i - \mathbf{R}_j) \rangle \langle \sigma_j \rangle
\]  

(100)

With the assumption of uniform chain expansion due to potential interactions, we have

\[
\langle \mathbf{G}(\mathbf{R}_i - \mathbf{R}_j) \rangle = \frac{1}{6\pi \eta_0} \left\langle \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \right\rangle
\]  

(101)

\[
= \frac{1}{\eta_0} \left( \frac{1}{6\pi^3 \ell \ell_1 |i - j|} \right)^{1/2}
\]  

(102)

Defining

\[
\langle \sigma_j \rangle \equiv \Phi_j \zeta \mathbf{R}^0
\]  

(103)

Eq. (100) yields

\[
\Phi_i = 1 - \frac{\zeta}{\eta_0} \frac{1}{(6\pi^3 \ell \ell_1)^{1/2}} \sum_{j \neq i} \frac{1}{|i - j|^{1/2}} \Phi_j
\]  

(104)

By going to continuous variables

\[
\frac{2i}{N} - 1 = x, \quad \frac{2j}{N} - 1 = y
\]  

(105)

Eq. (104) becomes

\[
\Phi(x) = 1 - h \int_{-1}^{1} dy \frac{1}{|x - y|^{1/2}} \Phi(y)
\]  

(106)

where

\[
h = \frac{\zeta}{\eta_0} \frac{\sqrt{N}}{(12\pi^3 \ell \ell_1)^{1/2}}
\]  

(107)
The integral equation for $\phi(x)$ was originally derived by Kirkwood and Riseman [1]. By defining the Fourier transforms

$$\hat{\phi}_v = \frac{1}{2} \int_{-1}^{1} dx \phi(x) e^{-i\pi vx}$$

we get from Eq. (106)

$$\hat{\phi}_v = \delta_{v,0} - h \sum_{\nu'} a_{\nu\nu'} \hat{\phi}_{\nu'}$$

where

$$a_{\nu\nu'} = \frac{1}{2} \int_{-1}^{1} dx \int_{-1}^{1} dy \frac{1}{|x-y|^{1/2}} e^{-i\pi vx + i\pi\nu'y}$$

For $\nu = 0 = \nu'$, we obtain

$$a_{00} = \frac{8\sqrt{2}}{3}$$

Although $a_{\nu\nu'}$ for $\nu \neq 0$ can be readily computed from Eq. (110), we use the Kirkwood–Riseman approximation of replacing $a_{\nu\nu'}$ by the values asymptotically valid for large $|\nu|$ and $|\nu'|$,

$$a_{\nu\nu'} \sim \begin{cases} \frac{8\sqrt{2}}{3} & \text{for } \nu = 0 = \nu' \\ \left( \frac{2}{|\nu|} \right)^{1/2} \delta_{\nu\nu'} & \text{for } \nu \neq 0 \end{cases}$$

It follows from Eqs. (103) and (108) that

$$\sum_i \langle \sigma_j \rangle = \zeta R^0 \sum_i \phi_i$$

$$= \zeta R^0 N \int_{-1}^{1} dx \phi(x)$$

$$= \zeta R^0 N \hat{\phi}_0$$

$$= \zeta \hat{\phi}_0$$
\( \hat{\phi}_0 \) is given by Eq. (110) as

\[
\hat{\phi}_0 = \frac{1}{1 + \frac{8\sqrt{2}}{3} \lambda}
\]

(115)

By combining Eqs. (98) and (114), the translational friction coefficient is given by

\[
f_t = \frac{\zeta N}{1 + \frac{8\sqrt{2}}{3} \lambda}
\]

(116)

\[
f_t = \frac{\zeta N}{1 + \frac{8\sqrt{2}}{3\eta_0} \left( \frac{\zeta \sqrt{N}}{(12\pi^3 N \ell_1)^{1/2}} \right)}
\]

(117)

In the free-draining limit of no hydrodynamic interactions, we have

\[
f_t = \zeta N
\]

(118)

When hydrodynamic interactions are present, we obtain

\[
f_t = \frac{3\eta_0}{8\sqrt{2}} \left( 12\pi^3 N \ell_1 \right)^{1/2}
\]

(119)

Recalling that \( \ell_1 / \ell \left( = \langle R^2 \rangle / N \ell^2 \right) \) is the expansion factor for the mean-square end-to-end distance and the radius of gyration \( R_g \) is \( \sqrt{\langle R^2 \rangle} / 6 \) within the uniform expansion approximation, we have

\[
f_t = \frac{9}{4} \pi^{3/2} \eta_0 R_g = \frac{3\sqrt{\pi}}{8} (6\pi \eta_0 R_g)
\]

(120)

\[
\sim \begin{cases} 
N, & \text{low salt} \\
N^{3/5}, & \text{high salt}
\end{cases}
\]

(121)

Although \( f_t \sim N \) in both the non-free-draining limit for low salt solutions and the free-draining limit, the terms appearing as prefactors are qualitatively different.

C. Electrophoretic Mobility

In this section we consider the motion of a uniformly charged flexible polyelectrolyte in an infinitely dilute solution under an externally imposed uniform electric field \( E \). The objective is to calculate the electrophoretic mobility \( \mu \) defined by

\[
R^0 = \mu E
\]

(122)
This is accomplished by balancing the total induced force on the polymer and the electrical force,

$$\sum_i \langle \sigma_i \rangle = QE$$  \hspace{1cm} (123)$$

where $Q = Nz_pe$, with $z_pe$ being the charge of each of the segments of the polymer molecule. The polymer chain is surrounded by $|Nz_p/z_c|$ counterions, each with a charge of $z_ce$. Let $\rho_i(r)$ be the charge density at $r$ due to the counterion surrounding the $i$th segment of the chain. The counterion charge density is related to the charge of the $i$th segment by the condition of electroneutrality,

$$z_pe = -\int d\mathbf{r} \rho_i(r)$$  \hspace{1cm} (124)$$

It follows from Eq. (16) that

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}_s(\mathbf{r}) + \sum_{i=0}^{N} \rho_i(\mathbf{r})\mathbf{E}$$  \hspace{1cm} (125)$$

In the equations below, we take the velocity field to be zero ($F_s = 0$), in the absence of the polymer. Substituting Eq. (125) in Eq. (43), we obtain

$$\mathbf{\sigma}_i = \zeta \left[ \mathbf{R}_i - \int d\mathbf{r}' \mathbf{G}(\mathbf{R}_i - \mathbf{r}') \cdot \sum_{i=0}^{N} \rho_i(\mathbf{r}')\mathbf{E} - \sum_{j \neq i} \mathbf{G}(\mathbf{R}_i - \mathbf{R}_j) \cdot \mathbf{\sigma}_j \right]$$  \hspace{1cm} (126)$$

By performing the average over chain configurations and using the preaveraging approximation, we get

$$\langle \sigma_i \rangle = \zeta \mathbf{R}^0 - \zeta \sum_{j=0}^{N} A_{ij} z_pe \mathbf{E} - \zeta \sum_{j \neq i} \langle \mathbf{G}(\mathbf{R}_i - \mathbf{R}_j) \rangle \langle \sigma_i \rangle$$  \hspace{1cm} (127)$$

where

$$A_{ij} z_pe = \left\langle \int d\mathbf{r}' \mathbf{G}(\mathbf{R}_i - \mathbf{r}') \cdot \rho_j(\mathbf{r}') \right\rangle$$  \hspace{1cm} (128)$$

When we use the Fourier representation of the Oseen tensor $\mathbf{G}$, $A_{ij}$ is given by

$$A_{ij} z_pe = \int d\mathbf{r}' \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{(1 - \hat{k}\hat{k})}{\eta_0 k^2} \langle e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{r}')} \rho_j(\mathbf{r}') \rangle$$  \hspace{1cm} (129)$$

$$= \int d\mathbf{r} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{(1 - \hat{k}\hat{k})}{\eta_0 k^2} \langle e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{r})} \rho_j(\mathbf{r}) \rangle$$  \hspace{1cm} (130)$$
where \( \mathbf{R} = \mathbf{R}_i - \mathbf{R}_j \) and \( \mathbf{r} = \mathbf{r}' - \mathbf{R}_j \). If we assume that \( \rho_j(\mathbf{r}) \) is radially symmetric, Eq. (130) becomes

\[
A_{ij} z_{pe} = \frac{2}{3 \eta_0} \left[ \int_0^R \, dr \, \frac{r^2}{R} \rho_j(r) + \int_R^\infty \, dr \, r \rho_j(r) \right]
\]

(131)

where

\[
\mathbf{R} = \mathbf{R}_i - \mathbf{R}_j \tag{132}
\]

The Poisson equation

\[
\rho_j(\mathbf{r}) = -\frac{\epsilon}{4\pi} \nabla^2 \psi_j(\mathbf{r})
\]

(133)

reduces to

\[
\rho_j(r) = -\frac{\epsilon}{4\pi} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \psi_j(r)}{dr} \right)
\]

(134)

\[
= -\frac{\epsilon}{4\pi} \frac{1}{r} \frac{d^2(r \psi_j(r))}{dr}
\]

(135)

for the radially symmetric \( \rho_j(\mathbf{r}) \), and \( \psi_j(r) \) is the electrostatic potential from the \( j \)th segment of charge \( z_{pe} \). The first integral in Eq. (131) simplifies to

\[
\frac{1}{R} \int_0^R \, dr \, r^2 \rho_j(r) = -\frac{\epsilon}{4\pi R} \int_0^R \, dr \frac{1}{dr} \left( r^2 \frac{d \psi_j(r)}{dr} \right)
\]

(136)

\[
= -\frac{\epsilon}{4\pi} \frac{d \psi_j(r)}{dr} \bigg|_R + \frac{\epsilon}{4\pi R} a^2 \frac{d \psi_j(r)}{dr} \bigg|_a
\]

(137)

where \( a \) is the effective radius of the polymer segment. However, by the condition of electroneutrality, we have

\[
-z_{pe} = \int d\mathbf{r} \rho_j(\mathbf{r})
\]

(138)

\[
= 4\pi \int_a^\infty \, dr \, r^2 \rho_j(r)
\]

(139)

\[
= \epsilon a^2 \frac{d \psi_j}{dr} \bigg|_a
\]

(140)
because the potential vanishes at $r \to \infty$. Combining Eqs. (137) and (140), we obtain

$$\frac{1}{R} \int_0^R dr \, r^2 \rho_j(r) = -\frac{\epsilon}{4\pi} R \left. \frac{d\psi_j}{dr} \right|_R - \frac{z_p e}{4\pi R}$$  \hspace{1cm} (141)

The second integral in Eq. (131) similarly simplifies to

$$\int_R^\infty dr \, r \rho_j(r) = -\frac{\epsilon}{4\pi} \int_R^\infty \frac{d^2(r\psi_j)}{dr^2} \Big|_R$$

$$= -\frac{\epsilon}{4\pi} \left. \frac{d(r\psi_j)}{dr} \right|_R$$

$$= \frac{\epsilon}{4\pi} \left. \frac{d\psi_j}{dr} \right|_R$$

$$= \frac{\epsilon}{4\pi} R \left. \frac{d\psi_j}{dr} \right|_R + \frac{\epsilon}{4\pi} \psi_j(R)$$  \hspace{1cm} (142)

By combining Eqs. (141) and (142), we get

$$A_{ij} z_p e = \left\langle \frac{2}{3 \eta_0} \left[ -\frac{z_p e}{4\pi R} + \frac{\epsilon}{4\pi} \psi_j(R) \right] \right\rangle$$  \hspace{1cm} (143)

Here $R$ is actually $|\mathbf{R}_i - \mathbf{R}_j|$. We take the potential $\psi_j$ as the Debye–Hückel potential,

$$\psi_j(R) = \frac{e z_p e^{-\kappa R}}{R}$$  \hspace{1cm} (144)

Therefore $A_{ij}$ becomes

$$A_{ij} = \frac{1}{6\pi \eta_0} \left\langle \left[ -\frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{e^{-\kappa |\mathbf{R}_i - \mathbf{R}_j|}}{|\mathbf{R}_i - \mathbf{R}_j|} \right] \right\rangle$$  \hspace{1cm} (145)

which is a function of $|i - j|$. We now repeat the calculation of the translational friction coefficient with the additional term ($A_{ij}$) to derive the desired expression for the electrophoretic mobility. Defining $\sum_j \langle \sigma_i \rangle$ as in Eq. (103) in terms of $\phi_i$ and going to the continuous variables for $i$ and $j$, we obtain from Eq. (127)

$$\zeta \mathbf{R}^0 \phi(x) = \zeta \mathbf{R}^0 - \frac{\zeta N}{2} z_p e \mathbf{E} \int_{-1}^1 dy A(x, y) - h \zeta \mathbf{R}^0 \int_{-1}^1 dy \frac{1}{|x - y|^{1/2}} \phi(y)$$  \hspace{1cm} (146)
Analogous to the Fourier transforms of Eq. (108), we expand $A(x,y)$ as

$$ A(x,y) = \sum_v \sum_v \hat{A}_{vv} e^{i\nu x - i\nu' y} $$

(147)

$$ \hat{A}_{vv} = \frac{1}{4} \int_{-1}^{1} dx \int_{-1}^{1} dy A(x,y) e^{-i\nu x - i\nu' y} $$

(148)

In terms of the Fourier transforms, Eq. (146) becomes

$$ \zeta \dot{\mathbf{R}}_0 \dot{\phi}_v = \zeta \mathbf{R}_0 - \zeta N z_p e \mathbf{E} \dot{A}_{vv} - h \zeta \mathbf{R}_0 \sum_v a_{vv} \dot{\phi}_v $$

(149)

The total hydrodynamic frictional force $\sum_i \langle \sigma_i \rangle$ is given by

$$ \sum_i \langle \sigma_i \rangle = \frac{N}{2} \int_{-1}^{1} dx \zeta \dot{\mathbf{R}}_0 \dot{\phi}(x) $$

(150)

$$ = N \zeta \mathbf{R}_0 \dot{\phi}_0 $$

(151)

By invoking the Kirkwood–Riseman approximation of diagonality in $a_{vv}$, we obtain

$$ \left(1 + \frac{8\sqrt{2}}{3} h \right) \phi_0 \zeta \mathbf{R}_0 = \zeta \mathbf{R}_0 - \zeta N z_p e \dot{A}_{00} \mathbf{E} $$

(152)

so that

$$ \zeta \mathbf{R}_0 \dot{\phi}_0 = \frac{\zeta \mathbf{R}_0}{\left(1 + \frac{8\sqrt{2}}{3} h \right)} - \frac{\zeta \dot{A}_{00} \mathbf{E}}{\left(1 + \frac{8\sqrt{2}}{3} h \right)} $$

(153)

Inserting this expression in Eq. (123), we obtain

$$ Q \mathbf{E} \left[1 + \frac{N \zeta \dot{A}_{00}}{\left(1 + \frac{8\sqrt{2}}{3} h \right)} \right] = \frac{N \zeta \mathbf{R}_0}{\left(1 + \frac{8\sqrt{2}}{3} h \right)} $$

(154)

providing the electrophoretic mobility as

$$ \mu = Q \left[ \frac{\left(1 + \frac{8\sqrt{2}}{3} h \right)}{\zeta N} + \dot{A}_{00} \right] $$

(155)

$$ = Q \left( \frac{1}{f_t} + \dot{A}_{00} \right) $$

(156)
where \( f_t \) is the translational friction coefficient of the chain. \( \hat{A}_{00} \) is the contribution from the counterion cloud. If this contribution is ignored, then the result is equivalent to the balancing of frictional force \( f_t \) and the electrical force \( Q \). However \( \hat{A}_{00} \) plays a crucial role in determining the electrophoretic mobility. \( \hat{A}_{00} \) is given by Eqs. (145) and (148) as

\[
\hat{A}_{00} = \frac{1}{4} \int_{-1}^{1} dx \int_{-1}^{1} dy A(x, y) 
\]

\[
= \frac{1}{6\pi\eta_0} \int_{0}^{L} ds \int_{0}^{L} ds' \left\langle \left[ \frac{1}{|R(s) - R(s')|} + e^{-\kappa|R(s) - R(s')|} \right] \rightangle \quad (157)
\]

Since the first term is the negative of the second term with \( \kappa = 0 \), we rewrite \( \hat{A}_{00} \) as

\[
\hat{A}_{00} = B(\kappa) - B(0) 
\]

where

\[
B = \frac{1}{6\pi\eta_0 L^2} \int_{0}^{L} ds \int_{0}^{L} ds' \left\langle \frac{e^{-\kappa|R(s) - R(s')|}}{|R(s) - R(s')|} \right\rangle
\]

\[
= \frac{1}{6\pi\eta_0 L^2} \int_{0}^{L} ds \int_{0}^{L} ds' \left( \frac{d\mathbf{k}}{2\pi^3 k^2 + \kappa^2} \right) e^{i\mathbf{k} \cdot (R(s) - R(s'))} \quad (158)
\]

where \( S(k) \) is the static structure factor of the polyelectrolyte chain. For a Gaussian chain, \( S(k) \) is the Debye structure factor,

\[
S_D(k) = \frac{2N}{k^4} \left( e^{-k^2 R_{g0}^2} - 1 + k^2 R_{g0}^2 \right) 
\]

where \( R_{g0}^2 = L \ell / 6 \). Substituting this result in Eq. (160) yields

\[
B(\kappa) = \frac{1}{6\pi\eta_0 \kappa R_{g0}^2} \left[ 1 - \frac{2}{\sqrt{\pi} R_{g0}} + \frac{1}{\kappa^2 R_{g0}^2} \left( 1 - e^{-k^2 R_{g0}^2} \text{erfc}(\kappa R_{g0}) \right) \right] 
\]

The \( \kappa \to 0 \) result is exactly the same as the result in Eq. (102).
For a polyelectrolyte chain that has non-Gaussian statistics, exact analytical expression for $B$ is not feasible. To get some insight, we notice that the static structure factor has the limiting behavior,

$$S(k) = \left\{ \begin{array}{l} N \left(1 - \frac{k^2 R_g^2}{2} + \cdots \right), \quad \kappa R_g \ll 1 \\ \sim \frac{1}{(k \ell)^{1/\nu}}, \quad \kappa R_g \gg 1 \end{array} \right.$$  \hspace{1cm} (163)

Therefore we construct an approximate interpolation for $S(k)$ as

$$S(k) = \frac{N}{\left(1 + \frac{2\nu}{3} k^2 R_g^2\right)^{1/2}}$$  \hspace{1cm} (164)

Substituting this expression for $S(k)$, Eq. (160) yields

$$B = \frac{1}{3\pi^2 \eta_0} \int_0^\infty dk \frac{k^2}{k^2 + \kappa^2} \frac{1}{\left(1 + \frac{2\nu}{3} k^2 R_g^2\right)^{1/2}}$$  \hspace{1cm} (165)

$$\sim \left\{ \begin{array}{l} \frac{1}{\eta R_g}, \quad \kappa \to 0 \\ \frac{1}{\eta R_g^{1/\nu} \kappa^{1/\nu - 1}}, \quad \kappa R_g \gg 1 \end{array} \right.$$  \hspace{1cm} (166)

This result reduces to Eq. (162) for Gaussian chains.

For $\kappa \to 0$, it follows from Eq. (159) that $A_{00} = 0$, so that

$$\mu = \frac{Q}{f_t}$$  \hspace{1cm} (167)

Since $f_t \sim R_g \sim N$ for $\kappa \to 0$, and $Q = N z_p e$,

$$\mu \sim N^0$$  \hspace{1cm} (168)

For $\kappa R_g \gg 1$, we get from Eqs. (156) and (166),

$$\mu = \frac{Q}{N} \left[ \frac{1}{\zeta} + \frac{\beta}{\eta_0 \ell \zeta^{1/\nu - 1}} \right]$$  \hspace{1cm} (169)

where $\beta$ is a known numerical coefficient [50]. Since $Q = N z_p e$, $\mu$ is independent of $N$ in the high salt limit also. Furthermore, since $\nu \simeq 3/5$ for high salt solutions, we expect

$$\mu \sim \frac{1}{\eta_0 \kappa^{2/3}}$$  \hspace{1cm} (170)

when hydrodynamic interaction dominates.
Summarizing, the electrophoretic mobility of a flexible polyelectrolyte chain in infinitely dilute solutions is given by Eq. (156):

\[
\mu = Q \left( \frac{1}{f_t} + \hat{A}_{00} \right)
\]

(171)

where the first and second terms are due to hydrodynamic interactions of polymer segments with other segments and counterion cloud, respectively. For \( \kappa = 0 \), \( \hat{A}_{00} \) is identically zero so that

\[
\mu = \frac{Q}{f_t} \sim \frac{N^0}{\eta_0}
\]

(172)

For \( \kappa \neq 0 \), a part of \( \hat{A}_{00} \) cancels \( 1/f_t \) exactly in the non-free-draining limit and the remainder is dependent on the structure factor of the polymer and the size exponent \( \nu \). For large values of \( \kappa R_g \), \( \mu \) becomes

\[
\mu \sim \frac{N^0}{\eta_0 \kappa^{\nu-1}}, \kappa R_g \gg 1
\]

(173)

While \( \mu \) is independent of \( N \) at all salt concentrations, it decreases with the salt concentration with an apparent power law,

\[
\mu \sim N^0 \kappa^{-\alpha}
\]

(174)

where \( \alpha \) changes smoothly from zero at low salt concentrations to 2/3 at high salt concentrations. In reaching these conclusions the role of hydrophobic effect is ignored.

D. Coupled Diffusion Coefficient

As seen in the preceding section, the counterions play a crucial role in the mobility of the polyelectrolyte molecules. Even in the absence of an external electric field, the counterions exert an induced electric field in the immediate environment of a charged segment which in turn significantly modifies the collective diffusion coefficient of the polymer. This additional contribution is absent for uncharged polymers, where the cooperative diffusion coefficient \( D_c \) is given by the Stokes–Einstein law in dilute solutions,

\[
D_c = \frac{k_BT}{f_t}
\]

(175)

We discuss below how this law is modified by counterions for the case of polyelectrolyte solutions.
The local concentration of the polyelectrolyte molecules, in number of chains per unit volume, as defined by

\[ c(r, t) = \sum_{x=1}^{n} \delta(r - R_x^{0}(t)) \]  \hspace{1cm} (176)

obeys the continuity equation

\[ \frac{\partial c(r, t)}{\partial t} = -\nabla \cdot J \]  \hspace{1cm} (177)

where the flux is given by

\[ J = -D_c \nabla c(r, t) + c(r, t)\mu E_{\text{ind}} \]  \hspace{1cm} (178)

Here the first term is the usual diffusive current, with \( D_c \) being the usual cooperative diffusion constant of the polymer molecule. The second term is a convective current due to the presence of induced electric field arising from all charged species in the system. \( \mu \) is the electrophoretic mobility of the polymer molecule derived in the preceding section. From the Poisson equation, we obtain

\[ \nabla \cdot E_{\text{ind}} = \frac{4\pi}{\epsilon} \sum_{\beta} z_{\beta} c_{\beta}. \]  \hspace{1cm} (179)

Focusing on the polyelectrolyte and the counterions by ignoring temporarily the presence of salt ions, we get

\[ \nabla \cdot E_{\text{ind}} = \frac{4\pi}{\epsilon} [Qc(r, t) + z_c \rho_c(r, t)] \]  \hspace{1cm} (180)

where \( Q \) is the polymer charge and \( \rho_c \) is the local concentration of counterions. It is evident from Eqs. (177)–(180) that the polymer concentration is coupled to the counterion concentration. Analogous to the continuity equation for the polymer concentration, the continuity equation for the counterion concentration is

\[ \frac{\partial \rho_c(r, t)}{\partial t} = D' \nabla^2 \rho_c(r, t) - \rho_c(r, t)\mu_c \nabla \cdot E_{\text{ind}} \]  \hspace{1cm} (181)

where \( D' \) and \( \mu_c \) are, respectively, the cooperative diffusion coefficient and electrophoretic mobility of the counterion, given by

\[ D' = \frac{k_BT}{f_c} \]  \hspace{1cm} (182)

\[ \mu_c = \frac{z_c}{f_c} = \frac{z_c D'}{k_BT} \]  \hspace{1cm} (183)
where $f_\epsilon$ is the translational friction coefficient of the counterion. Defining the fluctuations in polymer concentration and counterion concentration,

\[ c(\mathbf{r}, t) = \bar{c} + \delta c(\mathbf{r}, t) \quad (184) \]
\[ \rho_c(\mathbf{r}, t) = \bar{\rho}_c + \delta \rho_c(\mathbf{r}, t) \quad (185) \]

where $\bar{c}$ and $\bar{\rho}_c$ are, respectively, the average concentrations of the polymer and counterions, and performing Fourier transforms, we get

\[ \frac{\partial \delta c_k}{\partial t} = -D_c k^2 \delta c_k - \frac{4\pi}{\epsilon} \bar{c} \mu (Q \delta c_k + z_c \delta \rho_{c,k}) \quad (186) \]
\[ \frac{\partial \delta \rho_{c,k}}{\partial t} = -D' k^2 \delta \rho_{c,k} - \frac{4\pi}{\epsilon} \bar{\rho}_c \mu_c (Q \delta c_k + z_c \delta \rho_{c,k}) \quad (187) \]

If we define

\[ \kappa_c^2 = \frac{4\pi}{\epsilon k_B T} z_c^2 \bar{\rho}_c \quad (188) \]

and make the assumption that the relaxation of the counterions is much faster than that of the polymer, Eq. (187) simplifies to

\[ \delta \rho_{c,k} = -\frac{\kappa_c^2}{k^2 + \kappa_c^2} Q \delta c_k. \quad (189) \]

Therefore the terms in the parentheses of Eq. (186) reduce to

\[ Q \delta c_k + z_c \delta \rho_{c,k} = \frac{k^2}{(k^2 + \kappa_c^2)} Q \delta c_k \quad (190) \]

Substituting this result in Eq. (186), we obtain

\[ \frac{\partial \delta c_k}{\partial t} = - \left[ D_c + \frac{4\pi}{\epsilon} \frac{\bar{c} \mu Q}{(k^2 + \kappa_c^2)} \right] \delta c_k \quad (191) \]

Therefore, we can write the equation for the time evolution of fluctuations of polymer concentrations as

\[ \frac{\partial \delta c_k}{\partial t} = -D_f \delta c_k \quad (192) \]
where $D_f$ is the effective diffusion constant. Let us call $D_f$ as the coupled diffusion coefficient to contrast with the cooperative diffusion coefficient $D_c$. In general, $D_f$ depends on $k$.

$$D_f = D_c + \frac{4\pi \bar{\epsilon} \mu Q}{\epsilon (k^2 + \kappa_c^2)}$$  \hspace{1cm} (193)$$

In the limit of $k \rightarrow 0$, we get

$$D_f = D_c + \frac{4\pi \bar{\epsilon} \mu Q}{\epsilon \kappa_c^2}$$  \hspace{1cm} (194)$$

Noticing that the average counterion concentration is $N\bar{c}$ for fully ionized polyelectrolytes, we obtain

$$\kappa_c^2 = \frac{4\pi}{\epsilon k_B T} \frac{\bar{c}^2 N\bar{c}}{z_c}$$  \hspace{1cm} (195)$$

In addition, by recognizing that (for salt-free case)

$$\mu = \frac{QD_c}{k_B T}$$  \hspace{1cm} (196)$$

the coupled diffusion coefficient in dilute solutions becomes

$$D_f = D_c \left[ 1 + \frac{1}{N} \left(\frac{Q}{z_c}\right)^2 \right]$$  \hspace{1cm} (197)$$

For monovalent ions, $|z_p| = 1 = |z_c|$, we have

$$D_f = D_c (1 + N)$$  \hspace{1cm} (198)$$

Therefore, the coupling of polymer segments to the counterion cloud, which is directly responsible for the term $N$ in the above equation, dominates the collective diffusion coefficient. Since $R_g \sim N$ for salt-free solutions, $D_f$ is independent of $N$.

The above derivation can readily be extended [50] to the presence of salt ions. The formula is the same as Eq. (194) except that $\kappa_c^2$ includes terms from the dissociated salt ions and becomes the reciprocal of the square of the Debye length, and $\mu$ is now given by Eq. (156).
E. Viscosity

We now consider how the polymer dynamics in turn modifies the viscosity of the solution. Recalling from Eq. (41) that the no-slip boundary condition gives an expression for the velocity of the \(i\)th segment in terms of the induced forces, \(\sigma_i\), we obtain

\[
\dot{R}_i = \int dr' G(R_i - r') \cdot F(r') + \sum_{j=0}^{N} G(R_i - R_j) \cdot \sigma_j
\]  

(199)

Since intersegment hydrodynamic interaction dominates the friction coefficient, we ignore the \(i = j\) part that leads to the free-draining contribution. If we define the inverse propagator \(G^{-1}\) according to

\[
\sum_p G^{-1}(R_i - R_p) \cdot G(R_p - R_j) = \delta_{ij}
\]  

(200)

then \(\sigma_i\) is given formally by

\[
\sigma_i = \sum_j G^{-1}(R_i - R_j) \cdot \left[ \dot{R}_j - \int dr' G(R_j - r') \cdot F(r') \right]
\]  

(201)

Summing over \(i\) and taking the average over chain configurations, we get

\[
\sum_i \langle \sigma_i \rangle = \sum_i \sum_j \left\langle G^{-1}(R_i - R_j) \cdot \left[ \dot{R}_j - \int dr' G(R_j - r') \cdot F(r') \right] \right\rangle
\]  

(202)

Upon preaveraging, this reduces to

\[
\sum_i \langle \sigma_i \rangle = f_i \langle \dot{R}^0 \rangle - \int dr' G(R_j - r') \cdot F(r')
\]  

(203)

where

\[
f_i = \frac{3}{8\sqrt{2}} \frac{\zeta N}{h}
\]

\[
= \frac{3\sqrt{\pi}}{8} (6\pi \eta_0 R_g)
\]  

(204)
By iterating the elimination of the microscopic velocity of the \( j \)th segment in Eq. (201), we get

\[
\sum_i \delta(\mathbf{r} - \mathbf{R}_i) \sigma_i = -\int d\mathbf{r}' \left[ \delta(\mathbf{r} - \mathbf{R}_i) \mathbf{G}^{-1}(\mathbf{R}_i - \mathbf{R}_j) \delta(\mathbf{r}' - \mathbf{R}_j) \right] \\
\int d\mathbf{r}'' \mathbf{G}(\mathbf{r}' - \mathbf{r}'') \cdot \mathbf{F}(\mathbf{r}'') + \cdots \quad (205)
\]

Substituting this result in Eq. (31) and performing the average over chain configurations as in Eq. (33), we obtain

\[
\Sigma(\mathbf{r} - \mathbf{r}') = \left\langle \sum_i \sum_j \delta(\mathbf{r} - \mathbf{R}_i) \mathbf{G}^{-1}(\mathbf{R}_i - \mathbf{R}_j) \delta(\mathbf{r}' - \mathbf{R}_j) \right\rangle \quad (206)
\]

The Fourier transform of \( \Sigma(\mathbf{r} - \mathbf{r}') \) becomes

\[
\Sigma(\mathbf{k}) = \frac{n}{V} \int_0^L ds \int_0^L ds' \left\langle e^{i\mathbf{k} \cdot [\mathbf{R}(s) - \mathbf{R}(s')]} \mathbf{G}^{-1} [\mathbf{R}(s) - \mathbf{R}(s')] \right\rangle \quad (207)
\]

Using the Rouse mode variable \( q \) and employing the preaveraging approximation, we obtain

\[
\Sigma(\mathbf{k}) = \frac{c \ell}{\pi} \int_{2\pi/L}^{\infty} dq \, S(k, q) \mathbf{G}^{-1}(q) \quad (208)
\]

where \( c \) is the segment number density and

\[
S(k, q) = \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds' e^{iq(s-s')} \left\langle e^{i\mathbf{k} \cdot [\mathbf{R}(s) - \mathbf{R}(s')]} \right\rangle \quad (209)
\]

and

\[
G(q) = \frac{2}{3} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{1}{\eta_0 k^2} S(k, q) \quad (210)
\]

Assuming that the chain statistics is an effective Gaussian with the uniform expansion coefficient \( \ell_1 \), we obtain

\[
S(k, q) = \frac{(k^2 \ell_1)/3}{\left( \frac{k^2 \ell_1}{\eta_0} \right)^2 + q^2} \quad (211)
\]
Substituting this result in Eq. (210), we get

\[ G(q) = \frac{1}{\pi \eta_0} \frac{1}{(3 \ell_1 q)^{1/2}} \]  

(212)

When we combine Eqs. (208) and (212), \( \Sigma(k) \) becomes

\[ \Sigma(k) = \frac{c \ell_1 \eta_0}{\sqrt{3}} \int_{q^2}^{\infty} dq \frac{k^2 \ell_1}{\left[ \left( \frac{k^2 \ell_1}{6} \right)^2 + q^2 \right]} \sqrt{\ell_1 q} \]  

(213)

The change in viscosity therefore follows from Eq. (38) as

\[ \eta - \eta_0 = \lim_{\kappa \to 0} \frac{\Sigma(k)}{k^2} = \frac{c \ell_1 \eta_0}{3 \sqrt{3}} \int_{q^2}^{\infty} dq \left( \frac{\ell_1}{q} \right)^{3/2} \]  

(214)

Since \( \ell_1 \sim q^{1-2\nu} \), the intrinsic viscosity \([\eta]\) becomes

\[ [\eta] = \frac{\eta - \eta_0}{\eta_0 c} \sim L^{3\nu - 1} \]  

(215)

If we suppress the mode dependence of \( \ell_1 \) and consider only its lowest mode value \( \sim L^{2\nu - 1} \), then the intrinsic viscosity is given by

\[ [\eta] = \sqrt{\frac{2}{3\pi}} \ell_1^{3/2} L^{1/2} \]  

(216)

where \( \ell_1 / \ell \) is the expansion factor for the mean-square end-to-end distance of the chain.

### IV. SEMIDILUTE SOLUTIONS

The key ingredients in calculating the various dynamical properties of semidilute solutions are the effective Oseen tensor \( \mathcal{G} \) and \( \Sigma \), which contains all contributions from the chains. These quantities are calculated [50] using the effective medium approximation for interchain interactions, which is consistent with the nature of approximations utilized in obtaining the dilute solution properties. Under the effective medium theory, \( \sigma(k) \) is calculated self-consistently by assuming that \( \Sigma(k) \) arising from all of \( n \) polyelectrolyte chains is \( n \) times the contribution from one chain with an effective hydrodynamic interaction \( \mathcal{G} \), which is a functional of \( \Sigma(k) \). The details of this procedure are provided in Refs. 55–59; only the final result is given here. \( \Sigma(k) \) is given as a sum over the various Rouse modes.
\[ q = 2\pi p/L, \text{ with } p \text{ being the Rouse mode index and } L \text{ being the chain contour length}, \]

\[
\Sigma(k) = \frac{1}{\pi N} \int_{2\pi/L}^{\infty} dq S(k, q) G^{-1}(q) \quad (217)
\]

\[
G(q) = \int \frac{d\mathbf{j}}{(2\pi)^3} \frac{(1 - iyj_j)}{[\mathbf{\eta}_0 j^2 + \Sigma(j)]} S(\mathbf{j}, q) \quad (218)
\]

\[
S(k, q) = \int_{-\infty}^{\infty} d(s - s') e^{iq(s - s')} \langle \exp(\mathbf{i}k \cdot [\mathbf{R}(s) - \mathbf{R}(s')]) \rangle \quad (219)
\]

\( S(k, q) \) is the Fourier transform of the static structure factor.

In obtaining Eqs. (217)–(219), we have employed the preaveraging approximation and assumed that solvent motion is instantaneous in comparison to the motion of polyelectrolytes. For a solution of polyelectrolytes, the effective medium theory for the equilibrium properties gives

\[
\langle \exp(\mathbf{i}k \cdot [\mathbf{R}(s) - \mathbf{R}(s')]) \rangle \simeq \exp(-k^2 l_1 |s - s'|/6) \quad (220)
\]

where \( l_1/l \) is the square of the expansion factor for the mean-square end-to-end distance of a labeled polyelectrolyte chain

\[
\langle [R(L) - R(0)]^2 \rangle \equiv LI_1 \quad (221)
\]

\( l_1 \) is a complicated function [48] of \( c, L, \kappa, w, \) and \( z_p^2 l_B \). The asymptotic behavior of \( l_1 \) in the various limits is summarized in Table I. Equivalently, the polyelectrolyte chains can be described with bare Kuhn length but with an effective interaction \( \Delta \). Explicit formula for \( \Delta \) is derived in Ref. 48. Its Fourier transform is of the form

\[
\Delta_k = \frac{V_k}{\left(1 + e^{V_k/k_1^2}\right)} \quad (222)
\]

where \( \lambda_k \) is a functional of \( \Delta_k \) and \( l_1 \), and \( V_k \) is the Fourier transform of \( V \) in Eq. (24). In the high salt limit, \( \Delta_k \) becomes

\[
\Delta_k = \left(w + \frac{w_c}{k^2}\right)k^2\xi^2/(1 + k^2\xi^2) \quad (223)
\]

where \( \xi^2 = \lambda^2/c\left(w + \frac{w_c}{k^2}\right) \) and \( w_c = 4\pi z_p^2 e^2/\epsilon k_BT \). In the low salt limit, \( \Delta_k \)
The Dependencies of Radius of Gyration $R_g$, Static Correlation Length $\xi$, Hydrodynamic Screening Length $\xi_H$, Viscosity $\eta$, Self-Translational Diffusion Coefficient $D$, Cooperative Diffusion Coefficient $D_c$, Coupled Diffusion Coefficient $D_f$, and Electrophoretic Mobility $\mu$ on $c$ and $N$ for Various Regimes of Polyelectrolyte and Salt Concentrations

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Salt Level</th>
<th>Dilute (Zimm)</th>
<th>Semidilute (Rouse)</th>
<th>Concentrated (Entangled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{6\pi\eta}{L} = l_i$</td>
<td>High</td>
<td>$\left(\frac{4\pi\eta}{2}\right)^{2/3} N^{1/5}l$</td>
<td>$(w + \frac{4\pi\eta}{k^{3/4}})^{1/4}c^{-1/4}l^{3/2}$</td>
<td>$I$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$\frac{\sqrt{3}}{\pi} \left( \frac{6\pi}{3} \right)^{2/3} \left( \frac{4\pi\eta}{k^{3/4}} \right)^{1/6}c^{-1/2}l^{-1/2}$</td>
<td>$I$</td>
<td></td>
</tr>
<tr>
<td>$\xi$</td>
<td>High</td>
<td>$R_g \sim N^{-3/5}$</td>
<td>$\frac{3}{4\pi^{1/2}} \left( w + \frac{4\pi\eta}{k^{3/4}} \right)^{-1/4}c^{-3/4}l^{-1/2}$</td>
<td>$l\left[6c\left(w + \frac{4\pi\eta}{k^{3/4}}\right)^{-3/4}l^{-1/2}\right]$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$R_g \sim N$</td>
<td>$\left( \frac{6\pi^{3/2}}{3} \right)^{1/3} \left( \frac{4\pi\eta}{c^{3/4}} \right)^{-1/6} \left( cl \right)^{-1/2}$</td>
<td>$(\frac{3\pi^{1/4}l^{3/4}}{k^{3/4}})^{-1/4}$</td>
</tr>
<tr>
<td>$\xi_H$</td>
<td>High</td>
<td>$\infty$</td>
<td>$\frac{8}{\sqrt{3}\pi} \left( \frac{\pi}{6\pi^{1/2}} \right)^{2/3} \left( \frac{4\pi\eta}{c^{3/4}} \right)^{-1/6} \left( cl \right)^{-1/2}$</td>
<td>$c^{-1/2}$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$\infty$</td>
<td>$\frac{8}{\sqrt{3}\pi} \left( \frac{\pi}{6\pi^{1/2}} \right)^{2/3} \left( \frac{4\pi\eta}{c^{3/4}} \right)^{-1/6} \left( cl \right)^{-1/2}$</td>
<td>$c^{-1/2}$</td>
</tr>
<tr>
<td>$\frac{\eta - \eta_0}{\eta_0}$</td>
<td>High</td>
<td>$c\left(w + \frac{4\pi\eta}{k^{3/4}}\right)^{3/5}l^{5/4}N^{4/5}$</td>
<td>$\frac{1}{17} \left( \frac{c^{3/4}l}{c^{3/4}N} \right)^{1/2}L \sim c^{5/4}N$</td>
<td>$c^{4.25}N^{3.4}$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$cl f b^2N^2$</td>
<td>$\frac{1}{17} \left( \frac{c^{3/4}l}{c^{3/4}N} \right)^{1/2}L \sim \sqrt{c}N$</td>
<td>$c^{1.7}N^{3.4}$</td>
</tr>
<tr>
<td>$D$</td>
<td>High</td>
<td>$\frac{8}{\sqrt{3}\pi} \frac{k_B T}{\eta_0 l_i f b} \sim N^{-3/5}$</td>
<td>$\frac{k_B T}{\eta_0 l_i f b} \sim \frac{1}{N^{1/2}c}$</td>
<td>$c^{-7/5}N^{-2}$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$\frac{8}{\sqrt{3}\pi} \frac{k_B T}{\eta_0 l_i f b} \sim N^{-1}$</td>
<td>$\frac{k_B T}{\eta_0 l_i f b} \sim c^{0}N^{-1}$</td>
<td>$c^{-1/2}N^{-2}$</td>
</tr>
<tr>
<td>$D_c$</td>
<td>High</td>
<td>$D$</td>
<td>$\frac{k_B T}{\eta_0 l_i f b} \sim c^{3/4}N^{1/2}$</td>
<td>$c^{3/4}N^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$D$</td>
<td>$\frac{k_B T}{\eta_0 l_i f b} \sim c^{1/2}N^{1/2}$</td>
<td>$c^{1/2}N^{1/2}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>High</td>
<td>$\frac{N^0}{\eta_0 k^{3/4}}$</td>
<td>$\frac{Q D}{k_B T} \sim N^0 e^{-c^{-1/2}}$</td>
<td>$N^0 e^{-c^{-1/2}}$</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$\frac{N^0}{\eta_0}$</td>
<td>$\frac{Q D}{k_B T} \sim N^0 e^{0}$</td>
<td>$N^0 e^{0}$</td>
</tr>
<tr>
<td>$D_f$</td>
<td>High</td>
<td>$N^{-3/5}\left(1 + \frac{\xi_H}{c^{1/2}N^{0.17}}\right)$</td>
<td>$\frac{4\pi\eta_0 q c^{3/2}}{k^2c^{1/2}} \sim \sqrt{c}e^{-c^{1/2}}$</td>
<td>$\Delta_k = w_c k^{2}2^{-4}/(1 + k^{4}2^{-4})$ (224)</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>$N^{0}$</td>
<td>$\frac{4\pi\eta_0 q c^{3/2}}{k^2c^{1/2}} \sim N^0 e^{0}$</td>
<td>$\Delta_k = w_c k^{2}2^{-4}/(1 + k^{4}2^{-4})$ (224)</td>
</tr>
</tbody>
</table>

where $\xi^{-4} = w_c c/\lambda^2$. The scattering function $g(k)$ per segment ($S(k, q = 0)$) is related to $\Delta_k$ through the relation

$$g(k) = \frac{1}{cV_k} \left(1 - \frac{\Delta_k}{V_k}\right)$$(225)
Due to Eqs. (222)–(225), \( g(k) \) becomes in the high salt limit,

\[
g(k) = \frac{1}{(w + \frac{w}{k^2})c\xi^2 (k^2 + \xi^{-2})}
\]

(226)

and in the low salt limit,

\[
g(k) = \frac{k^2}{cw\xi^4 (k^4 + \xi^{-4})}
\]

(227)

In infinitely dilute solutions, \( l_1 \) is proportional to \( N \) and \( N^{1/5} \), and consequently the radius of gyration \( R_g \) is proportional to \( N \) and \( N^2 \), respectively, in low-salt (\( \kappa \simeq 0 \)) and high salt (\( \kappa R_g \gg 1 \)) limits as already pointed out. In semidilute solutions, \( l_1 \) is proportional to \( c^{-1/2} \) and \( c^{-1/4} \), and consequently \( R_g \) is proportional to \( c^{-1/4} \) and \( c^{-1/8} \), respectively, in low salt and high salt limits. As shown in Ref. 48, \( l_1 \) is intimately related to the static correlation length \( \xi \). In infinitely dilute solutions \( \xi \) is proportional to \( R_g \). In semidilute solutions, \( \xi \) is proportional to \( c^{-1/2} \) and \( c^{-3/4} \), respectively, in low and high salt limits. In concentrated solutions, \( \xi \) is proportional to \( c^{-1/4} \) and \( c^{-1/2} \), respectively, in low salt and high salt limits. All of these equilibrium results have been experimentally verified [52–54]. The hydrodynamic interaction \( G \) is given by Eq. (35),

\[
G(k) = \frac{1}{\eta_0 k^2 + \Sigma(k)}
\]

(28)

where \( \Sigma(k) \) is to be solved self-consistently according to

\[
\Sigma(k) = \frac{cl}{\pi} \int_{2\pi/L}^\infty dq \frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2 J(q)}
\]

(229)

\[
G(q) = \frac{1}{3\pi^2} \int_0^\infty dj \frac{j^2}{(\eta_0 j^2 + \Sigma(j))} \frac{j^2 l_1/3}{(j^2 l_1/6)^2 + q^2}
\]

(230)

In the limit of \( k \to 0 \), \( \Sigma(k) \) is proportional to \( k^2 \), as expected. On the other hand for \( \frac{1}{R_g} < k < \frac{1}{l_1} \), we expect the bare hydrodynamic interaction to be screened. Therefore we look for a solution of \( \Sigma \) from Eq. (229) so that \( \Sigma \) is independent of \( k \) to entail hydrodynamic screening. When large \( k \) behavior dominates the integrals in Eq. (229), \( \Sigma \) can be written as

\[
\Sigma(k) = \eta_0 \xi_H^{-2}
\]

(231)
so that $\mathcal{G}$ is screened hydrodynamic interaction

$$
\mathcal{G}(k) = \frac{1}{\eta_0 (k^2 + \xi_H^{-2})} \tag{232}
$$

where $\xi_H$ is the hydrodynamic screening length. It follows from Eq. (230) that

$$
G(q) = \frac{2\xi_H}{\pi \eta_0 l_1} \tag{233}
$$

and

$$
\xi_H^{-1} = \frac{\pi}{2} c l l_1 \tag{234}
$$

In view of the dependence of $l_1$ on $c$ as given in Table I, the hydrodynamic screening length has the following concentration dependence

$$
\xi_H = \begin{cases}
\frac{2}{\sqrt{\pi}} \left( \frac{1}{3} \right)^{1/4} \left( w + \frac{4\pi l_B}{\kappa^2} \right)^{-1/4} c^{-3/4} l^{-1/2} & \kappa R_g > 1 \\
\frac{8}{\sqrt{3\pi}} \left( \frac{\pi}{6\sqrt{2}} \right)^{2/3} \left( \frac{l}{4\pi l_B} \right)^{1/6} c^{-1/2} l^{-1/2}, & \kappa R_g < 1
\end{cases} \tag{235}
$$

It is to be noted that $\xi_H$ is proportional to the static correlation length $\xi$ and the numerical prefactor is not unity. $\xi_H$ is proportional to $c^{-1/2}$ and $c^{-3/4}$, respectively, for low salt and high salt conditions. Using the results of Eqs. (232)–(235), we now calculate the diffusion coefficients, electrophoretic mobility, and viscosity of semidilute polyelectrolyte solutions.

Using $\mathcal{G}$ and $\Sigma$, the translational friction coefficient and the electrophoretic mobility can be calculated by simply replacing $G$ by $\mathcal{G}$ in the respective formulas. Before we proceed to do this, we present the collective dynamics of monomer density and counterions.

Following the method of Ref. 59, we write the equation of motion for the collective coordinate of local segment density $\rho(\mathbf{r})$,

$$
\rho(\mathbf{r}) = \sum_{\alpha=1}^{n} \sum_{i=0}^{N-1} \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \tag{236}
$$

When we define the Fourier transform as

$$
\rho(\mathbf{k}) = \frac{n}{\Omega} \sum_{j=0}^{N-1} e^{i\mathbf{k}\cdot\mathbf{R}_{j}} \tag{237}
$$
the evolution of \( \rho(k) \) follows as

\[
\frac{\partial \rho(k)}{\partial t} = \frac{n}{\Omega} \sum_j ik \cdot \dot{R}_j e^{ikR_j} \tag{238}
\]

Analogous to the derivation of the effective Langevin equation for the chain in dilute solutions, we get in semidilute solutions

\[
\dot{R}_i = -\sum_{j=0}^{N-1} \mathcal{G}^{-1}(R_i - R_j) \cdot \frac{\partial U}{\partial R_j} + f_{vi} + \frac{\mu}{N} E \tag{239}
\]

where

\[
\frac{\partial U}{\partial R_i} = \sum_{j=0}^{N-1} \left[ \frac{3k_BT}{F} (2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1})R_j + \nabla_R V(R_i - R_j) \right] \tag{240}
\]

and

\[
f_{vi} = \sum_{j=0}^{N-1} \mathcal{G}^\prime(R_i - R_j) \cdot f_j \tag{241}
\]

so that

\[
\langle f_{vi}(t) \rangle = 0 \tag{242}
\]

\[
\langle f_{vi}(t)f_{vj}(t') \rangle = 2k_BT \mathcal{G}(R_i - R_j) \delta(t - t') \tag{243}
\]

The angular brackets indicate the thermal average for the noise \( f_{vi} \).

Substitution of Eq. (239) for \( \dot{R}_j \) in Eq. (238) enables us to write a phenomenological equation for \( \rho(k) \):

\[
\frac{\partial}{\partial t} \rho(k) = - \sum_{k'} L_{kk'} \frac{\partial U}{\partial \rho(k')} + f_\rho(k) + f_E(k) \tag{244}
\]

where

\[
f_\rho(k) = \frac{n}{\Omega} \sum_j ik \cdot f_{vj} e^{ikR_j} \tag{245}
\]

and

\[
f_E(k) = - \frac{\mu}{N} ik \cdot \sum_{k'} E(k') \rho(k - k') \tag{246}
\]
The Onsager coefficient \( L_{kk'} \) is given by the fluctuation–dissipation theorem:

\[
\langle f_p(k, t)f_p(k', t') \rangle = 2k_BT L_{kk'} \delta(t - t')
\]

(247)

and

\[
\langle f_p(k, t) \rangle = 0
\]

(248)

Combining Eqs. (35), (242), (243), (245), (247), and (248), we obtain

\[
L_{kk'} = \int \frac{dj}{(2\pi)^3} \frac{k \cdot (1 - \hat{j} \cdot \hat{j}) \cdot k'}{[\eta_0 j^2 + \Sigma(j)]} \rho(k + j)\rho(k' - j)
\]

(249)

Upon preaveraging, we obtain

\[
L_{kk'} = \delta(k + k')L_k
\]

(250)

where

\[
L_k = \frac{c}{\Omega} \int \frac{dj}{(2\pi)^3} \frac{k^2 [1 - (-\hat{k} \cdot \hat{j})^2]}{[\eta_0 j^2 + \Sigma(j)]} g(k + j)
\]

(251)

with \( g(k) \) being the scattering function per segment,

\[
g(k) = \frac{\Omega}{c} \langle \rho(k)\rho(-k) \rangle
\]

(252)

Within the effective medium theory, the potential functional can be written as [3]

\[
\frac{U}{k_BT} = \frac{\Omega}{2c} \sum_k \frac{\rho(k)\rho(-k)}{g(k)}
\]

(253)

Substituting the results of Eqs. (251)–(253) in Eq. (244), we get

\[
\frac{\partial}{\partial t} \rho(k) = -D_c k^2 \rho(k) + f_p(k) + f_E(k)
\]

(254)

where the cooperative diffusion coefficient is given by

\[
D_c = k_BT \frac{\int \frac{dj}{(2\pi)^3} \frac{[1 - (\hat{k} \cdot \hat{j})^2]}{[\eta_0 j^2 + \Sigma(j)]} g(k + j)}{g(k)}
\]

(255)
With the use of the preaveraging approximation, Eq. (246) becomes

\[ f_E(k) = -\frac{\mu c}{N} \mathbf{k} \cdot \mathbf{E}(k) \]  

(256)

which, in combination with the Poisson equation

\[ \mathbf{i} \cdot \mathbf{E}(k) = \frac{4\pi}{\epsilon} \sum_i z_i \rho_i(k) \]  

(257)

and Eq. (254), leads to

\[ \frac{\partial}{\partial t} \rho(k) = -D_c k^2 \rho(k) + f_\rho(k) - \frac{c\mu}{N} \frac{4\pi}{\epsilon} \sum_i z_i \rho_i(k) \]  

(258)

Here \( i = 1 \) represents the polyelectrolyte with \( z_1 = z_{pe} \) and \( \rho_1 = c \). For \( i \neq 1 \), \( \rho_i \) is the fluctuation in the number density of the \( i \)th charged species and \( z_i \) is its charge. The Eq. (258) for the segment density of the polyelectrolyte is coupled to the equation of motion for \( \rho_i \),

\[ \frac{\partial}{\partial t} \rho_i(k) = -D_c k^2 \rho_i(k) - \rho_{\rho i} \frac{4\pi}{\epsilon} \sum_i z_i \rho_i(k) \]  

(259)

where \( D_{ci} \) and \( \mu_i \) are the diffusion coefficient and the electrophoretic mobility of the \( i \)th species. The noise term is ignored in the above equation. Assuming that small ions, \( i \neq 1 \), relax faster than the polyelectrolyte chains, \( \frac{\partial}{\partial t} \rho_i(k) = 0 \), Eqs. (258) and (259) get decoupled to finally give

\[ \frac{\partial}{\partial t} \rho(k) = -D_c k^2 \left[ 1 + \frac{\kappa_1^2 M_1}{(k^2 + \kappa^2)} \right] \rho(k) \]  

(260)

where

\[ \kappa_1^2 = \frac{4\pi Q^2 c}{\epsilon k_B T \cdot N} \]  

(261)

and

\[ M_1 = \frac{k_B T \mu}{Q D_c} \]  

(262)

In obtaining Eq. (260), the condition

\[ \mu_i = \frac{z_i D_{ci}}{k_B T} \]  

(263)
valid for small ions $i \neq 1$ has been used. It readily follows from Eq. (262) that the time correlation function $\langle \rho(k, t) \rho(-k, 0) \rangle$ decays exponentially with time with rate $D_f k^2$,

$$\langle \rho(k, t) \rho(-k, 0) \rangle \sim \exp(-D_f k^2 t)$$ (264)

where the “coupled diffusion coefficient” $D_f$ is given by

$$D_f = D_c \left[ 1 + \frac{\kappa^2 M_1}{(k^2 + \kappa^2)} \right]$$ (265)

In the limit of $k \to 0$, $D_f$ becomes

$$D_f(k \to 0) = D_c(k \to 0) \left[ 1 + \frac{\kappa^2 M_1}{\kappa^2} \right]$$ (266)

The coupled diffusion coefficient $D_f$ is calculated using Eqs. (255)–(263).

We now present the key results of the above equations.

**A. Translational Friction Coefficient**

The translational friction coefficient is given by

$$f_t = \sum_{i=0}^{N-1} \sum_{p=0}^{N-1} \langle \mathcal{G}^{-1}(R_i, R_p) \rangle$$ (267)

The self-translational diffusion coefficient $D$ is related to $f_t$ by the Stokes–Einstein relation and is given by

$$D = \frac{k_B T}{f_t} = k_B T \mathcal{G}_{00} = \frac{k_B T}{N^2} \sum_{i=0}^{N-1} \sum_{p=0}^{N-1} \langle \mathcal{G}(R_i - R_p) \rangle$$ (268)

Using Eqs. (232) and (268), we get

$$D = \frac{k_B T}{6 \pi \eta_0 R_g} \left( \frac{2 \zeta_H}{R_g} \right) \left[ 1 - \frac{2}{\sqrt{\pi}} \frac{\zeta_H}{R_g} + \left( \frac{\zeta_H}{R_g} \right)^2 \left( 1 - e^{-\frac{\zeta_H^2}{\zeta_H^2}} \right) \right]$$ (269)

This reduces to the result of Eqs. (119) and (175) for dilute solutions ($\zeta_H \gg R_g$).

In the Rouse regime where hydrodynamic interaction is screened, $D$ becomes

$$D = \frac{k_B T \zeta_H}{3 \pi \eta_0 R_g^2}, \quad R_g \gg \zeta_H$$ (270)
Substituting the result of Eq. (234) and noticing that $R_g^2 = Ll_1/6$, $D$ is given by

$$D = \frac{4k_B T}{\pi^2 \eta_0} c Ll_1^2$$

(271)

Using the result of $l_1$ (Table I), the translational self-diffusion coefficient is given by the form

$$D \sim \begin{cases} \frac{1}{N\sqrt{c}}, & \kappa R_g \gg 1 \\ \frac{c_0}{N}, & \kappa R_g \ll 1 \end{cases}$$

(272)

where the prefactors readily follow from Eq. (271) and Table I. While the Rouse law of $D \sim N^{-1}$ is valid at all salt conditions, the dependence of $D$ on polyelectrolyte concentration is different for different salt conditions. At low salt conditions, $D$ is independent of polyelectrolyte concentration. The crossover between these asymptotic results is described by Eq. (271).

### B. Electrophoretic Mobility

Analogous to the derivation in dilute solutions, $\mu$ is given by

$$\mu = Q(G_{00} + A_{00})$$

(273)

Combining Eqs. (228) and (144), $A(r)$ is given by

$$A(r) = \frac{1}{6\pi \eta_0 r} \frac{\kappa^2 z_H^2}{(\kappa^2 z_H^2 - 1)} (e^{-\kappa r} - e^{-\frac{r}{z_H}})$$

(274)

Substituting this result in Eq. (148), $A_{00}$ becomes

$$A_{00} = \frac{1}{6\pi \eta_0 R_g} \frac{\kappa^2 z_H^2}{(\kappa^2 z_H^2 - 1)} [M(\kappa R_g) - M(\frac{R_g}{z_H})]$$

(275)

where the function $M$ is defined as

$$M(xR_g) \equiv \frac{R_g}{N^2} \sum_{i=0}^{N-1} \sum_{j=0}^{N-1} e^{-xR_{ij}} = \frac{2R_g}{\pi N} \int_0^\infty dk \frac{k^2}{(k^2 + x^2)} S(kR_g)$$

(276)

Using Eqs. (268), (273), and (275), the electrophoretic mobility $\mu$ is given by

$$\mu = \frac{Q}{6\pi \eta_0 R_g} \frac{1}{(1 - \kappa^2 z_H^2)} [M(\frac{R_g}{z_H}) - M(\kappa R_g)]$$

(277)
This reduces to Eq. (156) in the infinite dilution limit ($\xi_H \to \infty$). In the Rouse regime ($\xi_H$ small), the electrophoretic mobility becomes

$$\mu = \frac{Q}{6\pi \eta_0 R_g} \mathcal{M}\left(\frac{R_g}{\xi_H}\right)$$

(278)

Substituting the asymptotic form of $M(R_g/\xi_H)$, we obtain

$$\mu = \frac{Q\xi_H}{2\pi \eta_0 R_g^2}$$

(279)

Noticing the expression for $D$ in the Rouse limit, Eq. (270), we see that $\mu$ becomes

$$\mu = \frac{QD}{k_BT}$$

(280)

in the Rouse regime. The power laws of $\mu$ on $N$ and polyelectrolyte concentration $c$ follow from Eq. (272) to be

$$\mu \sim \begin{cases} N^0 c^{-\frac{1}{2}} \left(1 + \frac{4\pi n_c}{\kappa^2}ight)^{-1/2}, & \kappa R_g > 1 \\ N^0 c^0, & \kappa R_g < 1 \end{cases}$$

(281)

### C. Cooperative and Coupled Diffusion Coefficients

When we substitute Eq. (231) into Eq. (255), the cooperative coefficient $D_c$ is given by

$$D_c = \frac{k_BT}{\eta_0} \int \frac{dj}{(2\pi)^3} \frac{[1 - (k \cdot j)^2]g(k + j)}{j^2 + \xi_H^2} g(k)$$

(282)

The scattering function $g(k)$ is a function of static correlation length $\xi$ as given by Eqs. (225)–(227). For semidilute solutions at high salt concentrations, $D_c$ follows from Eqs. (226) and (282) in the $k \to 0$ limit,

$$D_c = \frac{k_BT}{6\pi \eta_0 \xi \xi_H}$$

(283)

In infinitely dilute solutions we have $\xi_H \to \infty$ and the static correlation $\xi = R_g/\sqrt{3}$ as already discussed. In this limit, $D_c$ of Eq. (175) is therefore recovered. On the other hand, in the Rouse regime, Eq. (283) yields

$$D_c \sim \frac{T}{\eta_0 \xi} \sim c^{3/4}$$

(284)
since $\xi_H \sim \xi \sim c^{-3/4}$. For semidilute solutions at low salt concentrations, $D_c$ follows from Eqs. (227) and (282):

$$D_c = \frac{2k_BT}{3\eta_0} \int \frac{dj}{(2\pi)^3} \frac{1}{(j^2 + \xi_H^{-2})} \frac{(k + j)^2}{[(k + j)^4 \xi^4 + 1]} \frac{(k^4 \xi^4 + 1)}{k^2}$$

(285)

The cooperative diffusion coefficient in the salt-free limit is thus strongly $k$-dependent. In this limit the equilibrium scattering function $g(k)$ exhibits a peak at $k^* = \xi^{-1}$. Approximating $g(k)$ in Eqs. (282) and (285) by its value at the peak position $k^*$, Eq. (285) yields

$$D_c = \frac{k_BT}{6\pi\eta_0 \xi} \frac{\sqrt{2}}{1 + \left(\frac{\xi}{\xi_H}\right)^4} \left[ 1 - \left(\frac{\xi}{\xi_H}\right)^2 + \sqrt{2} \left(\frac{\xi}{\xi_H}\right)^3 \right]$$

(286)

In the Rouse regime (for low salt concentrations)

$$D_c \sim \frac{T}{\eta_0 \xi} \sim N^0 c^{1/2}$$

(287)

because $\xi_H \sim \xi \sim c^{-1/2}$.

The coupled diffusion coefficient $D_f$ can be now obtained from $D_c$ of Eqs. (283)–(287) and $\mu$ of Eq. (281). In the Rouse regime (where the second term on the right-hand side of Eqs. (265) and (266) dominates, $D_f$ becomes

$$D_f = \frac{4\pi QC\mu}{\epsilon\kappa^2N}$$

(288)

Writing $\mu$ explicitly in terms of $R_g$ and $\xi_H$, $D_f$ is given by

$$D_f = \frac{k_BT}{2\pi\eta_0} \frac{Z^2 c}{(Z^2 c + 2c_s)} \frac{N\xi_H}{R_g^2}$$

(289)

where salt ions are taken to be monovalent. In the salt-free limit, $\xi_H \sim c^{-1/2}$ and $R_g^2 \sim Nc^{-1/2}$ so that

$$D_f \sim \frac{T}{\eta_0} N^0 c^0$$

(290)

Therefore, remarkably, the coupled diffusion coefficient becomes independent of $N$ and $c$ in the Rouse regime of salt-free polyelectrolyte solutions. This is to be
contrasted with Eq. (287) for the cooperative diffusion coefficient $D_c$ and with Eq. (272) for the translational diffusion coefficient $D$. In the Rouse regime at high salt concentrations, $\xi_H \sim c^{-3/4}$ and $R_g^2 \sim Nc^{-1/4}$ so that Eq. (289) yields

$$D_f \sim \frac{T}{\eta_0} \frac{Z_p^2 \sqrt{c}}{Z_c^2 (c + 2c_s)}$$

(291)

The coupled diffusion coefficient $D_f$ decreases from the value of Eq. (290) to that of Eq. (291) as the salt concentration is increased.

### D. Viscosity

The virial series of viscosity in polyelectrolyte concentration $c$ can be obtained from Eq. (229) by iterating $\Sigma(k)$ to the desired order in $c$ and then combining with Eq. (38). To the leading order in $c$, Eq. (229) yields

$$G(q) = \frac{1}{\pi \eta_0 \sqrt{3l_1 q}} \left[ 1 - \frac{\pi}{2\sqrt{3}q} cll^{3/2} + \ldots \right]$$

(292)

so that viscosity change becomes from Eq. (38)

$$\frac{\eta - \eta_0}{\eta_0} = \left( \frac{2}{3\pi} \right)^{1/2} cll^{3/2} L^{1/2} \left[ 1 + \frac{1}{4} \sqrt{\frac{\pi}{6}} cll^{3/2} L^{1/2} + \ldots \right]$$

(293)

Defining the overlap concentration $c^*$ to be

$$c^* = \frac{3}{4\pi R_g^2}$$

(294)

where $R_g^2 = lL_1 / 6$, viscosity change can be written as

$$\frac{\eta - \eta_0}{\eta_0} = \frac{9}{\pi^{3/2}} \left( \frac{c}{c^*} \right)^{3/2} \left[ 1 + \frac{9}{2\sqrt{\pi} c^*} + \ldots \right]$$

(295)

Alternatively, Eq. (295) can be rewritten in terms of the intrinsic viscosity given by Eq. (216) as

$$\frac{\eta - \eta_0}{\eta_0} = c[\eta] + k_H c^2 [\eta]^2 + \ldots$$

(296)

where

$$[\eta] \approx \frac{1.616}{c^*}$$

(297)
and the Huggins coefficient $k_H$ is

$$k_H \simeq 1.57 \quad (298)$$

This value of $k_H$ is actually low by an order of magnitude for dilute suspensions of charged spheres of radius $R_g$. This is due to the neglect of interchain correlations for $c < c^*$ in the structure factor used in the derivation of Eqs. (295)–(298). If the repulsive interaction between polyelectrolyte chains dominates, as expected in salt-free solutions, the virial expansion for viscosity may be valid over considerable range of concentrations where the average distance between chains scales as $c^{-1/3}$. This virial series may be approximated by

$$\frac{\eta - \eta_0}{\eta_0} = [\eta] c \exp(k_H[\eta] c) \quad (299)$$

Substituting Eqs. (233) and (234) into Eq. (229) and (38), the viscosity change in the Rouse regime becomes

$$\frac{\eta - \eta_0}{\eta_0} = \frac{1}{24} c^2 l_1^3 L \quad (300)$$

Using the concentration dependence of $l_1$ under different salt conditions, we get

$$\frac{\eta - \eta_0}{\eta_0} \sim \begin{cases} c^{5/4} N, & \kappa R_g \gg 1 \\ c^{1/2} N, & \kappa R_g \ll 1 \end{cases} \quad (301)$$

E. Frequency Dependence

The theory given above can be readily extended [60] to the frequency $\omega$ dependence of shear viscosity $\eta(\omega)$ and shear modulus $G(\omega) = i\omega \eta(\omega)$. Generalizing the equations in the preceding sections for $\omega$ dependence, we get

$$\eta(\omega) - \eta_0 = \lim_{k \to 0} \frac{1}{k^2} (1 - \hat{k} \hat{k}) \cdot \Sigma(k, \omega) \quad (302)$$

$$\Sigma(k, \omega) = \frac{1}{\pi} \int_{\frac{2 \pi}{\omega}}^{\infty} dq S(k, q, \omega) J^{-1}(q, \omega) \quad (303)$$

$$J(q, \omega) = \int \frac{dj}{(2\pi)^3 [I(\eta_0 j^2 + i\omega) + \Sigma(j, \omega)]} S(j, q, \omega) \quad (304)$$

$$S(k, q, \omega) = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d(s - s') \exp(i k \cdot [R(s, t) - R(s', 0)]) \quad (305)$$
The key results from these equations are summarized in Table II. Naturally, in the $\omega \to 0$ limit, results of Table I are recovered. Only the high frequency limit is mentioned now.

### 1. Dilute

In infinite dilute solutions, the intrinsic viscosity $[\eta]$ is given by $[3, 4, 61]$

$$[\eta] = \frac{RT}{M \eta_0} \sum_{j=1}^{N} \frac{\tau_j}{1 + i\omega \tau_j} \quad (306)$$

where $R$, $T$, $M$, and $\tau_j$ are, respectively, the gas constant, absolute temperature, molecular weight (proportional to the number of Kuhn segments $N$ per chain), and relaxation time of the $j$th Rouse–Zimm mode. The intrinsic storage $[G']$ and loss $[G'']$ moduli are

$$[G'] = \frac{RT}{M} \sum_{j=1}^{N} \frac{\omega^2 \tau_j^2}{1 + \omega^2 \tau_j^2}$$

$$[G''] = \frac{RT}{M} \sum_{j=1}^{N} \frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} \quad (307)$$

In the high frequency limit, the intrinsic viscosity follows from Eq. (306) as

$$[\eta] \sim \int dq \frac{\tau_q}{1 + i\omega \tau_q} \quad (308)$$
so that both the real and imaginary parts are proportional to

\[ [\eta] \sim \omega \int dq \frac{1}{q^{\alpha v} + \omega^2} \]

\[ \sim \omega^{-(3v-1)/3v} \]  
(309)

Equation (307) gives the intrinsic modulus as

\[ [G] \sim \omega^{1/3v} \]  
(310)

2. Semidilute

At high frequencies, we have

\[ \frac{\eta - \eta_0}{\eta_0 c} \sim \omega \int dq \frac{\tau_q^2}{(1 + \omega^2 \tau_q^2)} \]

\[ \sim \frac{1}{\sqrt{\omega}} c^{(2-3v)/2} \]  
(311)

and

\[ \frac{G - G_0}{G_0 c} \sim \sqrt{\omega} c^{(2-3v)/2} \]  
(312)

Therefore in this Rouse regime of unentangled semidilute solutions where hydrodynamic interaction is screened, both the reduced viscosity and reduced modulus decrease with increase in polymer concentration in salt free solutions \((v \rightarrow 1)\),

\[ \frac{\eta - \eta_0}{\eta_0 c} \sim \begin{cases} \frac{N c^{-1/2}}{\omega^{-1/2} c^{-1/4}}, & \omega \rightarrow 0 \\ \omega \rightarrow \infty \end{cases} \]  
(313)

and

\[ \frac{G - G_0}{G_0 c} \sim \begin{cases} \omega N c^{-1/2}, & \omega \rightarrow 0 \\ \omega^{1/2} c^{-1/4}, & \omega \rightarrow \infty \end{cases} \]  
(314)

These apparent strange results are to be contrasted with the results at high salt concentrations \((v \rightarrow 3/5)\),

\[ \frac{\eta - \eta_0}{\eta_0 c} \sim \begin{cases} \frac{N c^{1/4}}{\omega^{-1/2} c^{1/8}}, & \omega \rightarrow 0 \\ \omega \rightarrow \infty \end{cases} \]  
(315)
and

\[
\frac{G - G_0}{G_0 c} \sim \begin{cases} 
\omega N c^{1/4}, & \omega \to 0 \\
\omega^{1/2} c^{1/8}, & \omega \to \infty
\end{cases}
\] (316)

The above general results and the asymptotic values for high and low salt concentrations are included in Table II.

Although several experimental studies [22, 62, 63] have been reported on \( \eta, G, \) and the compliance of polyelectrolyte solutions, systematic investigations on the frequency dependence is still lacking.

## F. Entanglement Effects

It is nontrivial to calculate the various diffusion coefficients and viscosity of polyelectrolyte solutions at very high concentrations when entanglement effects dominate. However, because of screening of electrostatic, excluded volume, and hydrodynamic interactions as the polyelectrolyte concentration is increased, we can expect the applicability of scaling arguments as in neutral solutions. Assuming that, in the asymptotic regime of very high entanglement density, reptation dynamics is valid, \( D \) is proportional to \( N^{-2} \). The concentration dependence of \( D \) in this limit can be obtained by assuming that \( D \) is proportional to \( R_g^{-1} f_e(c/c^*) \) and that the \( N \)-dependence of \( D \) should be consistent with the reptation law,

\[
D \sim \begin{cases} 
\frac{1}{\sqrt{c} N^2}, & \kappa R_g \ll 1 \\
\frac{1}{c^{7/5} N^2}, & \kappa R_g \gg 1
\end{cases}
\] (317)

For concentrations between the Rouse and reptation regimes, \( D \) can depend more sensitively on \( N \) due to the entropic barrier mechanism [6, 64]. In this crossover region, \( D \) can be written as

\[
D \sim N^{-\delta}
\] (318)

where \( \delta \) can be 3 or even higher, depending on the concentration range and the system. Similarly, the electrophoretic mobility follows from the formula \( \mu \sim QD \) as

\[
\mu \sim N^{1-\delta}
\] (319)

so that \( \mu \sim N^{-2} \) if entropic barriers dominate and \( \mu \sim N^{-1} \) if reptation limit is approached. There has been substantial experimental support for the presence of entropic barrier mechanism for polymer dynamics [65, 66]. Recently, there have been several electrophysiology experiments [67–71], where translocation of
single polyelectrolyte molecules through protein channels is investigated. Under the conditions of these experiments, the entropic barrier mechanism is the dominant polymer dynamics [72–76].

The concentration dependence of \( \eta \) at very high concentrations of polyelectrolytes can be obtained by assuming that \( \eta - \eta_0 \) is a function of \( c/c^* \) and that this function is consistent with \( \eta \sim N^{3.4} \),

\[
\eta \sim \begin{cases} 
  c^{1.7}N^{3.4}, & \kappa R_g \ll 1 \\
  c^{4.25}N^{3.4}, & \kappa R_g \gg 1
\end{cases}
\]  

(320)

V. CONCLUSIONS

The main results derived from the theory of polyelectrolyte dynamics are as follows.

A. Electrophoretic Mobility

In infinitely dilute solutions where full hydrodynamic interaction between segments is present as in the Kirkwood–Riseman–Zimm model, the electrophoretic mobility is independent of \( N \) in both low (\( \kappa R_g \ll 1 \)) and high (\( \kappa R_g \gg 1 \)) salt concentrations:

\[
\mu \sim \begin{cases} 
  N^0, & \kappa R_g \ll 1 \\
  N^0 \kappa^{-2/3}, & \kappa R_g \gg 1
\end{cases}
\]  

(321)

But \( \mu \) decreases with salt concentration with an apparent exponent of \( \kappa \) which changes from 0 at low salt concentration to \(-\frac{2}{3}\) at high salt concentrations. The \( N \)-independence of \( \mu \) arises from a cancellation between hydrodynamic interaction and electrostatic coupling between the polyelectrolyte and other ions in the solution. It is to be noted that the self-translational diffusion coefficient \( D \) is proportional to \( \frac{T}{\eta_0 R_g} \) as in the Zimm model with full hydrodynamic interaction. The results of Eq. (321) are in agreement with experimental data [35]. In semidilute solutions, the hydrodynamic interaction is screened. But the electrostatic coupling between various ions are always present. When entanglement effects are unimportant, the solution is in the Rouse regime. Even in semidilute solutions, Eqs. (278)–(281) show that \( \mu \) is independent of \( N \):

\[
\mu \sim \begin{cases} 
  c^0 N^0, & \kappa R_g \ll 1 \\
  \frac{N^0}{\sqrt{c}}, & \kappa R_g \gg 1
\end{cases}
\]  

(322)

In addition, we predict that \( \mu \) is independent of polyelectrolyte concentration \( c \) at low salt concentrations and decreases with \( c \) as the salt concentration is
increased. There is also an additional salt concentration dependence of $\mu$ as shown in Eq. (281). It is to be remarked that in the Rouse regime, the Hückel law of electrophoretic mobility is valid,

$$\mu = \frac{Q D}{k_B T}$$  \hspace{1cm} (323)

whereas in dilute solutions this law is significantly modified,

$$\mu = \frac{Q D}{k_B T} \mathcal{M}(\kappa R_g)$$  \hspace{1cm} (324)

where $\mathcal{M}(\kappa R_g)$ is defined in Eq. (276). The predictions of Eq. (323) need to be verified in order to identify the range of concentrations where Rouse regime exists.

### B. Diffusion Coefficients

We have identified three diffusion coefficients. These are the self-translational diffusion coefficient $D$, cooperative diffusion coefficient $D_c$, and the coupled diffusion coefficient $D_f$. $D_c$ is the cooperative diffusion coefficient in the absence of any electrostatic coupling between polyelectrolyte and other ions in the system. $D_f$ is the cooperative diffusion coefficient accounting for the coupling between various ions. For neutral polymers, $D_f$ and $D_c$ are identical. Furthermore, we identify $D_f$ as the fast diffusion coefficient as measured in dynamic light scattering experiments. The fourth diffusion coefficient is the slow diffusion coefficient $D_s$ discussed in the Introduction. A satisfactory theory of $D_s$ is not yet available.

#### 1. Self-Translational Diffusion Coefficient

Equations (116) and (271) give $D$ in dilute and semidilute limits. For low polyelectrolyte concentrations, we have

$$D \sim \begin{cases} \frac{1}{N}, & \kappa R_g \ll 1 \\ \frac{1}{N^{1/5}}, & \kappa R_g \gg 1 \end{cases}$$  \hspace{1cm} (325)

In the Rouse regime we have derived

$$D \sim \begin{cases} \frac{\nu^0}{N}, & \kappa R_g \ll 1 \\ \frac{1}{N^{1/\nu_1}}, & \kappa R_g \gg 1 \end{cases}$$  \hspace{1cm} (326)

The numerical prefactors for the relations in the above two equations are given in Eqs. (116) and (271).
2. **Cooperative Diffusion Coefficient**

In dilute solutions, $D_c = D$. In the Rouse regime, $D_c$ depends on both static and hydrodynamic screening lengths $\xi$ and $\xi_H$,

$$D_c = \frac{k_B T}{6 \pi \eta_0 \xi} f_d \left( \frac{\xi}{\xi_H} \right)$$  \hspace{1cm} (327)

where $f_d$ is given in Eqs. (283)–(287). $\xi_H$ is given in Eqs. (234) and (235) and $\xi$ was already reported in Ref. (48) and summarized in Table 1. $\xi_H$ is proportional to $\xi$. As discussed in the previous section, $D_c$ can be strongly $k$-dependent. The asymptotic results for $D_c$ follow from Eqs. (283)–(287) as

$$D_c \sim \begin{cases} N^0 c^{1/2}, & \kappa R_g \ll 1 \\ N^0 c^{3/4}, & \kappa R_g \gg 1 \end{cases}$$  \hspace{1cm} (328)

These results can readily be obtained by a scaling argument, $D_c \sim R_g^{-1} f_c(c/c^*)$, where we insist on the behavior of $f_c$ on $c/c^*$ so as to produce independence of $D_c$ an $N$. The details of the prefactors are provided by formulas used in the derivation of Eq. (328).

3. **Coupled Diffusion Coefficient**

By accounting for the coupling between the dynamics of polyelectrolyte chains and their counterions and salt ions and assuming that small ions relax faster than polyelectrolyte chains, we have derived $D_f$ to be

$$D_f = D_c + \frac{4 \pi Q_{c\mu}}{\epsilon k^2 N}$$  \hspace{1cm} (329)

In dilute polyelectrolyte solutions containing monovalent salt ions, $D_f$ is given by

$$D_f \sim \begin{cases} \frac{T}{\eta_0} \left( 1 + \frac{1}{N} \right), & \kappa R_g \ll 1 \\ \frac{T}{\eta_0} \left( \frac{1}{w + \frac{4 \pi d^2}{\xi^2}} \right)^{1/5} N^{1/5} \left[ 1 + \frac{\xi^2 N c}{(\xi^2 + 2 c_\xi)} \left( \frac{1.17}{\kappa R_g} \right)^{2/3} \right], & \kappa R_g \gg 1 \end{cases}$$  \hspace{1cm} (330)

Therefore we expect $D_f$, identified as the fast diffusion coefficient measured in dynamic light-scattering experiments, in infinitely dilute polyelectrolyte solutions to be very high at low salt concentrations and to decrease to self-diffusion coefficient $D(\kappa R_g \gg 1)$ as the salt concentration is increased. The above result for $\kappa R_g \ll 1$ limit is analogous to the Nernst–Hartley equation reported in Ref. 33. The theory described here accounts for structural correlations inside polyelectrolyte chains.
In the Rouse regime \( (c > c^*) \), the result is

\[
D_f \sim \begin{cases} 
\frac{T}{\eta_0} N^0 c^0, & \kappa R_g \ll 1 \\
\frac{T}{\eta_0} \frac{\sqrt{c}}{\left(c c + 2c^0\right)^2}, & \kappa R_g \gg 1 
\end{cases}
\]

(331)

Thus in salt-free semidilute solutions, the fast diffusion coefficient is expected to be independent of both \( N \) and \( c \), although the polyelectrolyte concentration is higher than the overlap concentration. This remarkable result is in agreement with experimental data [31, 33, 34] discussed in the Introduction. Upon addition of salt, \( D_f \) decreases from this value as given by the above formulas.

C. Viscosity

In dilute solutions, the viscosity is given by

\[
\frac{\eta - \eta_0}{\eta_0} = c[\eta][1 + k_H c[\eta] + \cdots]
\]

(332)

where the intrinsic viscosity \([\eta]\) follows the Kirkwood–Riseman–Zimm formula as given by Eq. (216):

\[
[\eta] \sim \begin{cases} 
l_B l^2 N^2, & \kappa R_g \ll 1 \\
\left(w + \frac{4\pi l_B^3}{\kappa^2}\right)^{3/5} \rho^{4/5} N^{4/5}, & \kappa R_g \gg 1 
\end{cases}
\]

(333)

The Huggins coefficient \( k_H \) is of order unity for neutral chains and for polyelectrolyte chains at high salt concentrations. In low salt concentrations, the value of \( k_H \) is expected to be an order of magnitude larger, due to the strong Coulomb repulsion between two polyelectrolyte chains, as seen in the case of colloidal solutions of charged spheres. While it is in principle possible to calculate the leading virial coefficients in Eq. (332) for different salt concentrations, the essential feature of the concentration dependence of \( \eta \) can be approximated by

\[
\frac{\eta - \eta_0}{\eta_0} = c[\eta] \exp(k_H[\eta]c), \quad c < c^*
\]

(334)

in dilute solutions. Therefore, in dilute solutions where Zimm dynamics is valid, the specific viscosity increases roughly with concentration according to

\[
\frac{\eta - \eta_0}{\eta_0} = 1.616 \left(\frac{c}{c^*}\right) \exp\left[1.616 k_H \left(\frac{c}{c^*}\right)\right], \quad c < c^*
\]

(335)
where the relation of Eq. (297) is used. The increase of $\eta$ with $c$ in dilute solutions is steeper at low salt concentrations due to the higher value of $k_H$. This behavior is sketched as regime I in Figs. 1 and 2. The concentration dependencies of $(\eta - \eta_0)/\eta_0$ and $(\eta - \eta_0)/\eta_0 c$ are sketched in Figs. 1a and 1b, respectively, where I, II, and III represent Zimm, Rouse, and entanglement regimes, respectively. The expected slopes are also indicated.

Figure 1. Sketch of double logarithmic plot of $(\eta - \eta_0)/\eta_0$ and $(\eta - \eta_0)/\eta_0 c$ versus $c$ in (a) and (b), respectively, in salt-free solutions. I, II, and III represent Zimm, Rouse, and entanglement regimes, respectively. The expected slopes are also indicated.

Figure 2. Same as in Fig. 1, except now the salt concentration is high.
for polyelectrolyte solutions in salt-free conditions. Figures 2a and 2b are similar sketches for high salt concentrations. In the Rouse regime where hydrodynamic interaction is screened, the viscosity is given by Eqs. (300) and (301) to be

$$\frac{\eta - \eta_0}{\eta_0} \sim \begin{cases} c^{1/2} N, & \kappa R_g \ll 1 \\ c^{5/4} N, & \kappa R_g \gg 1 \end{cases}$$

(336)

This behavior is sketched as regime II in Figs. 1 and 2. It is to be remarked that the viscosity change is monotonic with concentration in both salt-free and salty polyelectrolyte solutions. However, a plot of \((\eta - \eta_0)/\eta_0 c\) against \(c\) will show a peak in salt-free solutions, because \((\eta - \eta_0)/\eta_0\) is proportional to \(\sqrt{c}\) in the Rouse regime. In such a plot, the peak will be absent at high salt concentrations as shown in Fig. 2, because now \((\eta - \eta_0)/\eta_0\) is proportional to \(c^{5/4}\) (with \(\frac{5}{4}\) being greater than unity) in the Rouse regime. Thus we identify the empirical Fuoss law observed for salt-free polyelectrolyte solutions to be the same as the Rouse regime (with screened hydrodynamic interaction and no entanglements).

When entanglement effects dominate, scaling arguments suggest

$$\eta \sim \begin{cases} c^{1.7} N^{3.4}, & \kappa R_g \ll 1 \\ c^{4.25} N^{3.4}, & \kappa R_g \gg 1 \end{cases}$$

(337)

These expectations are indicated as regime III in Figs. 1 and 2 for polyelectrolyte concentrations greater than the entanglement concentration \(c_e\).

**D. Unresolved Issues**

Although the theory of polyelectrolyte dynamics reviewed here provides approximate crossover formulas for the experimentally measured diffusion coefficients, electrophoretic mobility, and viscosity, the validity of the formulas remains to be established. In spite of the success of one unifying conceptual framework to provide valid asymptotic results, in qualitative agreement with experimental facts, it is desirable to establish quantitative validity. This requires (a) gathering of experimental data on well-characterized polyelectrolyte solutions and (b) obtaining the relationships between the various transport coefficients. Such data are not currently available, and experiments of this type are out of fashion. In addition to these experimental challenges, there are many theoretical issues that need further elaboration. A few of these are the following:

1. Although the coupling of counterion dynamics and polyelectrolyte dynamics has been accounted for at the mean field level, the relaxation of counterion cloud needs to be included in comparing with experimental data.
2. The crossover between the Kirkwood–Riseman–Zimm behavior and the Rouse behavior requires a better understanding, in terms of the contributing factors for the occurrence of a maximum in the plot of reduced viscosity against polyelectrolyte concentration at low salt concentrations. A firm understanding of the structure factor of polyelectrolyte solutions at concentrations comparable to the overlap concentration is necessary.

3. The role of semiflexibility of the polymer backbone on the dynamical properties is necessary to explore the dynamical properties of biologically relevant polyelectrolytes. Orientational correlations among molecules are expected to enhance the richness of the dynamical properties.

4. As discussed extensively in this chapter, most of the surprising properties of polyelectrolyte dynamics are due to the coupling of counterion dynamics with polymer dynamics. But, there is no adequate understanding of how much of the counterions are mobile and how much are effectively condensed on polymer chain backbone. Theoretical attempts \([77, 78]\) on counterion condensation need to be extended to concentrated polyelectrolyte solutions.

5. The effective dielectric function of polyelectrolyte solutions remains as a mystery, demanding a better understanding of structure of solvent surrounding polyelectrolyte molecules.

6. The origins of experimentally observed slow mode need to be explored in terms of hydrophobic effects arising from the intrinsic chemical properties of polymer molecules.

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