

Electro-osmosis of polymer solutions: linear and nonlinear behavior

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1. INTRODUCTION

1.1. General introduction

Electro-osmosis is widely observed in many systems such as colloids, porous materials, and biomembranes. It characterizes the properties of interfaces between solids and electrolyte solutions.[1–4] Interests in the applications of electro-osmosis have been growing recently. For instance, it is used to pump fluids in microfluidic devices, as it is more easily implemented than pressure-driven flow.[5] Application to an electrical power conversion is also of great interest in chemical engineering.[6, 7] Fig. 1 shows a schematic illustration of energy conversion. A saline solution and fresh water are separated by a membrane, and one nanotube connects them. The narrow tube causes a giant osmotic current driven by the gradient of the electrochemical potential of ions. Such a device suggests the possibility of converting oceanic energy.[8]

When the electrokinetic properties of a surface are characterized by the zeta potential, the Smoluchowski equation is often employed with measurements of the electro-osmotic or electrophoretic mobilities. However, one has to consider the validity of this equation seriously. It is derived from the Poisson-Boltzmann equation and Newton’s constitutive equation for viscous fluids. The zeta potential is defined as the electrostatic potential at the plane where a no-slip boundary condition is assumed. When these equations are not valid, the Smoluchowski equation is also questionable. For a strong-coupling double layer,[9] inhomogeneity of the viscosity and dielectric constant near the interface,[10, 11] and non-Newtonian fluids,[12–15] for example, the Poisson-Boltzmann and/or simple hydrodynamic equations sometimes do not work well.

To control the electrokinetic properties of charged capillaries, the structures of liquid interfaces in contact with charged surfaces are modified by grafting or adding polymers.[16] In capillary electrophoresis, for example, the electro-osmotic flow is reduced by polymers grafted on the interfaces. Several studies of surfaces with end-grafted charged and uncharged polymers have also been reported.[17–22] Under a weak applied electric field, the grafted polymer remains in the equilibrium configuration, and the resultant electro-osmotic velocity behaves linearly with respect to the electric field. To measure the mobility of such a surface, the hydrodynamic screening and anomalous charge distributions due to the grafted

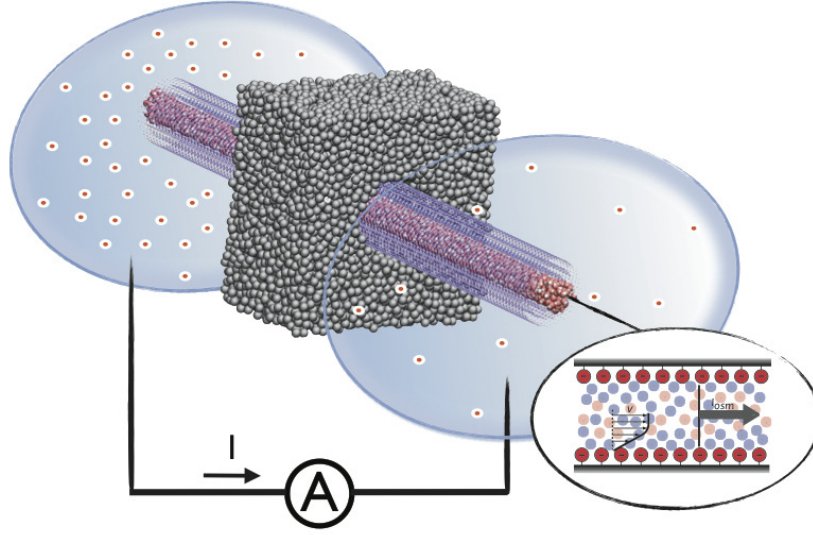


FIG. 1. Schematic illustration of energy conversion. Reprinted by permission from Macmillan Publishers Ltd: ref. [8], copyright (2013). [doi:10.1038/nature11876](https://doi.org/10.1038/nature11876)

polymers are important.[17–22] When a sufficiently large electric field is applied, the polymers are deformed by the flow and electric field; thus, the electro-osmotic velocity becomes nonlinear.[19] Note that the end-grafted polymers cannot migrate toward the bulk because one of the ends is fixed on the surfaces.

When we add polymers to solutions, a depletion or adsorption layer is often formed near a solid wall as well as diffuse layers of ions in equilibrium states. The interaction between the polymers and the wall determines whether the polymers are depleted from or adhere to the surfaces. The thickness of the depletion or adsorption layer is of the same order as the gyration length of the polymers. When the polymers adhere to the wall, the viscosity near the wall becomes large, so the electro-osmotic mobility is strongly suppressed.[23] Moreover, it is known that an adsorption layer of charged polymers can change the sign of the mobility.[10, 24–27] The curvature of the surface also modulates the surface charge density and even increases the mobility beyond the suppression caused by the viscosity enhancement.[23]

Fig. 2 shows the electrophoretic mobility as a function of the polyelectrolyte concentration. Feng *et al.* measured the electrophoretic mobility of polystyrene latex with a diameter of $1.356\,\mu\text{m}$ in a polyelectrolyte solution.[26] They added the positively charged polyelec-

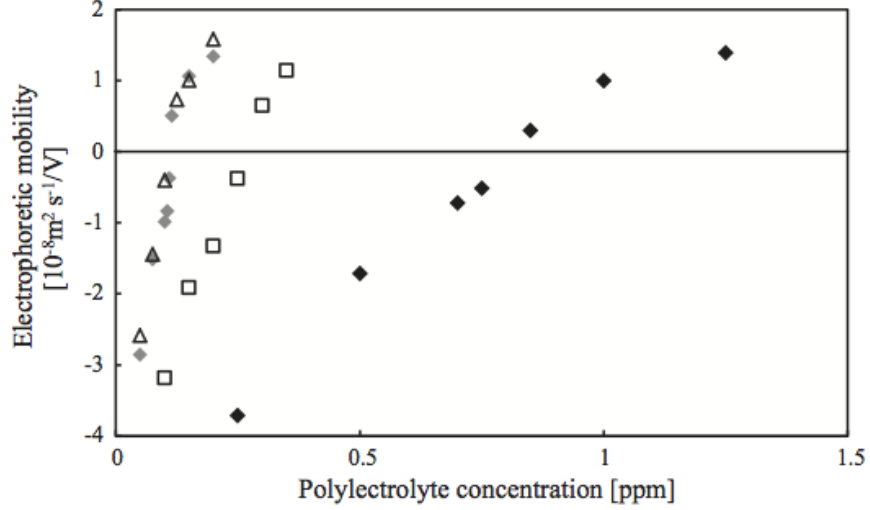


FIG. 2. Electrophoretic mobility as a function of polyelectrolyte concentration under different ionic strength: in the absence of KCl(open triangles), in the presence of 1 mM KCl(gray diamonds), 10 mM KCl (open squares) and 0.5 M KCl (black diamonds). Reprinted from ref. [26]. Copyright (2014), with permission from Elsevier. [doi:10.1016/j.colsurfa.2012.09.023](https://doi.org/10.1016/j.colsurfa.2012.09.023)

trolyte dimethylamino ethylmethacrylate with a molecular weight of 4.9×10^6 to a colloidal suspension. The polymer size in a 0.5 M KCl solution is 79.39 nm, and the charge density is 100 percent. Fig. 2 shows that without polyelectrolyte, the colloid is negatively charged, and the mobility is negative. The mobility increases with the polyelectrolyte concentration, approaching the point where the mobility is zero. When we add further polyelectrolyte, the sign of the mobility is changed, and the colloid migrates as if it were positively charged. The point at which the mobility is zero depends on the ionic strength; the dosage of polyelectrolyte increases with increasing ionic strength.

Electro-osmosis of a non-adsorbing polymer solution was analyzed using two length scales: the equilibrium depletion length δ_0 and the Debye length λ . [10, 28] In the depletion layer, the viscosity is estimated approximately as that of the pure solvent, and it is smaller than the solution viscosity in the bulk. When the Debye length is smaller than the depletion length, the electro-osmotic mobility is larger than that estimated using the bulk value of the viscosity. Typically, for 10 mM monovalent electrolyte solutions, one has $\lambda \approx 3$ nm and $\delta_0 \approx 100$ nm. In this case, [29–31] an electro-osmotic flow with a high shear rate is localized at a distance λ from the wall. Thus, the electro-osmotic flow profile and resultant electro-osmotic

mobility are almost independent of the polymers. Such behaviors were experimentally observed in solutions of carboxymethyl cellulose (CMC) with urea.[30] On the other hand, in solutions of small polymers with low salinity, typically, for 0.1 mM electrolyte solutions, $\lambda \approx 30$ nm and $\delta_0 \approx 5$ nm, and the electro-osmotic mobility is suppressed by the polymeric stress.[28]

Fig. 3 shows the effective zeta potential as a function of the polymer concentration for polyethylene glycol (PEG) dissolved in water. The panel on the left shows that when $\lambda > \delta_0$, the effective zeta potential does not change. In other words, the electro-osmotic mobility decreases with increasing polymer concentration, as the denominator of the mobility is the solution viscosity. On the other hand, for high-molecular-weight polymers ($\lambda < \delta_0$), the effective zeta potential increases with increasing polymer concentration. This means that the viscosity in the double layer remains lower than the bulk value of the solution viscosity. The panel on the right shows various ionic strengths for a high-molecular-weight polymer. For a high ionic strength, the Debye layer becomes thinner, and the effective zeta potential is larger than the value without 10 mM NaCl. This means that the viscosity of the double layer decreases when the salinity is high.

When a sufficiently strong electric field is applied, the electro-osmosis of a polymer solution shows nonlinear behaviors.[30, 32] These nonlinearities are theoretically analyzed using models of uniform non-Newtonian shear thinning fluids.[12–15] Assuming that the polymers remain localized in interfacial layers and the viscosity depends on the local shear rate, as in power-law fluids, their phenomenological parameters differ from those in the bulk, since the concentration in the interfacial layers differs from the bulk concentration.[30] Thus, the understanding of nonlinear electro-osmosis remains phenomenological. Furthermore, when shear flow is applied to polymer solutions near a wall, it is experimentally and theoretically confirmed that cross-stream migration toward the bulk is induced.[33–35] The concentration profiles of the polymer near the wall have been calculated, and the depletion length was found to dynamically grow tenfold larger than the gyration radius.[34] However, these hydrodynamic effects in electrokinetics have not been studied to date, to the best of our knowledge.

Fig. 4 shows the mobility as a function of the applied electric field. The polymer is CMC which is weakly negatively charged at pH 7. The Debye length of the background electrolyte solution (BGE) is $\lambda \approx 3.5$ nm, whereas that of the CMC solution is around

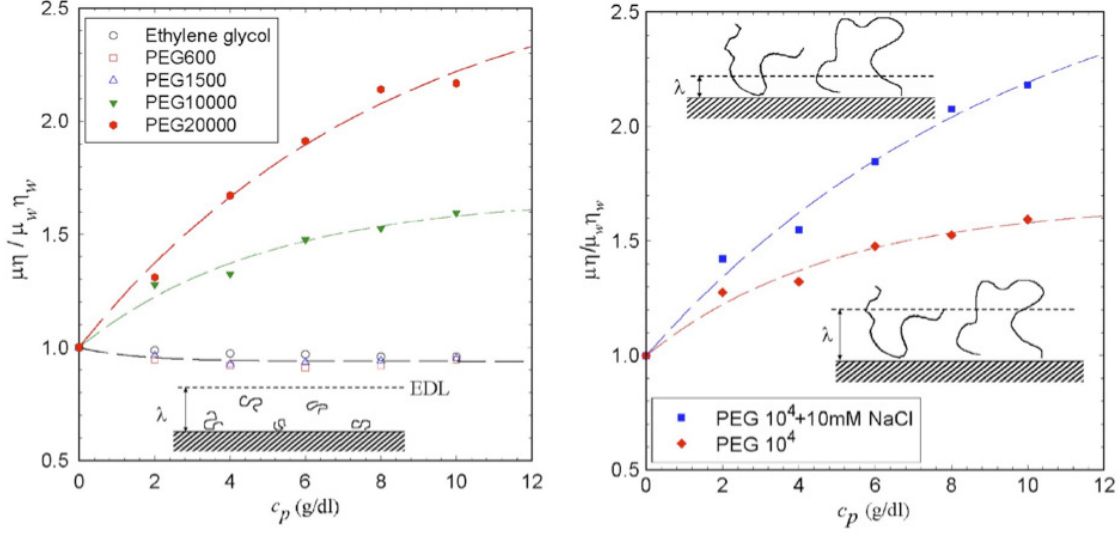


FIG. 3. Variation of the effective zeta potential $\mu(c)\eta(c)/\mu_w\eta_w$ with PEG concentration for various polymer molecular weights, where $\mu(c)$ is the electro-osmotic mobility at the polymer concentration c , $\mu_w = \mu(0)$ is the mobility of pure water, $\eta(c)$ is the solution viscosity at the polymer concentration c , and $\eta_w = \eta(0)$ is the viscosity of pure water. The lines are drawn only to guide the eyes. (left) Schematic drawing of the condition ($\lambda > \delta_0$) is shown. (right) For $M_w = 10^4$ with and without 10 mM NaCl, schematic drawing of the condition $\lambda < \delta_0$. Reprinted with permission from ref. [28]. Copyright 2007, AIP Publishing LLC. [doi:10.1063/1.2735279](https://doi.org/10.1063/1.2735279)

1 nm or less because of sodium ions from CMC molecules. In the figure, the results for the BGE, CMC solution with urea, and BGE with urea show constant electro-osmotic mobility, that is, linear behavior, whereas the results for the CMC solution show variations in the mobility, that is, nonlinear behavior. The solid line is the mobility calculated using the model of a uniform non-Newtonian liquid, which has a power-law constitutive equation with the parameters determined by bulk rheological measurement. The discrepancies between the solid line and the results for the CMC solution appear to come from the assumption of a uniform distribution of the polymer near the surface.

In this context, the present thesis discusses the linear and nonlinear behavior of electro-osmosis when we apply an external electric field to a polymer solution. For this purpose, this thesis is organized as follows. In the rest of section 1, the necessary background on electrokinetics is presented. Section 2 discusses the linear electro-osmotic flow of charged and uncharged polymer solutions. Section 3 discusses the nonlinear electro-osmotic flow

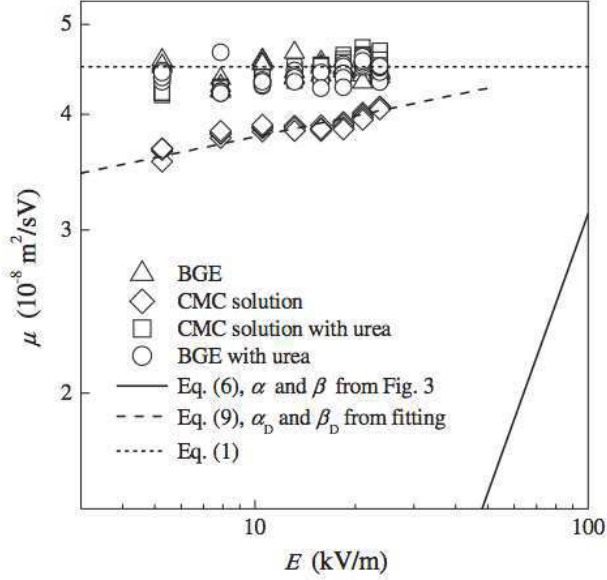


FIG. 4. Electro-osmotic mobility as a function of the applied electric field. Symbols are experimental results obtained with 1 percent CMC solution in fused silica capillaries (pH 7; 25 °C). The solid line is calculated using the theory of nonlinear electro-osmosis of non-Newtonian liquids with the parameters obtained by bulk rheology. The broken and dotted lines are guides to the eyes. The labels in the graph such as “Eq. (···)...” refer to the equations in the original publication. Reproduced from ref. [30] by permission of John Wiley & Sons Ltd. [doi:10.1002/elps.200800578](https://doi.org/10.1002/elps.200800578)

of non-adsorbing polymer solutions with low ionic strength. Section 4 outlines the main conclusions and discusses the future prospects.

1.2. Electrolyte solution

Salts such as sodium chloride and potassium iodide exist as ionic crystals at room temperature in the absence of a solvent. The salts are dissociated into two types of electrolytes: cations and anions, when we dissolve them in water. The energy difference between the two states in water is estimated simply as[36]

$$\Delta E = E_{\text{disassociated}} - E_{\text{associated}} = 0 - \left(-\frac{e^2}{4\pi\epsilon\epsilon_0} \frac{1}{a_+ + a_-} \right) > 0, \quad (1.1)$$

where e is the elementary charge, ϵ is the dielectric constant of water, ϵ_0 is the electric permittivity of vacuum, and a_+ (a_-) is the radius of the cation (anion). According to the

TABLE 1. Properties of electrolytes with $\ell_B = 0.709$ nm at $T = 293.15$ K.

	a_+ [nm][37]	a_- [nm][37]	X_s (theory)	M_w [g/mol][38]	M_s [g/l][38]	X_s (reference)
LiCl	0.074	0.181	0.0620	42.39	832	0.2613
NaCl	0.102	0.181	0.0817	58.44	359	0.0997
KCl	0.138	0.181	0.1083	74.55	344	0.0768
KBr	0.138	0.196	0.1197	119.002	652	0.0899
KI	0.138	0.220	0.1380	166.003	1445	0.1356

equation for the mixing entropy, the free energy is

$$\Delta F = \Delta E + k_B T \ln X_s, \quad (1.2)$$

where $k_B T$ is the thermal energy, and X_s is the molar fraction of the electrolyte. The dissolution is saturated at $\Delta F = 0$, and it gives

$$X_s = \exp \left(-\frac{\ell_B}{a_+ + a_-} \right), \quad (1.3)$$

where ℓ_B is the Bjerrum length,

$$\ell_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}, \quad (1.4)$$

and $\ell_B \approx 0.7$ nm at room temperature. Tab. 1 shows the molar fraction estimated using the above theory and the value from ref. [38]. The two values are of the same order except for lithium chloride. The saturation molar fraction $X_s \sim 0.1$ corresponds to the molar concentration ~ 5 M. For the salt in a vacuum, $X_s \approx \exp(-\epsilon\ell_B/(a_+ + a_-))$, and it cannot be dissociated. In this thesis, the concentration below 1 M is considered.

Mobile ions in an electrolyte solution can produce electrical currents. The conductivity is proportional to the concentration of each ion in the dilute limit as[39]

$$\Lambda_0 = e^2 \left(\frac{c^+}{\zeta^+} + \frac{c^-}{\zeta^-} \right), \quad (1.5)$$

where Λ_0 is the conductivity, which is the current density divided by the electric field; ζ^+ (ζ^-) is the friction coefficient of cations (anions); and c^+ (c^-) is the concentration of cations (anions).

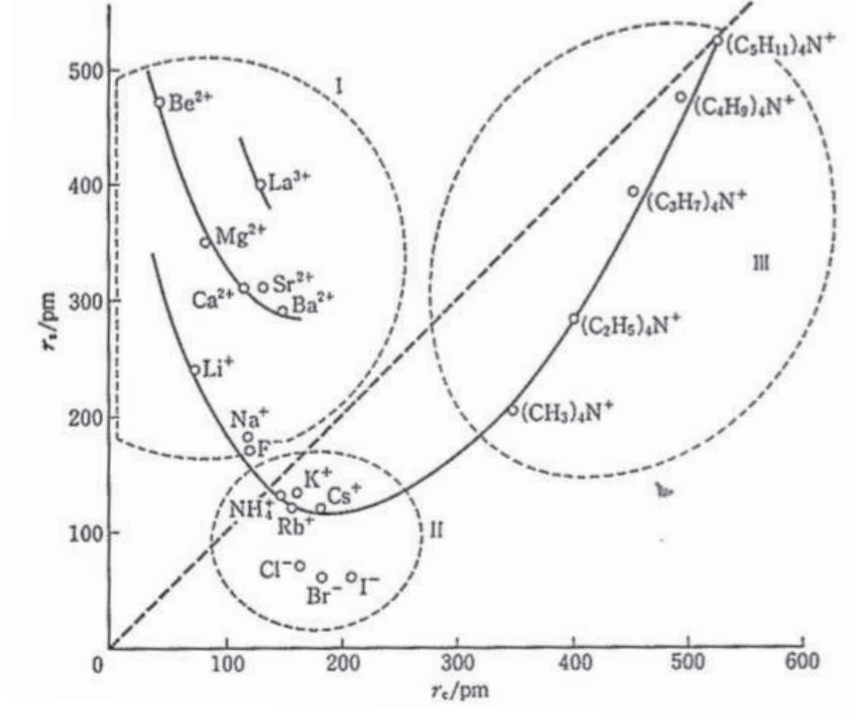


FIG. 5. Relation between the ionic radii and Stokes radii. Reprinted with permission from ref. [39]. Copyright 1985 Shokabo.

Assuming that the Stokes law is still valid on the atomistic scale, we can estimate the Stokes radius of the ions a_s^+ (a_s^-) as

$$a_s^\pm = \frac{\zeta^\pm}{6\pi\eta}, \quad (1.6)$$

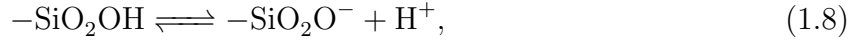
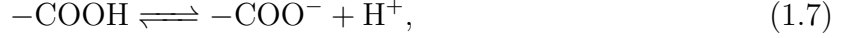
where η is the viscosity of water.

Fig. 5 shows the relation between the ionic radii and Stokes radii. Small cations such as Li^+ , and Be^{2+} have larger Stokes radii than their ionic radii, because the electrostatic interaction between the ions and water molecules hydrates the ion. On the other hand, K^+ , Cl^- , Br^- , and I^- have smaller Stokes radii than ionic radii. The reason for this is still problematic, and further discussions are reported in refs. [40–42].

1.3. Structure of electric double layer

A solid surface in contact with an electrolyte solution is often charged. The origin of the surface charge varies; (a) induced charge in metals and dielectrics, (b) dissociable groups on the surface (including metal oxides), (c) ion adsorption from the solution, (d) an imbalance of

insoluble ionic crystals, and (e) crystal lattice defects.[3, 4] The most important and common mechanism in electrokinetics is (b), dissociable groups on the surface, for example, a colloidal surface or fused silica. Examples of the dissociable group include carboxyl ($-\text{COOH}$), sulfonate ($-\text{SO}_2\text{OH}$), and amine ($-\text{NH}_2$). They dissociate ions as



An ion that has a sign opposite to that of the surface charge is called a counterion, and an ion that has the same sign is called a coion. In this thesis, we consider mainly a 1:1 electrolyte solution at a concentration of 10^{-5} – 1 M. Because of spontaneous water self-dissociation, the concentration of hydroxide ions and hydrogen ions is 10^{-7} M at pH 7. Therefore, we can neglect water dissociation because the salt concentration is much larger than the concentration of the hydroxide and hydrogen ions.

In the solution phase, the ion distribution becomes nonuniform owing to the electrified surface. The nanoscale layer structure is called the electric double layer. It is known that there is an interfacial layer of 0.1–0.5 nm in which water molecules have anomalous structure. This layer is called the Stern layer and is discussed further in section 1.5. The layer above the Stern layer is called the diffuse layer, and its thickness is characterized using the Debye length. The diffuse layer is well modeled using the Poisson-Boltzmann equation. However, modeling the Stern layer is difficult, and many ideas are still being proposed.

Outsides of the Stern layer, the ion distribution obeys the Boltzmann distribution. The concentrations of cations and anions are

$$c_{\pm} = c_0 \exp\left(-\frac{\pm e\psi}{k_{\text{B}}T}\right), \quad (1.10)$$

where ψ is the local electrostatic potential, and c_0 is the ion concentration at $\psi = 0$. Combining eq. (1.10) with the Poisson equation as

$$\nabla \cdot (\varepsilon \varepsilon_0 \nabla \psi) = -\rho = -e(c_+ - c_-), \quad (1.11)$$

where ρ is the charge density, we obtain the Poisson-Boltzmann equation as

$$\nabla \cdot (\varepsilon \varepsilon_0 \nabla \psi) = ec_0 \sinh\left(\frac{e\psi}{k_{\text{B}}T}\right). \quad (1.12)$$

We develop the theory of the diffuse layer of charged planar surfaces. For simplicity, the charged surface extends in the xy direction at $z = 0$, and we ignore the Stern layer. The dielectric constant is assumed to be uniform; thus, the Poisson-Boltzmann equation is given by

$$\frac{d^2\Psi}{dz^2} = \kappa^2 \sinh \Psi, \quad (1.13)$$

where $\Psi = e\psi/k_B T$ is the reduced potential, and κ is given by

$$\kappa = \left(\frac{2e^2 c_0}{\varepsilon \varepsilon_0 k_B T} \right)^{1/2}, \quad (1.14)$$

where κ^{-1} is the Debye length. The boundary conditions of eq. (1.13) are

$$\varepsilon \varepsilon_0 \left. \frac{d\Psi}{dz} \right|_{z=0} = -\frac{e\sigma_0}{k_B T}, \quad (1.15)$$

or

$$\Psi|_{z=0} = \Psi_0 = \frac{e\psi_0}{k_B T}, \quad (1.16)$$

where σ_0 is the surface charge density, and ψ_0 is the surface potential. In the limit $z \rightarrow \infty$, the potential should be zero:

$$\Psi|_{z \rightarrow \infty} = 0. \quad (1.17)$$

First, we linearize eq. (1.13) and obtain the approximated solution that is valid for a small surface potential. The linearized Poisson-Boltzmann equation is

$$\frac{d^2\Psi}{dz^2} = \kappa^2 \Psi, \quad (1.18)$$

and its solution that satisfies the boundary conditions is

$$\psi = \psi_0 e^{-\kappa z}. \quad (1.19)$$

This equation shows that the potential decays with the Debye length scale κ^{-1} . Using this solution, the surface charge density is given as

$$\sigma_0 = \varepsilon \varepsilon_0 \kappa \psi_0, \quad (1.20)$$

which is a linear relationship.

Exact solutions of eq. (1.13) with the boundary conditions are easily obtained. Multiplying both side of eq. (1.13) by $d\Psi/dz$, we can integrate it as

$$\frac{1}{2} \left(\frac{d\Psi}{dz} \right)^2 - \kappa^2 \cosh \Psi = \text{const.}, \quad (1.21)$$

where the constant is $-\kappa^2$ using the boundary condition at $z \rightarrow \infty$. We assume $\psi_0 > 0$; then $d\Psi/dz < 0$, and

$$\frac{d\Psi}{dz} = -\sqrt{2\kappa^2(\cosh \Psi - 1)} = -2\kappa \sinh \frac{\Psi}{2}. \quad (1.22)$$

Therefore, we can integrate it again as

$$\int_{\Psi_0}^{\Psi} \frac{d(\Psi/2)}{\sinh(\Psi/2)} = -\kappa \int_0^z dz. \quad (1.23)$$

The left-hand side of the equation can be calculated using the relation $\int (\sinh x)^{-1} dx = \ln |\tanh(x/2)|$ as

$$\ln \frac{\tanh(\Psi/4)}{\tanh(\Psi_0/4)} = -\kappa z, \quad (1.24)$$

and finally, we obtain

$$\psi = \frac{4k_B T}{e} \operatorname{arctanh} [e^{-\kappa z} \tanh(\Psi_0/4)] = \frac{2k_B T}{e} \ln \frac{1 + e^{-\kappa z} \tanh(\Psi_0/4)}{1 - e^{-\kappa z} \tanh(\Psi_0/4)}, \quad (1.25)$$

where this solution is also valid when $\psi_0 < 0$. The derivative of eq. (1.25) is eq. (1.22). At $z = 0$, the equation gives the relation between σ_0 and ψ_0 as

$$\sigma_0 = \frac{2\varepsilon\varepsilon_0 k_B T \kappa}{e} \sinh \left(\frac{e\psi_0}{2k_B T} \right), \quad (1.26)$$

which is the nonlinear version of eq. (1.20).

Fig. 6 is a plot of the potential profiles. The solid line is the nonlinear solution, eq. (1.25) whereas the dotted line is the linear solution, eq. (1.19). We use the same surface charge density, $\sigma_0 = -0.5 \text{ e/nm}^2$, and the salt concentration $c_0 = 100 \text{ mM}$. Note that the magnitude of the surface potential obtained by the nonlinear solution is smaller than that obtained using the linear solution at the same surface charge density.

The static property of the double layer is characterized by the differential capacitance. For the interface between mercury and an electrolyte solution, the differential capacitance can be easily obtained by measuring the surface tension.[3, 4] The differential capacitance C is defined as

$$C = \frac{d\sigma_0}{d\psi_0}. \quad (1.27)$$

The derivative of eq. (1.20) is

$$C = \varepsilon\varepsilon_0 \kappa, \quad (1.28)$$

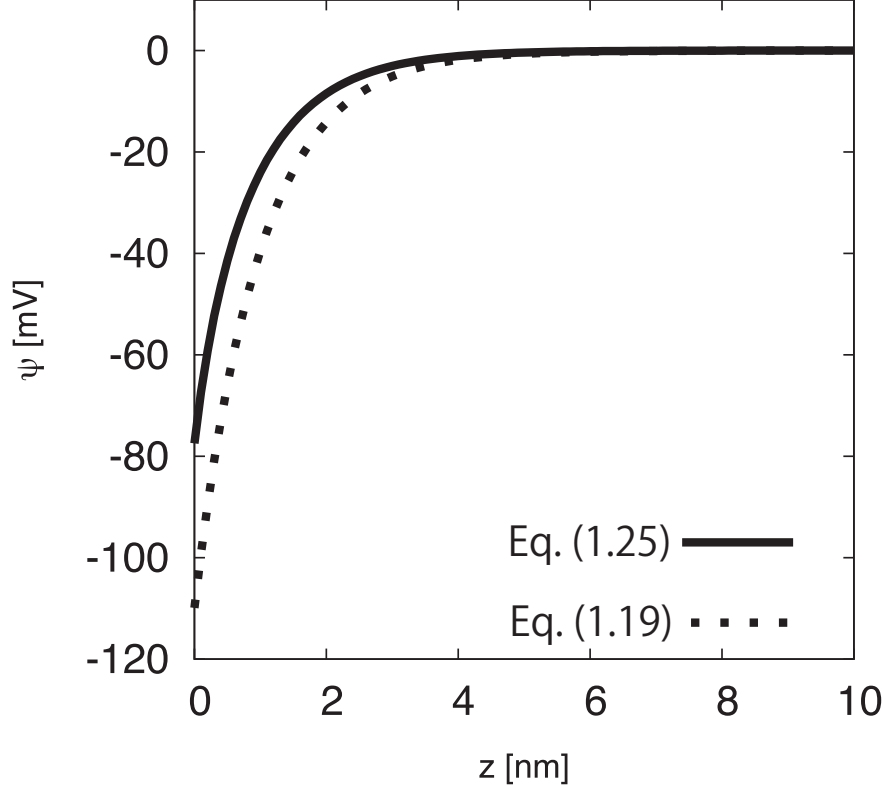


FIG. 6. Plot of the potential profiles for the nonlinear solution [solid line, eq. (1.25)] and linear solution [dotted line, eq. (1.19)]. We use the same surface charge density, $\sigma_0 = -0.5 e/\text{nm}^2$, and the salt concentration $c_0 = 100 \text{ mM}$.

which indicates the capacitance of a conductor of electric permittivity $\varepsilon\varepsilon_0$ with thickness κ^{-1} .

The derivative of eq. (1.26) is

$$C = \varepsilon\varepsilon_0\kappa \cosh\left(\frac{e\psi_0}{2k_B T}\right) = \varepsilon\varepsilon_0\sqrt{\kappa^2 + \lambda_{\text{GC}}^{-2}}, \quad (1.29)$$

where λ_{GC} is the Gouy-Chapman length,

$$\lambda_{\text{GC}} = \frac{2\varepsilon\varepsilon_0 k_B T}{e|\sigma_0|}. \quad (1.30)$$

In the limit of high surface charge density, $\sigma_0 \rightarrow -\infty$, the capacitance behaves as

$$C \rightarrow \frac{\varepsilon\varepsilon_0\kappa}{2} \exp\left(-\frac{e\psi_0}{2k_B T}\right) = \frac{\varepsilon\varepsilon_0}{\lambda_{\text{GC}}}, \quad (1.31)$$

which is the capacitance of a conductor of permittivity $\varepsilon\varepsilon_0$ with thickness λ_{GC} .

Fig. 7 shows the differential surface capacitance for different concentrations. The panel on the left was obtained experimentally by measuring the surface tension of a mercury NaF

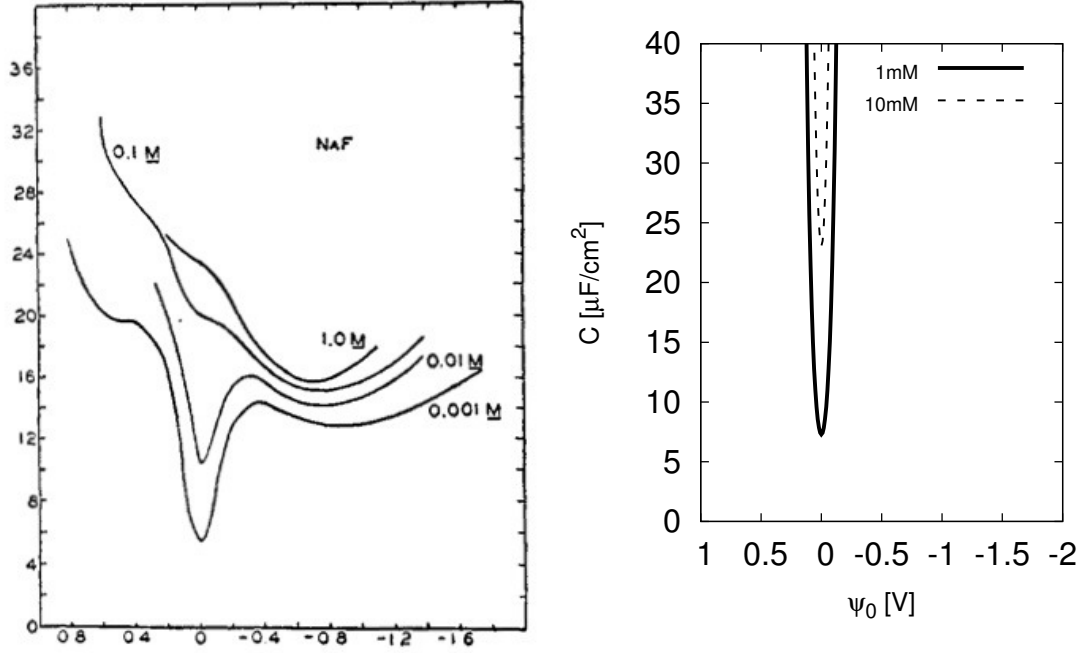


FIG. 7. Plot of the differential capacitance ($\mu\text{F}/\text{cm}^2$) as a function of the surface potential (V). (left) The electrolyte is NaF at different concentrations at 25 °C. Reprinted with permission from ref. [43]. Copyright (1947) American Chemical Society. [doi:10.1021/cr60130a002](https://doi.org/10.1021/cr60130a002) (right) Theoretical curves calculated using eq. (1.29).

solution.[43] For dilute solutions and low surface potential, the experimentally measured capacitances exhibit as parabolic behavior. However, in concentrated solution or at high surface potential, the curves have other peaks and are complicated. The panel on the right shows the theoretical curves predicted by eq. (1.29). Without the Stern layer, the capacitance abruptly diverges to infinity with increasing surface potential. Thus, the Gouy-Chapman model exhibits a large discrepancy from the experimental observations.

1.4. Electrokinetic transport

When a charged-surface capillary is filled with an electrolyte solution and subjected to an electric field E and a pressure difference $P(= -\nabla_x p)$, a volume flux and electric current are induced along the external fields. Here p is the pressure. When E and P are sufficiently

weak, the volume flux and the electric current are given by

$$V = L_{11}P + L_{12}E, \quad (1.32)$$

$$J = L_{21}P + L_{22}E. \quad (1.33)$$

V and J are the mean volume flux and mean electric current, respectively, and L_{ij} represents the electrokinetic transport coefficients. This thesis focuses on $L_{12}(= \mu)$, which is known as the *electro-osmotic mobility*.

We derive a standard model that can describe the hydrodynamics of an electrolyte solution. The velocity field $\mathbf{u}$ obeys the Navier-Stokes equation as

$$\rho_m \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = \nabla \cdot \boldsymbol{\sigma}, \quad (1.34)$$

where ρ_m is the mass density, and $\boldsymbol{\sigma}$ is the stress tensor. The stress tensor has contributions from

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^U + \boldsymbol{\sigma}^E, \quad (1.35)$$

where $\boldsymbol{\sigma}^U$ is the mechanical part of the stress tensor, and $\boldsymbol{\sigma}^E$ is the Maxwell stress tensor. They are given by

$$\boldsymbol{\sigma}^U = -p' \mathbf{I} + \eta \left[\nabla \otimes \mathbf{u} + (\nabla \otimes \mathbf{u})^t \right], \quad (1.36)$$

$$\boldsymbol{\sigma}^E = \varepsilon \varepsilon_0 (\nabla \psi \otimes \nabla \psi) - \frac{\varepsilon \varepsilon_0}{2} |\nabla \psi|^2 \mathbf{I}, \quad (1.37)$$

where p' is the renormalized pressure, $\mathbf{I}$ is the unit tensor, η is the viscosity of the solution, and $\otimes$ is the tensor product operator. The renormalized pressure is given by

$$p' = p + k_B T (c^+ + c^-), \quad (1.38)$$

where the first term is the mechanical pressure, and the second is the osmotic pressure. In addition, the velocity field satisfies the incompressible condition given by

$$\nabla \cdot \mathbf{u} = 0. \quad (1.39)$$

The concentration dynamics are given by

$$\frac{\partial c^+}{\partial t} = -\nabla \cdot (c^+ \mathbf{u}^+), \quad (1.40)$$

$$\frac{\partial c^-}{\partial t} = -\nabla \cdot (c^- \mathbf{u}^-), \quad (1.41)$$

where

$$\mathbf{u}^\pm = \mathbf{u} - \frac{1}{\zeta^\pm} \nabla \mu^\pm. \quad (1.42)$$

The electro-chemical potential of ions, $\mu^\pm$, is given by

$$\mu^+ = k_B T \ln(c^+ a_+^3) + e\psi, \quad (1.43)$$

$$\mu^- = k_B T \ln(c^- a_-^3) - e\psi. \quad (1.44)$$

The local electrostatic potential satisfies the Poisson equation eq. (1.11).

We consider an aqueous electrolyte solution in a charged slit of width $2L$. We calculate the volume flux and electric current when we apply the electric field and pressure difference in the x direction.

$$V = \frac{1}{2L} \int_0^{2L} u_x(z) dz, \quad (1.45)$$

$$J = \frac{1}{2L} \int_0^{2L} j_x(z) dz, \quad (1.46)$$

where

$$\mathbf{j} = e (c^+ \mathbf{u}^+ - c^- \mathbf{u}^-). \quad (1.47)$$

On the assumption that the ion distribution is uniform in the xy direction and the velocity field has only an x component, the ion distribution and potential are determined by the Poisson-Boltzmann equation eq. (1.13), and the velocity field is determined by the steady-state solution of the Navier-Stokes equation, given by

$$P + \frac{d}{dz} \left(\eta \frac{du_x}{dz} \right) + \rho E = 0. \quad (1.48)$$

This can be solved with the boundary condition

$$\psi|_{z=0} = \psi|_{z=2L} = \psi_0, \quad (1.49)$$

and we impose the no-slip boundary condition as

$$u_x|_{z=0} = u_x|_{z=2L} = 0, \quad (1.50)$$

as

$$u_x = \frac{z(2L - z)}{2\eta} P + \frac{\varepsilon \varepsilon_0 (\psi - \psi_0)}{\eta} E. \quad (1.51)$$

The potential can be obtained using the Debye-Hückel approximation as

$$\psi(z) = \frac{e^{-\kappa(z-L)} + e^{\kappa(z-L)}}{e^{\kappa L} + e^{-\kappa L}} \psi_0. \quad (1.52)$$

The integral of eq. (1.51) gives L_{11} and μ as

$$L_{11} = \frac{L^2}{3\eta}, \quad (1.53)$$

$$\mu = -\frac{\varepsilon\varepsilon_0\psi_0}{\eta} \left[1 - \frac{\sinh(\kappa L)}{\kappa L \cosh(\kappa L)} \right]. \quad (1.54)$$

The current density is given by

$$j_x = e(c^+ - c^-) \frac{z(2L - z)}{2\eta} P + \left[e(c^+ - c^-) \frac{\varepsilon\varepsilon_0(\psi - \psi_0)}{\eta} + e^2 \left(\frac{c^+}{\zeta^+} + \frac{c^-}{\zeta^-} \right) \right] E. \quad (1.55)$$

The first term is the mechanical current and is related to L_{21} as

$$L_{21} = \frac{1}{2L} \int_0^{2L} \rho \frac{z(2L - z)}{2\eta} dz = \frac{1}{2L} \int_0^{2L} \frac{\varepsilon\varepsilon_0(\psi - \psi_0)}{\eta} dz = \mu, \quad (1.56)$$

which is equal to the electro-osmotic mobility. The equivalence of the two transport coefficients is the result of the Lorentz reciprocal theorem in Stokes hydrodynamics.[44, 45] The second term is the convective contribution of the current, given by

$$L_{22}^{\text{conv}} = \frac{1}{2L} \frac{(\varepsilon\varepsilon_0)^2}{\eta} \int_0^{2L} \left(\frac{d\psi}{dz} \right)^2 dz = \frac{1}{2L} \frac{(\varepsilon\varepsilon_0)^2}{\eta} \frac{\kappa\psi_0^2}{\sinh^2(\kappa L)} [\sinh(2\kappa L) - 2\kappa L]. \quad (1.57)$$

The third term is the conductive contribution of the current, and is divided into the bulk and surface components as

$$L_{22}^{\text{cond,bulk}} = e^2 c_0 \left(\frac{1}{\zeta^+} + \frac{1}{\zeta^-} \right), \quad (1.58)$$

which is equal to Λ_0 in eq. (1.5), and

$$L_{22}^{\text{cond,surf}} = \frac{e^2}{2L} \int_0^{2L} \left(\frac{c^+ - c_0}{\zeta^+} + \frac{c^- - c_0}{\zeta^-} \right) dz, \quad (1.59)$$

where the concentration difference in the Debye-Hückel limit is given by

$$c^\pm - c_0 = \mp \frac{e\psi}{k_B T} c_0. \quad (1.60)$$

Therefore,

$$L_{22}^{\text{cond,surf}} = e^2 c_0 \left(-\frac{e\psi_0}{k_B T} \right) \frac{\sinh(\kappa L)}{\kappa L \cosh(\kappa L)} \left(\frac{1}{\zeta^+} - \frac{1}{\zeta^-} \right). \quad (1.61)$$

Finally,

$$L_{22} = L_{22}^{\text{conv}} + L_{22}^{\text{cond,bulk}} + L_{22}^{\text{cond,surf}}. \quad (1.62)$$

When the cation and anion have the same Stokes radius, the conductivity due to the surfaces is of the same order as $\mathcal{O}(\psi_0^2)$ and is quite small under the Debye-Hückel approximation.

An analysis without the Debye-Hückel approximation in a slit geometry is described in refs. [46, 47], and an analysis in cylindrical geometry is described in ref. [48].

To discuss the electro-osmosis and surface conductivity further, we consider the upper half of the space on an infinite plane using the nonlinear solution eq. (1.25). The electro-osmotic mobility is then defined as

$$\mu = \frac{u_x|_{z \rightarrow \infty}}{E} = -\frac{\varepsilon\varepsilon_0\psi_0}{\eta}, \quad (1.63)$$

which is linear with respect to the surface potential, although the potential profile is nonlinear with respect to the surface potential. This nonlinearity is violated in the electrophoresis of spherical particles with high surface potential.[49] The convective contribution of the surface current is given by

$$L_{22}^{\text{conv}} = \frac{1}{2L} \frac{(\varepsilon\varepsilon_0)^2}{\eta} \int_{\psi_0}^0 \frac{d\psi}{dz} d\psi = \frac{2}{\eta} \left(\frac{2\varepsilon\varepsilon_0 k_B T \kappa}{e} \sinh \frac{\Psi_0}{4} \right)^2, \quad (1.64)$$

where L is the characteristic system size, although we consider the upper half of the space. The conductive contribution of the surface current is

$$L_{22}^{\text{cond,surf}} = \frac{e^2}{2L} \int_0^\infty \left[\frac{c_0}{\zeta^+} (e^{-\Psi} - 1) + \frac{c_0}{\zeta^-} (e^{\Psi} - 1) \right] \frac{dz}{d\Psi} d\Psi = \frac{e^2 c_0}{\kappa L} \left(\frac{e^{-\Psi_0/2} - 1}{\zeta^+} + \frac{e^{\Psi_0/2} - 1}{\zeta^-} \right). \quad (1.65)$$

$$L_{22}^{\text{conv}} + L_{22}^{\text{cond,surf}} = \frac{e^2 c_0}{\kappa L} \left[\frac{e^{-\Psi_0/2} - 1}{\zeta^+} (1 + m^+) + \frac{e^{\Psi_0/2} - 1}{\zeta^-} (1 + m^-) \right], \quad (1.66)$$

where

$$m^\pm = \frac{\zeta^\pm}{2\pi\eta\ell_B} \quad (1.67)$$

is the ratio of the convective contribution compared to the conductive contribution. We assume $\zeta_0 = \zeta^+ = \zeta^-$ for simplicity; thus,

$$L_{22}^{\text{conv}} + L_{22}^{\text{cond,surf}} = \frac{4}{\kappa L} \sinh^2 \frac{\Psi_0}{4} \left[\frac{e^2 c_0}{\zeta_0} + \frac{(\varepsilon\varepsilon_0 k_B T \kappa)^2}{\eta e^2} \right]. \quad (1.68)$$

$$Du = \frac{L_{22}^{\text{conv}} + L_{22}^{\text{cond,surf}}}{L_{22}^{\text{cond,bulk}}} \quad (1.69)$$

is the Dukhin number, which characterizes the surface conduction of a system with a high surface charge and small Debye length.[1, 3]

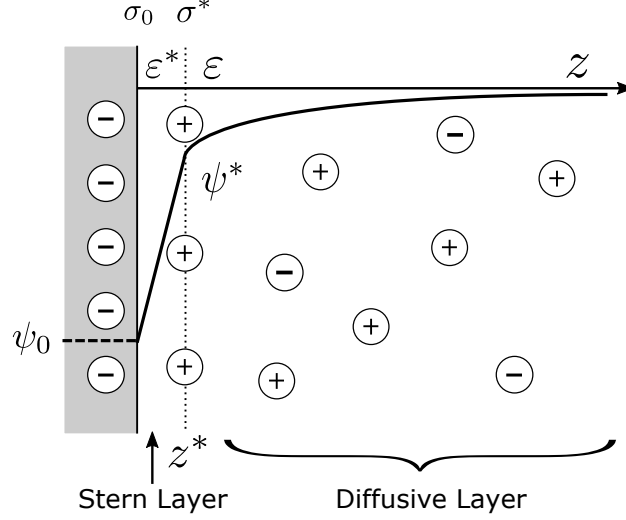


FIG. 8. Sketch of the Gouy-Stern double-layer model with specific adsorption of ions.

1.5. Theory of the Stern layer

1.5.1. Gouy-Stern double-layer model with specific adsorption of ions

We introduce a charge-free layer with thickness z^* and the dielectric constant ε^* as the Stern layer and assume that specific adsorption of ions occurs on the boundary between the Stern layer and the diffuse layer.[43] If we consider only the adsorption of cation, the surface charge density at the boundary induced by specific adsorption, σ^* , is expressed using the equilibrium constant K as

$$\sigma^* = \sigma_M \frac{K c_0 e^{-\Psi^*}}{1 + K c_0 e^{-\Psi^*}}, \quad (1.70)$$

where σ_M is the maximum surface charge density at the boundary, and $\Psi^* = e\psi^*/k_B T$ is the reduced electrostatic potential at the boundary. Fig. 8 shows the sketch of this model. The potential at the boundary is obtained solving the equation as

$$\sigma_0 + \sigma^* = \frac{2\varepsilon\varepsilon_0 k_B T \kappa}{e} \sinh\left(\frac{\Psi^*}{2}\right), \quad (1.71)$$

and eq. (1.70). The surface potential is

$$\psi_0 = \psi^* + \frac{\sigma_0}{C_s}, \quad (1.72)$$

where C_s is the capacitance of the Stern layer. When it is modeled as a layer with thickness z^* and dielectric constant ε^* , the capacitance of the Stern layer is

$$C_s = \frac{\varepsilon^* \varepsilon_0}{z^*}. \quad (1.73)$$

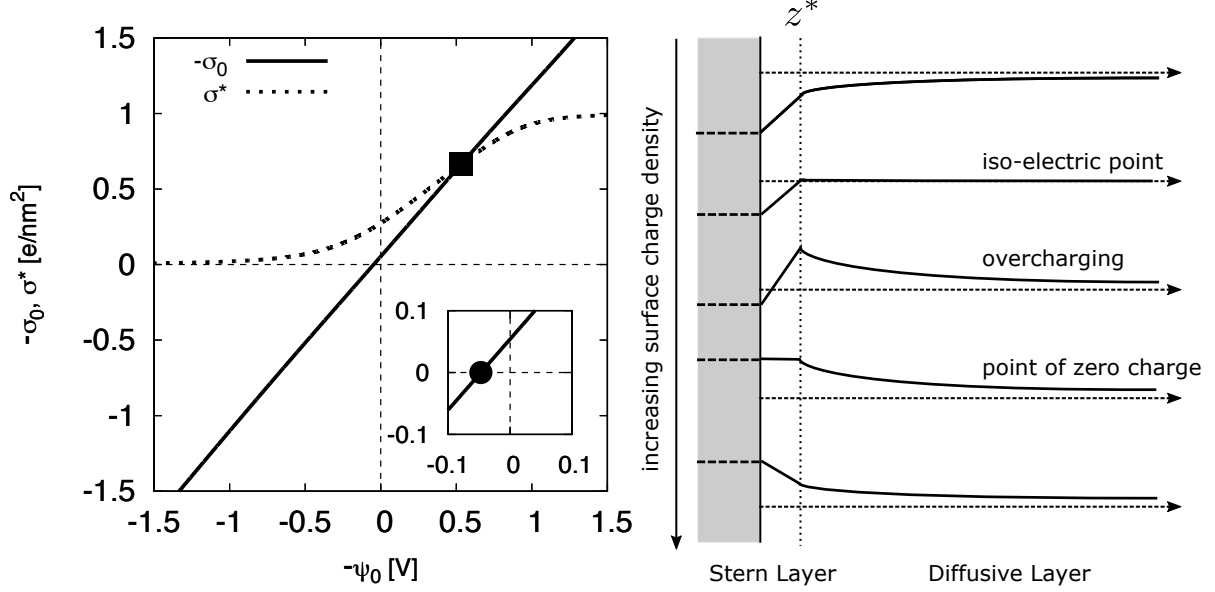


FIG. 9. (left) Surface charge density is plotted as a function of surface potential (solid line) and charge density of specific adsorption (broken line). Black square is the isoelectric point. Inset shows a magnification of the region near the origin; black circle is the point of zero charge. The concentration of salts is 100 mM, $K = 20 \text{ M}^{-1}$, $C_s = 20 \mu\text{F}/\text{cm}^2$, and $\sigma_M = 1.0 e/\text{nm}^2$. (right) Sketch of the potential profile with increasing surface charge density.

In the left-hand panel of Fig. 9, the surface charge density and adsorbed charge density are plotted as a function of the surface potential. When

$$\sigma_0 = -\sigma_M \frac{Kc_0}{1 + Kc_0}, \quad (1.74)$$

the surface charge is totally neutralized, as $\sigma_0 + \sigma^* = 0$ and $\psi^* = 0$. We call this point the isoelectric point and indicate it by a black square in Fig. 9. Above the isoelectric point, the amount of adsorbed ions becomes saturated. The inset in the panel on the left shows a magnification of the main graph. When the surface potential is zero, a finite negative surface charge remains on the surface. The black circle in the inset is the point of zero charge, where $\sigma_0 = 0$. At the point of zero charge, the surface potential is positive finite because of the adsorption of cations. The panel on the right in Fig. 9 shows the potential profiles with increasing surface charge density. Between the isoelectric point and the point of zero charge, we have a peak in the potential profile. We call these states overcharging, charge inversion, or super-equivalent. In the overcharging states, we can find the case that the signs of ψ_0 and ψ^* differ.

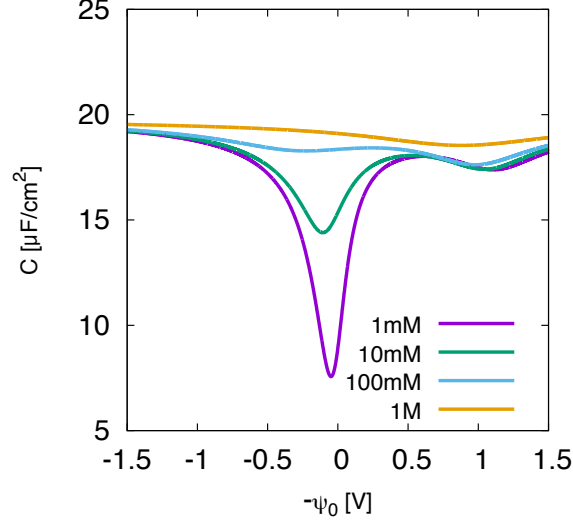


FIG. 10. Capacitances calculated using eq. (1.76) (solid lines) for different concentrations. $K = 20 \text{ M}^{-1}$, $C_s = 20 \mu\text{F}/\text{cm}^2$, and $\sigma_M = 1.0 e/\text{nm}^2$ are chosen arbitrarily.

Differentiation of eqs. (1.70) and (1.71) yields

$$\frac{d\sigma_0}{d\psi^*} = \frac{e}{k_B T} \left[\frac{\sigma_M K c_0 e^{-\Psi^*}}{(1 + K c_0 e^{-\Psi^*})^2} + \frac{\varepsilon \varepsilon_0 k_B T \kappa}{e} \cosh \frac{\Psi^*}{2} \right], \quad (1.75)$$

and thus, the capacitance is

$$C = \left(\frac{d\psi^*}{d\sigma_0} + C_s^{-1} \right)^{-1}. \quad (1.76)$$

When the specific adsorption is neglected ($\sigma^* = 0$), the total capacitance is

$$C = \left(\frac{1}{\varepsilon \varepsilon_0 \sqrt{\kappa^2 + \lambda_{GC}^{-2}}} + C_s^{-1} \right)^{-1}. \quad (1.77)$$

Fig. 10 shows the differential capacitances as a function of the surface potential for an arbitrarily chosen K , C_s , and σ_M . The shape is antisymmetric with respect to $\psi_0 = 0$, and we have a maximum around $\psi_0 = -0.5 \text{ V}$ due to the saturation of adsorption. The same behavior is obtained for theoretical models that include the volume effect of ions.[50, 51] The appearance of the lines is more consistent with the experimental results (Fig. 7, left) than with the Gouy-Chapman theory (Fig. 7, right).

1.5.2. Shear plane and saturation of electrokinetic charge

So far we have discussed the static properties of the Stern layer. In this section, we consider the dynamic properties of the Stern layer.

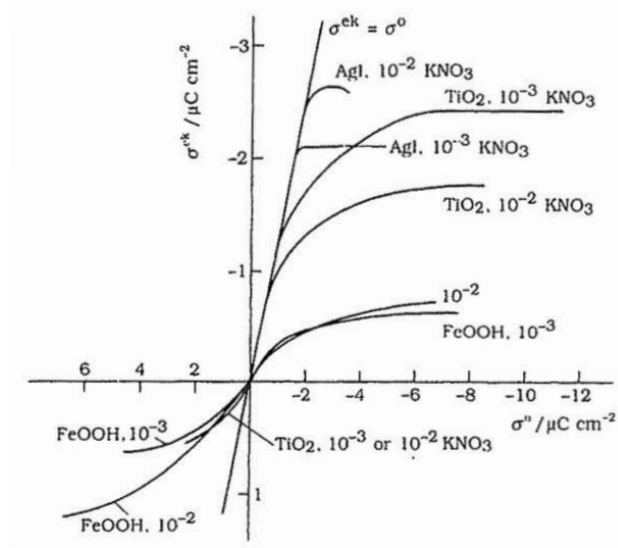


FIG. 11. Plot of the electrokinetic surface charge density as a function of the surface charge density obtained by titration. Reprinted from ref. [52]. Copyright (1994), with permission from Elsevier. doi:10.1016/0927-7757(94)02727-7

In section 1.4, the zeta potential is defined as the potential at the slip plane. By measuring the electro-osmotic mobility, we can obtain the zeta potential as

$$\zeta = -\frac{\eta\mu}{\varepsilon\varepsilon_0} \quad (1.78)$$

and the electrokinetic surface charge density as

$$\sigma_{ek} = \frac{2\varepsilon\varepsilon_0 k_B T \kappa}{e} \sinh\left(\frac{e\zeta}{2k_B T}\right). \quad (1.79)$$

If the slip plane is identical to the solid surface, we obtain $\zeta = \psi_0$ and $\sigma_{ek} = \sigma_0$.

In Fig. 11, the electrokinetic surface charge density is plotted as a function of the surface charge density measured by titration.[52] We find that for a strongly charged surface, the electrokinetic charge is saturated. We call this *saturation of the electrokinetic charge*. This behavior implies the existence of a stagnant layer.

Next, we consider the thickness of the stagnant layer. In this thesis, we assume that the boundary between the Stern layer and the diffuse layer is equivalent to the slip plane. Therefore,

$$\zeta = \psi^*. \quad (1.80)$$

This assumption is validated by comparing the ψ^* obtained from the critical coagulation

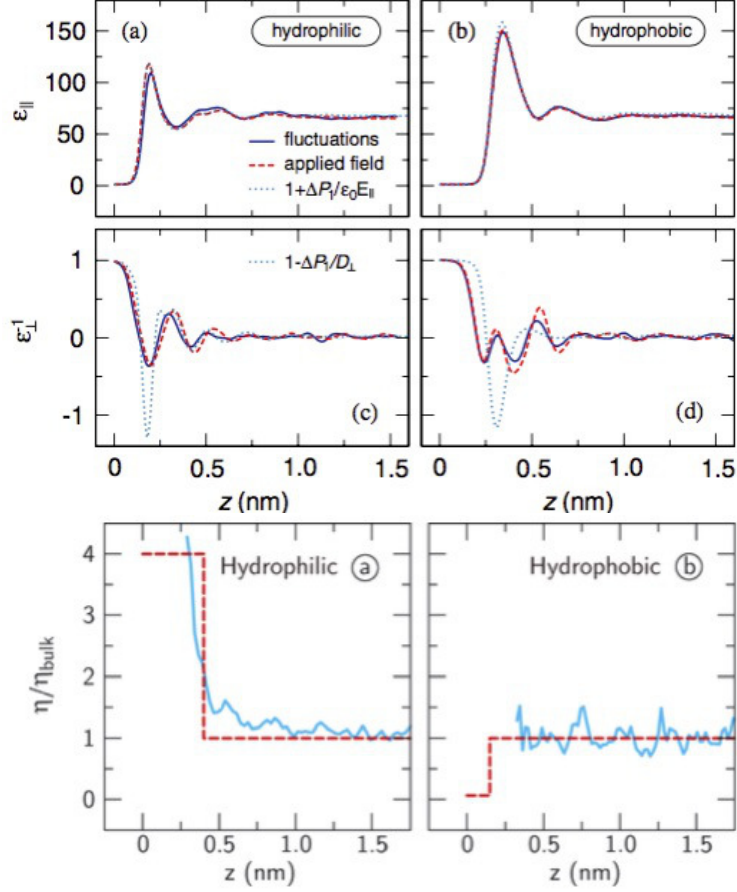


FIG. 12. (top) Profile of the dielectric constant normal and parallel to the surface measured by molecular dynamics simulation. Box functions are determined by conserving $\int_0^\infty \varepsilon_\perp^{-1}(z)dz$. Reprinted figure with permission from ref. [54]. Copyright (2011) by the American Physical Society. [doi:10.1103/PhysRevLett.107.166102](https://doi.org/10.1103/PhysRevLett.107.166102) (bottom) Profile of the shear viscosity measured by molecular dynamics simulation. Reprinted with permission from ref. [55]. Copyright 2013 American Chemical Society. [doi:10.1021/jp402482q](https://doi.org/10.1021/jp402482q)

concentration and the ζ values obtained from electrophoresis experiments.[53] Under this assumption, the contents of section 1.4 can be reproduced by taking ψ_0 as ψ^* .

1.5.3. Continuum model using nonuniform permittivity and viscosity

The structure of the Stern layer was revealed recently using a molecular dynamics simulation. Fig. 12 shows the dielectric and viscosity profiles of the electric double layer for hydrophilic and hydrophobic surfaces.[54, 55] The surfaces are composed of face-centered

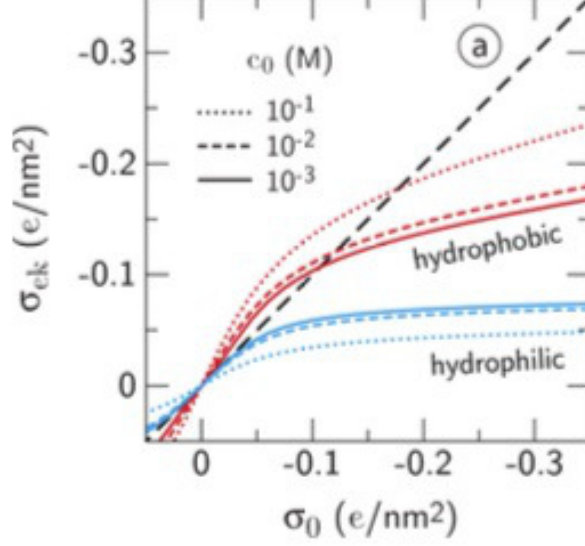


FIG. 13. Electrokinetic surface charge density as a function of the bare surface charge density at various salt concentrations, for hydrophilic surfaces calculated using $z_s = 0.30$ nm and $\eta/\eta_i = 1/3$ in combination with $z^* = 0.10$ nm, and for hydrophobic surfaces calculated using $z_s = 0.15$ nm and $\eta/\eta_i = 15$ in combination with $z^* = 0.12$ nm. Reprinted with permission from ref.[11]. Copyright 2012 American Chemical Society. [doi:10.1021/la3020089](https://doi.org/10.1021/la3020089)

cubic diamond with either OH termination (hydrophilic) or H termination (hydrophobic) and zero net charge, and the liquid is composed of simple extended point charge water without ions. The dielectric profiles oscillate strongly, like the density profile, and the difference between the hydrophilic and hydrophobic surfaces seems to be small. When we approximate these profiles by box functions as

$$\varepsilon_{\perp}(z) = \begin{cases} 1 & \text{for } 0 < z < z^*, \\ \varepsilon & \text{for } z > z^*, \end{cases} \quad (1.81)$$

while conserving $\int_0^{\infty} \varepsilon_{\perp}^{-1}(z) dz$, $z^* = 0.10$ nm for a hydrophilic surface, and $z^* = 0.12$ nm for a hydrophobic surface.[54] On the other hand, the viscosity profile differs greatly between the two types of surface. For a hydrophilic surface, the viscosity increases as the surface is approached. For a hydrophobic surface, a depletion layer of water showing a positive slip length is formed. The profiles are approximated by box functions as

$$\eta(z) = \begin{cases} \eta_i & \text{for } 0 < z < z_s, \\ \eta & \text{for } z > z_s. \end{cases} \quad (1.82)$$

From the simulation, $z_s = 0.4 \text{ nm}$ and $\eta_i = 4\eta$ for the hydrophilic surface, and $z_s = 0.15 \text{ nm}$ and $\eta_i = \eta/15$ for the hydrophobic surface.[55]

Using these non-uniform profiles, the researchers in ref. [55] modeled the double layer using the modified Poisson-Boltzmann equation as

$$\frac{d}{dz} \left[\varepsilon(z)_{\perp} \varepsilon_0 \frac{d\psi}{dz} \right] = 2ec_0 \sinh \left(\frac{e\psi}{k_B T} \right) \quad (1.83)$$

and the force balance of the Navier-Stokes equation as

$$\frac{d}{dz} \left[\eta(z) \frac{du_x}{dz} \right] + \rho E = 0. \quad (1.84)$$

Fig. 13 shows the electrokinetic charge density as a function of the bare surface charge density calculated using the above theory. It can reproduce the saturation of the electrokinetic charge shown in Fig. 11. For a hydrophobic surface, the saturated charge density increases with increasing salinity, which corresponds to the curve for TiO_2 in Fig. 11. For a hydrophilic surface, the saturated charge density decreases with increasing salinity, which corresponds to the curve for AgI in Fig. 11.

1.6. Basis of polymer physics

Macromolecules or polymers are giant molecules composed of a large number of monomeric units. The concept was proposed and established by Staudinger in the early 20th century.[56] Since then, polymers and their solutions have been used in a variety of industrial applications.

1.6.1. Gyration radius of a polymer

To estimate the sizes of macromolecules experimentally, the scattering method is used. Macromolecules are modeled theoretically as chains of beads connected by springs. We introduce the Gaussian chain model in this section. We consider $N + 1$ beads connected by a Hookian spring with the spring constant

$$H = \frac{3k_B T}{a^2}, \quad (1.85)$$

where a is the bead radius. The position of the beads is defined as $\mathbf{x}_n$, and the displacement vector is defined as $\mathbf{r}_n = \mathbf{x}_n - \mathbf{x}_{n-1}$; then the elastic energy function is

$$E_0(\{\mathbf{r}_n\}) = \sum_{n=1}^N \frac{H}{2} \mathbf{r}_n^2 = \frac{H}{2} \int_0^N dn \left(\frac{\partial \mathbf{x}_n}{\partial n} \right)^2, \quad (1.86)$$

where the last expression is in the continuum limit, and the probability function is

$$P(\{\mathbf{r}_n\}) = \left(\frac{3}{2\pi a^2} \right)^{3N/2} \exp \left[\sum_{n=1}^N \frac{3(\mathbf{x}_n - \mathbf{x}_{n-1})^2}{2a^2} \right]. \quad (1.87)$$

An important property of the Gaussian chain is that the distribution of the end-to-end vector is also Gaussian:

$$G_N^0(\mathbf{x}_N, \mathbf{x}_0) = \int d\{\mathbf{r}_n\} \delta\left(\sum_{n=1}^N \mathbf{r}_n - \mathbf{x}_N + \mathbf{x}_0\right) P(\{\mathbf{r}_n\}) = \left(\frac{3}{2\pi a^2 N} \right)^{3/2} \exp \left[-\frac{3(\mathbf{x}_0 - \mathbf{x}_N)^2}{2Na^2} \right], \quad (1.88)$$

where the relation

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (1.89)$$

and the Gaussian integral is used in the calculation. The average magnitude of the end-to-end vector is

$$\langle (\mathbf{x}_N - \mathbf{x}_0)^2 \rangle = a^2 N, \quad (1.90)$$

where $\langle \dots \rangle$ denotes the average of the probability function. The gyration radius obeys

$$R_g = \sqrt{\frac{1}{N} \sum_{n=1}^N \langle (\mathbf{x}_n - \mathbf{x}_G)^2 \rangle} = \sqrt{\frac{a^2 N(N+2)}{6(N+1)}} \approx aN^{1/2}, \quad (1.91)$$

where $\mathbf{x}_G$ is the position of the center of mass. Therefore, the gyration radius is proportional to the square root of the polymerization index.

The Gaussian chain is an ideal chain, and a solvent in which a polymer swells according to the relation eq. (1.91) is called a theta solvent. In many cases, the chain swells more than the ideal chain because of repulsive forces between monomeric units. We can model this repulsive force by the excluded volume interaction as

$$E_v = k_B T v \sum_{n \neq n'} \delta_a(\mathbf{x}_n - \mathbf{x}_{n'}), \quad (1.92)$$

where v is the volume interaction parameter, and $\delta_a(\mathbf{x})$ is an overlap function such as a delta function. According to the Flory theory for excluded volume effects, the free energy

is given by

$$F(R_g) = -k_B T \ln G_N^0 + k_B T v c^2 R_g^3 \approx k_B T \left(\frac{R_g}{a N^{1/2}} \right)^2 + k_B T v \left(\frac{N}{R_g} \right)^2 R_g^3, \quad (1.93)$$

where the first term is the entropic elastic energy and the second is the repulsive energy, $k_B T v c^2$, per volume. We minimize the above free energy with respect to R_g , and then we obtain

$$R_g \approx a(v/a^3)^{1/5} N^{3/5}, \quad (1.94)$$

where the exponent of the power-law behavior with respect to the polymerization index is larger than 1/2. From a renormalization group calculation, the gyration radius is given by[57]

$$R_g \approx a N^\nu, \quad (1.95)$$

where

$$\nu = 0.588 \pm 0.001, \quad (1.96)$$

which is very similar to the Flory's exponent. A solvent in which a polymer swells as $R_g \approx a N^{3/5}$ is called a good solvent. On the other hand, a solvent in which polymers cannot dissolve is called a poor solvent.

Fig. 14 shows the gyration radius of polyethylene oxide (PEO) in water as a function of the molecular weight.[58] Fitting of the exponent with data yielded the power law relation of the gyration radius and molecular weight as

$$R_g = 0.0215 M_w^{0.583 \pm 0.031} \text{ nm}, \quad (1.97)$$

where M_w is the molecular weight.

1.6.2. Continuum model of polymer solution

Three types of concentration of a polymer solution are considered theoretically. (i) In a dilute solution, the macromolecules do not overlap each other. We can treat it as one macromolecule in a good or theta solvent. (ii) In a semidilute solution, the macromolecules overlap each other, but the concentration is still dilute. The threshold of overlap c^* is determined by

$$c^* = \frac{N}{R_g^3} \approx a^{-3} N^{1-3\nu}, \quad (1.98)$$

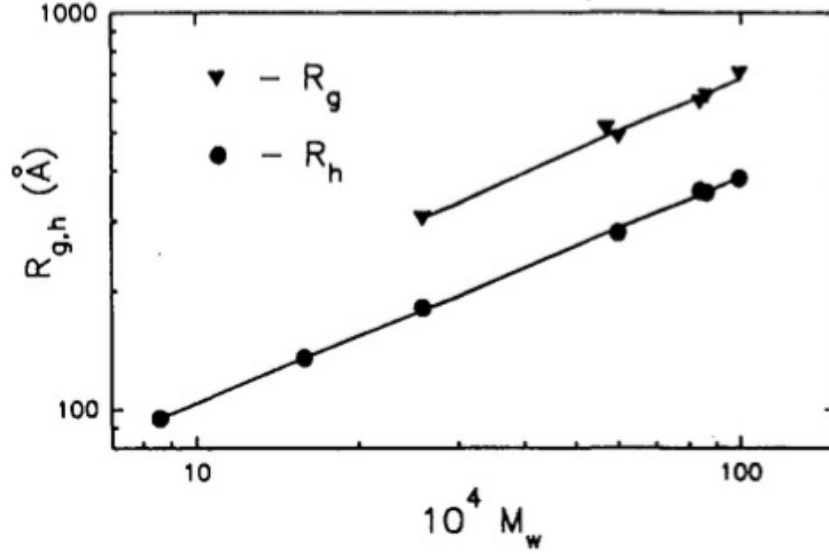


FIG. 14. Log-log plot of the PEO radius of gyration and the hydrodynamic radius versus the molecular weight. Reprinted with permission from ref. [58]. Copyright 1991 American Chemical Society. [doi:10.1021/ma00022a008](https://doi.org/10.1021/ma00022a008)

where c^* is the overlap concentration, and ν is $3/5$ ($1/2$) for a good (theta) solvent. Slightly above this concentration, we have universal behavior independent of the polymerization index N or molecular weight. (iii) For a concentrated solution, a polymer interacts with other polymer segments as well as segments of itself. In this case, entanglement is another problem in modeling.

One of the simple theories that describes the solution behavior over a wide range of concentrations is the Flory-Huggins theory, which is an extension of the thermodynamics of solutions. We consider a lattice in which each site is occupied by a solvent molecule or polymeric unit. For simplicity, they have the same volume, and we define the volume fraction of the polymer as Φ . Then the free energy per site is given by

$$\frac{f_{\text{FH}}}{k_B T} = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi(1 - \Phi) \quad (1.99)$$

where f is the free energy per site, and χ is a parameter describing the interaction between the polymer and the solvent. From this free energy, we can obtain the phase diagram of dissolution of the polymers. Fig. 15 is a typical phase diagram from the Flory-Huggins theory. With increasing χ , the solution become unstable and separates into two phase. The critical volume fraction is as small as $N^{-1/2}$; thus, one of the phases is almost pure solvent.

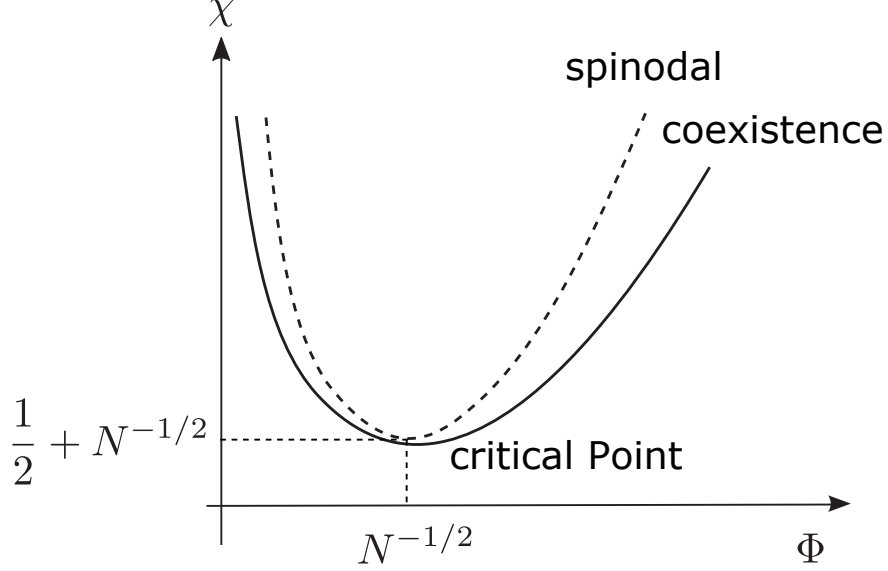


FIG. 15. Schematic of phase diagram of polymer solution calculated using the Flory-Huggins theory.

The panel on the left in Fig. 16 shows the phase diagram of polyisobutylene in diisobutyl ketone with different molecular weights.[59] The solid lines are obtained from experiments, and the broken lines are calculated by the Flory-Huggins theory. The critical temperature that has an unstable state at lower temperature is the upper critical solution temperature. The panel on the right in Fig. 16 shows the phase diagrams of PEG-water and polypropylene glycol-water solutions.[60] Unlike the solutions shown in the left-hand panel, these solutions exhibit the lower critical solution temperature.

A semidilute solution is equivalent to one in which one infinitely long macromolecule is dissolved with the same polymer concentration. This is a significant property of semidilute solutions. To describe the fluctuations of the concentration field or inhomogeneity near the surface, we construct the variational theory of the concentration field. First, we consider an ideal chain under the external potential field $U(\mathbf{r})$. To discuss the statistical properties of such a system, it is convenient to define the Green function as

$$G_N(\mathbf{r}, \mathbf{r}') = \int_{\mathbf{x}_0=\mathbf{r}}^{\mathbf{x}_N=\mathbf{r}'} d\{\mathbf{x}_n\} \exp \left[-\beta E_0(\{\mathbf{x}_n\}) - \beta \int_0^N dn U(\mathbf{x}_n) \right]. \quad (1.100)$$

We consider the difference $G_{N+\Delta N}(\mathbf{r}, \mathbf{r}') - G_N(\mathbf{r}, \mathbf{r}')$ and expand it to the order ΔN : [57, 61]

$$-\frac{\partial G_N}{\partial N} = -\frac{a^2}{6} \nabla^2 G_N + \frac{U(\mathbf{r})}{k_B T} G_N. \quad (1.101)$$

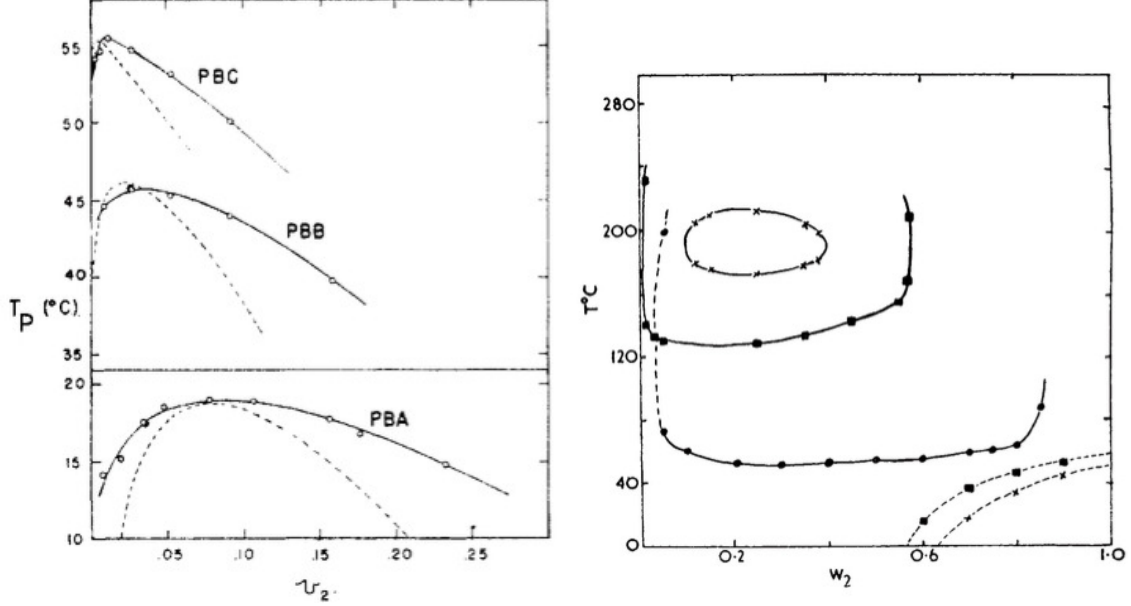


FIG. 16. (left) Precipitation temperatures T_p for polyisobutylene in diisobutyl ketone plotted against the concentration expressed as the volume fractions v_2 of the polymer. Molecular weights of polyisobutylene are different as 2.27×10^4 (PBA), 2.85×10^5 (PBB), and roughly 6.0×10^6 (PBC), respectively. The broken lines are the corresponding theoretical curves. Reprinted with permission from ref. [59]. Copyright 1952 American Chemical Society. [doi:10.1021/ja01139a010](https://doi.org/10.1021/ja01139a010) (right) Phase diagram for aqueous solutions of PEGs and polypropylene glycols. Squares and crosses, PEGs 5000 and 3000, respectively; circles, polypropylene glycol 400. Lower right-hand curves, solid-liquid boundaries. Reproduced from ref. [60] with permission of The Royal Society of Chemistry. [doi:10.1039/TF9575300921](https://doi.org/10.1039/TF9575300921)

The solution of this equation is

$$G_N(\mathbf{r}, \mathbf{r}') = a^3 \sum_k \phi_k^*(\mathbf{r}') \phi_k(\mathbf{r}) e^{-\epsilon_k N}, \quad (1.102)$$

where ϕ_k and ϵ_k are the eigenfunction and eigenvalue, respectively, of the equation:

$$\left[-\frac{a^2}{6} \nabla^2 + \frac{U(\mathbf{r})}{k_B T} \right] \phi_k = \epsilon_k \phi_k. \quad (1.103)$$

Then the concentration is proportional to the probability as

$$c(\mathbf{x}) \propto \int d\mathbf{r}' \int d\mathbf{r} \sum_{n=1}^N G_n(\mathbf{r}', \mathbf{x}) G_n(\mathbf{x}, \mathbf{r}). \quad (1.104)$$

When the ground state ($k = 0$) is dominant, we set $\phi(\mathbf{r}) = \phi_0(\mathbf{r})$, and

$$c(\mathbf{r}) = |\phi(\mathbf{r})|^2. \quad (1.105)$$

The mean field of the excluded volume interaction is given by

$$U(\mathbf{r}) = k_B T v c(\mathbf{r}) = k_B T v |\phi(\mathbf{r})|^2, \quad (1.106)$$

and the self-consistent field equation is given by

$$-\frac{a^2}{6} \nabla^2 \phi + v |\phi|^2 \phi = \epsilon \phi. \quad (1.107)$$

This is equivalent to the variation problem of the free energy:

$$F = k_B T \int d\mathbf{r} \left[-\epsilon \phi^2 + \frac{1}{2} v \phi^4 + \frac{a^2}{6} |\nabla \phi|^2 \right]. \quad (1.108)$$

1.6.3. Polymer at an interface

In this section, we calculate non-uniform profiles of the polymer concentration near a surface using self-consistent field theory.[\[61–63\]](#) First, we consider a repulsive surface in a good solvent. The boundary condition at the surface is

$$\frac{1}{\phi(0)} \frac{d\phi}{dz} \Big|_{z=0} = \frac{1}{2D}, \quad (1.109)$$

where D is a positive parameter characterizing the interfacial length, and in the bulk,

$$c(z) \rightarrow \phi_b^2. \quad (1.110)$$

Then we obtain $\epsilon = v \phi_b^2$. The solution is

$$\phi(z) = \phi_b \tanh \left(\frac{z + z_0}{\xi_b} \right), \quad (1.111)$$

where ξ_b is the correlation length in the bulk as

$$\xi_b = \frac{a}{\sqrt{3v\phi_b^2}}, \quad (1.112)$$

and

$$z_0 = \frac{\xi_b}{2} \operatorname{arcsinh} \left(\frac{4D}{\xi_b} \right). \quad (1.113)$$

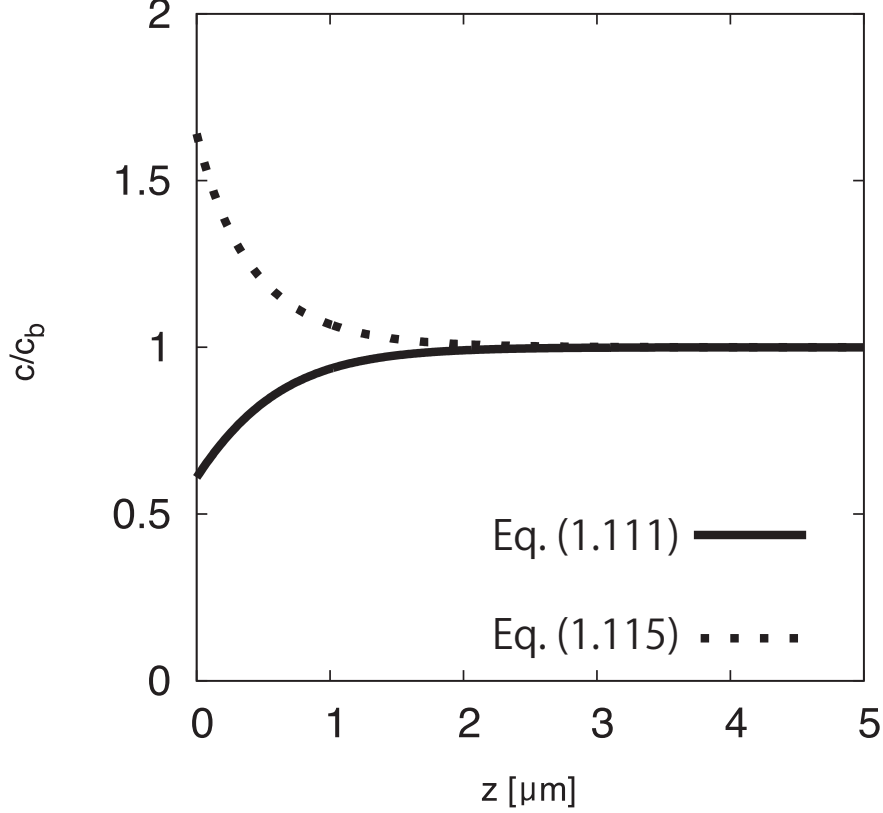


FIG. 17. Concentration profiles of polymers near surfaces. The solid and dotted lines are calculated using eqs. (1.111) and (1.115), respectively. $D = 1 \mu\text{m}$, and $\xi_b = 1 \mu\text{m}$.

Next, we consider an attractive surface in a good solvent. In this case, the boundary condition at the surface is

$$\left. \frac{1}{\phi(0)} \frac{d\phi}{dz} \right|_{z=0} = -\frac{1}{2D}. \quad (1.114)$$

The solution is

$$\phi(z) = \phi_b \coth \left(\frac{z + z_0}{\xi_b} \right). \quad (1.115)$$

Fig. 17 is the profile calculated using eqs. (1.111) and (1.115) for $D = 1 \mu\text{m}$ and $\xi_b = 1 \mu\text{m}$. The scaling theory is studied in refs. [64, 65], and experimental and theoretical results are reviewed in ref. [66].

1.6.4. Charged polymers

Charged polymers or polyelectrolytes are macromolecules that contain dissociable groups in their monomers.[62, 67–70] Polyelectrolytes tend to dissolve in polar liquids such as water

because of their electric charge, although most neutral polymers can dissolve only in organic solvents. The difference between neutral polymers and polyelectrolytes is the existence of an electric repulsive force between charged monomers. In contrast to the short-ranged excluded volume interaction, the electrostatic interaction is long-range as

$$E = k_{\text{B}}T \frac{\ell_{\text{B}}}{r}, \quad (1.116)$$

where r is the separation distance of two charged monomers.

First, we consider a weakly charged flexible chain using the Flory theory. We define f as the fraction of charged monomers, and the free energy as a function of R_{g} is

$$F(R_{\text{g}}) \approx k_{\text{B}}T \left(\frac{R_{\text{g}}}{aN^{1/2}} \right)^2 + \frac{(Nf)^2 \ell_{\text{B}}}{R_{\text{g}}}. \quad (1.117)$$

Minimization with respect to R_{g} gives an equilibrium size of

$$R_{\text{g}} \sim N f^{2/3} (\ell_{\text{B}} a^2)^{1/3}, \quad (1.118)$$

which establishes the result that the chain size is proportional to the number of monomers. However, in realistic situations counterions and salts exist in polyelectrolyte solutions. We assume that the salt concentration c_0 and the electric repulsive force are well described by the screened Coulomb interaction as

$$E = k_{\text{B}}T \frac{\ell_{\text{B}}}{r} e^{-\kappa r}. \quad (1.119)$$

The electrostatic repulsive force is short-range which implies that at a very large size, a charged chain has the same structure as a neutral polymer in a good solvent. At the intermediate length scale, the polyelectrolytes behave as a semi-flexible chain with a persistence length ℓ_{eff} . [62, 69, 71–74]

Polyelectrolytes are more swollen in the solution than neutral polymers; thus, the overlap concentration defined by eq. (1.98) behaves as

$$c^* \sim N^{-2} f^{-2} \ell_{\text{B}}^{-1} a^{-2}, \quad (1.120)$$

which is very small. To discuss the phase separation and concentration fluctuation in a polyelectrolyte solution, the electrostatic and ion contributions to the free energy are added to the free energy of a neutral polymer solution, eq. (1.99) or eq. (1.108). These theories can describe the intermediate peak of the scattering function and mesophase separation. [69] The scaling theory of polyelectrolyte solutions is studied in ref. [75]. Polyelectrolytes at an interface are studied in refs. [76–81].

2. LINEAR ELECTRO-OSMOSIS OF CHARGED AND UNCHARGED POLYMER SOLUTIONS

In this section, we present the characteristic behavior of linear electro-osmosis of charged and uncharged polymer solution using self-consistent field theory and fluid mechanics.

Main part of this section is published in ref. [10].

2.1. Mean-field equations for concentrations, electrostatic potential and flow

We consider an aqueous solution of sufficiently long polyelectrolyte chains in a slit (see Fig. 18). A fraction f of the polyelectrolytes is positively charged, whereas the slit wall is negatively charged. Counterions from the polyelectrolytes and salts are also dissolved in the solution. For simplicity, we assume that the anions from the salt and the counterions from the polymers are the same species and all the small ions are monovalent. The free energy of the system is contributed by polymer conformations, ion distributions, and electrostatic interactions as follows:

$$F = F_{\text{poly}} + F_{\text{ions}} + F_{\text{ele}}. \quad (2.1)$$

The polymer free energy is given by[61]

$$F_{\text{poly}} = k_{\text{B}}T \int d\mathbf{r} \left[\frac{a^2}{6} |\nabla\phi|^2 + \frac{v}{2} \phi^4 \right], \quad (2.2)$$

where ϕ is an order parameter related to the local polymer concentration $c(\mathbf{r})$, given by $\phi(\mathbf{r}) = \sqrt{c(\mathbf{r})}$. $k_{\text{B}}T$ is the thermal energy, a is the monomer size, and v is the second virial (excluded volume) coefficient of the monomers.

The ion free energy, contributed by the translational entropy of the ions, is given by

$$F_{\text{ion}} = k_{\text{B}}T \int d\mathbf{r} \sum_{i=\pm} [c^i \ln(c^i a_i^3) - c^i], \quad (2.3)$$

where $c^+(\mathbf{r})$ and $c^-(\mathbf{r})$ are the concentrations of the cations and anions, respectively. The electrostatic free energy is given by

$$F_{\text{ele}} = \int d\mathbf{r} \left[\rho\psi - \frac{\varepsilon\varepsilon_0}{2} |\nabla\psi|^2 \right]. \quad (2.4)$$

where $\psi(\mathbf{r})$ is the local electrostatic potential, ε is the dielectric constant of the aqueous solution, and $\rho(\mathbf{r})$ is the electric charge density defined as

$$\rho = e(fc + c^+ - c^-), \quad (2.5)$$

where e is the elementary electric charge.

The control parameters in this study are the bulk concentrations of the cation c_b^+ and the charged monomer fraction f . These parameters should satisfy the neutral charge condition, $f c_b + c_b^+ - c_b^- = 0$, in the bulk. Here c_b and c_b^- are the bulk concentrations of the monomers and anions, respectively, whose steady profiles are obtained by minimizing the following grand potential

$$\Xi = F - \mu \int \phi^2 d\mathbf{r} - \sum_{i=\pm} \mu^i \int c^i d\mathbf{r}, \quad (2.6)$$

where μ and μ^i ($i = \pm$) denote the chemical potential of each component.

The solution is confined within a slit bounded by two parallel walls. We assume that the above variables change only along the z axis, and are homogeneous along the x and y axes. In this scenario, the mean-field equations are

$$\begin{aligned} \frac{a^2}{6} \frac{\partial^2 \phi}{\partial z^2} &= v(\phi^3 - c_b \phi) + f \phi \beta e \psi, \\ \varepsilon \varepsilon_0 \frac{\partial^2 \psi}{\partial z^2} &= -e f (\phi^2 - c_b \exp[\beta e \psi]) + 2e c_b^+ \sinh(\beta e \psi), \end{aligned} \quad (2.7)$$

(2.8)

where $\beta = 1/k_B T$. Eq. (2.7) is the Edwards equation that accounts for the charge effect, while eq. (2.8) is the Poisson-Boltzmann equation for the system containing the salts and polyelectrolytes.

Applying a sufficiently weak electric field E in the x direction, the system evolves to steady state in which ion fluxes are induced along E . Because E is weak and orthogonal to $-\nabla\psi(z)$, we assume that it influences neither the concentration fields nor the polymer conformations (see Appendix 2.A). In steady state, the mechanical forces are balanced. This force balance is expressed by the Navier-Stokes equation, whose simplified form is

$$\frac{\partial}{\partial z} \left[\eta(\phi) \frac{\partial v_x}{\partial z} \right] + \rho E = 0, \quad (2.9)$$

where $v_x(z)$ is the x component of the velocity field. In this case, because we impose no pressure difference on the system, $P = 0$ in eqs. (1.32) and (1.33). $\eta(\phi)$ is the viscosity, which is a function of the concentration order parameter ϕ . In this study, we set

$$\eta(\phi) = \eta_0 \{1 + h(\phi/\sqrt{c_b})^\alpha\}, \quad (2.10)$$

where h and α are nondimensional parameters. Here η_0 is the solvent viscosity and $\eta_b = \eta_0(1 + h)$ denotes the viscosity in the bulk. Because $\eta(\phi)$ usually increases from η_0 as ϕ

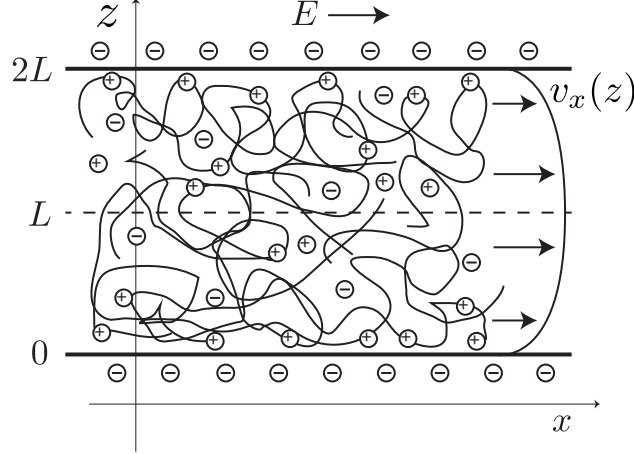


FIG. 18. Schematic of the investigated system. A positively charged polyelectrolyte solution is confined within a negatively charged slit and an external electric field is applied along the slit walls. The long-chain polymers are interspersed with polymer counterions and anions derived from salt. Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. [doi:10.1063/1.4820236](https://doi.org/10.1063/1.4820236)

increases, h and α are assumed positive. As described in Appendix 2.B, h and α depend on the physical parameters N , f , and c_b^+ , in which N is the polymer length. In this study, however, h is assumed as an independent parameter. According to Fuoss law [75], we set $\alpha = 1$. Later, we demonstrate that these simplifications do not alter the essential results.

As shown in Fig. 18, the surfaces are placed at $z = 0$ and $2L$, where $2L$ is the slit width and the electrostatic potentials are the same at both surfaces. Because all profiles are symmetric with respect to $z = L$, we consider only the range $[0, L]$. At the bottom surface ($z = 0$), we assume $\phi(0) = 0$, implying that the intermolecular interactions between the surfaces and polymers are strongly repulsive. We also set $v_x(0) = 0$ and $\psi(0) = \psi_s$. The former is the nonslip boundary condition for the flow. ψ_s is negative because the surfaces are negatively charged and the electrostatic interaction between the polymer and surfaces is attractive. Because the system is symmetric, all z derivatives vanish at $z = L$;

$$\left. \frac{\partial \phi}{\partial z} \right|_{z=L} = 0, \left. \frac{\partial \psi}{\partial z} \right|_{z=L} = 0, \left. \frac{\partial v_x}{\partial z} \right|_{z=L} = 0. \quad (2.11)$$

In this study, we assume that the electric field is sufficiently weak so that the flow speed is proportional to the field strength. Specifying a coefficient $\lambda_{12}(z)$, the flow profile is expressed as $v_x(z) = \lambda_{12}(z)E$. In other words, the solution is Newtonian and the nonlinear dependence

of the flow on E can be ignored, and considered in the next section. Having obtained the static profiles (which are difficult to solve analytically), λ_{12} is calculated as

$$\lambda_{12}(z) = \varepsilon\varepsilon_0 \int_0^z \frac{dz'}{\eta(\phi(z'))} \frac{\partial\psi}{\partial z} \Big|_{z'}. \quad (2.12)$$

This quantity is related to the macroscopic electro-osmotic coefficient in eq. (1.32) by

$$L_{12} = \frac{1}{L} \int_0^L \lambda_{12}(z) dz. \quad (2.13)$$

To study the effects of the near-surface polyelectrolyte structures on electro-osmosis in this system, we numerically evaluate eqs. (2.7), (2.8) and (2.9). The parameter settings are $c_b = 10^{-3} \text{ nm}^{-3}$, $v = 0.05 \text{ nm}^3$, $L = 102.4 \text{ nm}$, $\ell_B = 0.7 \text{ nm}$, $T = 300 \text{ K}$, $\psi_S = -k_B T/e = -25.8 \text{ mV}$, $a = 0.5 \text{ nm}$, and $\eta_0 = 0.01 \text{ P}$. Here ℓ_B is the Bjerrum length, given by $\ell_B = e^2/(4\pi\varepsilon\varepsilon_0 k_B T)$. The polymer chains are assumed so long that $c_b > c^*$, where c^* is the overlap concentration of the polymer solution (see Appendix 2.B).

The electro-osmotic coefficient is evaluated from the L_{12}^0 of a solution without polyelectrolytes, given by $L_{12}^0 = -\varepsilon\varepsilon_0\psi_S/\eta_0 = 1.82 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$. The space discretization in the numerical calculations is $d = 0.1 \text{ nm}$.

2.2. Electrically neutral polymer solution with chemically repulsive surfaces

First, we assume that polymers are electrically neutral, *i.e.*, $f = 0$. In this case, the mean-field equations (2.7) and (2.8) are exactly solved as

$$\phi = \sqrt{c_b} \tanh\left(\frac{z}{\xi_b}\right), \quad (2.14)$$

$$\psi = \frac{2k_B T}{e} \ln \frac{1 + e^{-\kappa z} \tanh(\beta e \psi_S/4)}{1 - e^{-\kappa z} \tanh(\beta e \psi_S/4)}. \quad (2.15)$$

where $\kappa = (8\pi\ell_B c_b^+)^{1/2}$ is the Debye wave number and $\xi_b = a/\sqrt{3vc_b} = 40.8 \text{ nm}$ is the correlation length of the polymer concentration fluctuation. e is Napier's constant. Note that these analytical solutions are valid only when $\lambda \ll L$ and $\xi_b \ll L$ because they are solved under the boundary conditions at $z = 0$ and L . If $|\beta e \psi_S| \ll 1$, eq. (2.15) reduces to

$$\psi = \psi_S e^{-\kappa z}, \quad (2.16)$$

using the Debye-Hückel approximation.

If the slit width is much larger than all other length scales in the system, L_{12} is approximately equal to $L_{12} \approx \lambda_{12}(L)$. Therefore, we write

$$L_{12} \approx \frac{\varepsilon \varepsilon_0}{\eta_0 i} \int_0^L \frac{dz}{1 + \eta_1 \phi} \frac{\partial \psi}{\partial z}. \quad (2.17)$$

Because $\psi(z)$ is a monotonically increasing function of z in eqs. (2.15) and (2.16), the integral $\int \cdots dz$ in eq. (2.17) can be replaced by $\int \cdots d\psi$, using $e^{z/\xi_b} = \zeta^{-1/\kappa \xi_b}$. L_{12} is then calculated as

$$\frac{L_{12}}{L_{12}^0} = \int_0^1 \frac{(\zeta^{-1/\kappa \xi_b} + \zeta^{1/\kappa \xi_b}) d\zeta}{(h+1)\zeta^{-1/\kappa \xi_b} - (h-1)\zeta^{1/\kappa \xi_b}}, \quad (2.18)$$

where $\zeta = \psi/\psi_S$ is a reduced electrostatic potential. After some calculations, eq. (2.18) can be expanded as

$$\begin{aligned} \frac{L_{12}}{L_{12}^0} &= \frac{2}{h+1} \frac{\kappa \xi_b + 1}{\kappa \xi_b + 2} + \frac{1}{h+1} \sum_{n=1}^{\infty} \left(\frac{h-1}{h+1} \right)^n \\ &\times \left[\frac{1}{2n/(\kappa \xi_b) + 1} + \frac{1}{2(n+1)/(\kappa \xi_b) + 1} \right]. \end{aligned} \quad (2.19)$$

When $h = 1$, eq. (2.19) reduces to

$$L_{12} = L_{12}^0 \left(\frac{\kappa \xi_b + 1}{\kappa \xi_b + 2} \right). \quad (2.20)$$

Clearly, eq. (2.20) is an increasing function of $\kappa \xi_b$.

The electro-osmotic coefficient calculated by eq. (2.19) is plotted as a function of salt concentration in Fig. 19. Shown are the coefficients for several values of the bulk viscosity parameter h . As the salt concentration increases, the electro-osmotic coefficient increases and approaches L_{12}^0 , regardless of h . By contrast, in the low salt concentration regime, L_{12} decreases as $(c_b^+)^{1/2}$ to $L_{12}^b = L_{12}^0/(1+h)$, the electro-osmotic coefficient estimated at the viscosity of the bulk solution.

We interpret these results as follows. In the neutral polymer solution, the electrostatic interaction does not influence the polymer concentration profile. The polymers are depleted from the surface by short-ranged surface forces, and the near-surface viscosity is smaller than that in the bulk. Only the region near the surface, where $\rho \neq 0$, responds to the applied electric field. The charged region is characterized by the Debye length λ from the surface. If the Debye length is smaller than the correlation length ξ_b , the electro-osmosis is enhanced; otherwise it is suppressed.

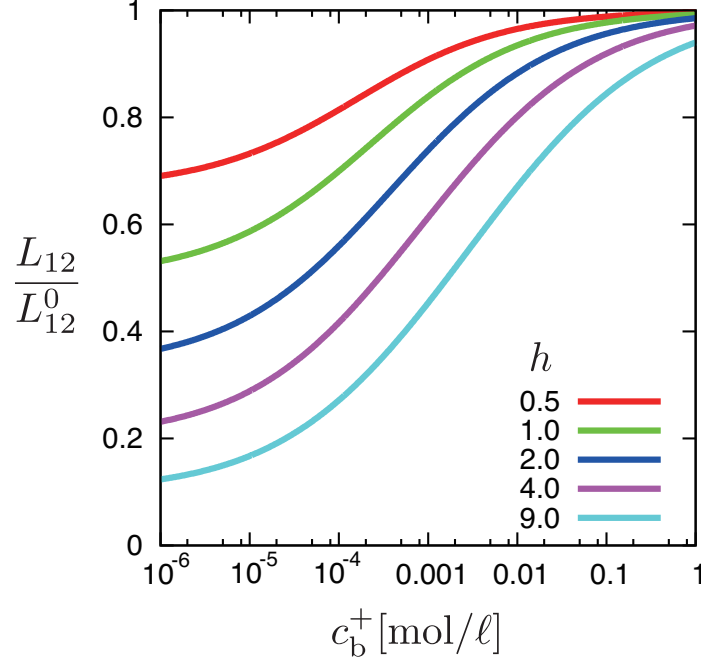


FIG. 19. Electro-osmotic coefficients L_{12} in the solution without polyelectrolytes, plotted as functions of salt concentration c_b^+ . In place of polyelectrolytes, electrically neutral polymers are dissolved. The viscosity parameter h is varied. Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. [doi:10.1063/1.4820236](https://doi.org/10.1063/1.4820236)

Given the effective viscosity η_S , the electro-osmotic coefficient is calculated by the usual Smoluchowski's formula, $L_{12} = -\varepsilon\varepsilon_0\psi_S/\eta_S$. As noted above, the formation of the depletion layer near the surface effectively lowers the viscosity of the solution. From eq. (2.19), the effective viscosity decreases with $\kappa\xi_b$ as

$$\eta_S \approx \eta_0(1+h) \left\{ 1 - \kappa\xi_b \frac{h}{h-1} \ln \frac{h+1}{2} \right\}, \quad (2.21)$$

when $\kappa\xi_b \ll 1$, using $\sum_{n=1}^{\infty} n^{-1}r^n = \ln[1/(1-r)]$. On the other hand, when $\kappa\xi_b \gg 1$, the viscosity approaches the solvent viscosity, $\eta_S \approx \eta_0$. This phenomenon can be explained as follows. In the high salt limit, the electrostatic interaction between ions and walls is screened by a short length scale. If the wall is chemically repulsive to the polymers, the polymers are depleted from the surface with a correlation length far exceeding the Debye screening length.

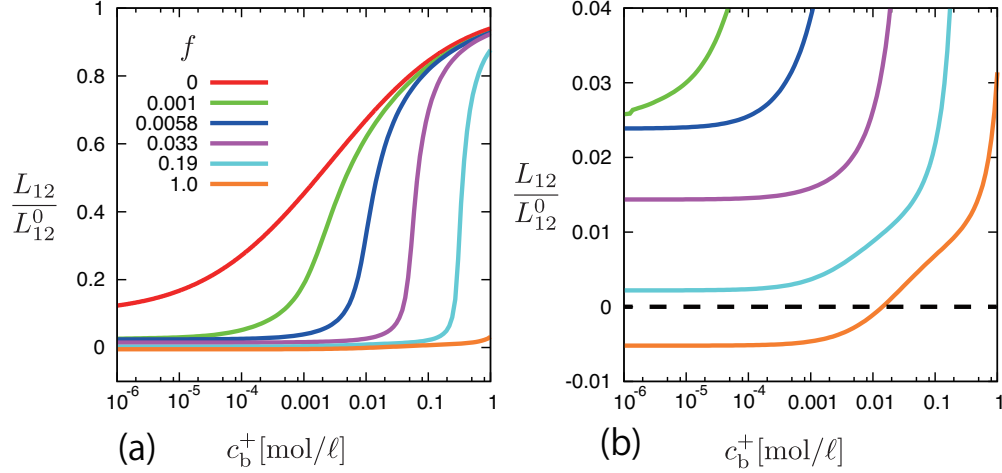


FIG. 20. (a) Electro-osmotic coefficients L_{12} , plotted as functions of salt concentration c_b^+ . The fraction of charged monomers in the polyelectrolyte f is varied for fixed $h = 9$. At $f = 0$, the curve is that of the electrically neutral polymer solution, and it increases with c_b^+ as shown in Fig. 19. At sufficient salt concentrations, all curves approach L_{12}^0 . (b) Magnification of the same plots around a small range of L_{12} . Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. [doi:10.1063/1.4820236](https://doi.org/10.1063/1.4820236)

2.3. Polyelectrolyte solution with electrically attractive and chemically repulsive surfaces

Next, we consider polyelectrolyte solutions, *i.e.*, $f \neq 0$. Fig. 20(a) shows the electro-osmotic coefficients as functions of salt concentration. Here we fix $h = 9$ and vary the fraction of charged monomers f . We find that, as in neutral polymer solutions (see Fig. 19), electro-osmosis is suppressed in the low salt regime. At high salt concentrations, the electro-osmotic coefficient approaches L_{12}^0 . Fig. 20(a) also indicates that, with increasing electric charge on the polyelectrolytes, electro-osmosis becomes more suppressed and salinity exerts a more drastic effect. In Fig. 20(b), these plots are magnified around $L_{12} = 0$. Interestingly, the electro-osmotic coefficient can become negative at sufficiently dilute salt and when the polyelectrolytes are highly charged. Such inversion of electro-osmotic flow is never observed in neutral polymer solutions.

The electro-osmotic coefficients are plotted as functions of f in Fig. 21(a). Here the salt concentration is fixed at a low concentration $c_b^+ = 10^{-6}$ [mol/l], and the bulk viscosity parameter h is changed. We observe that the electro-osmotic flow is weakened if the

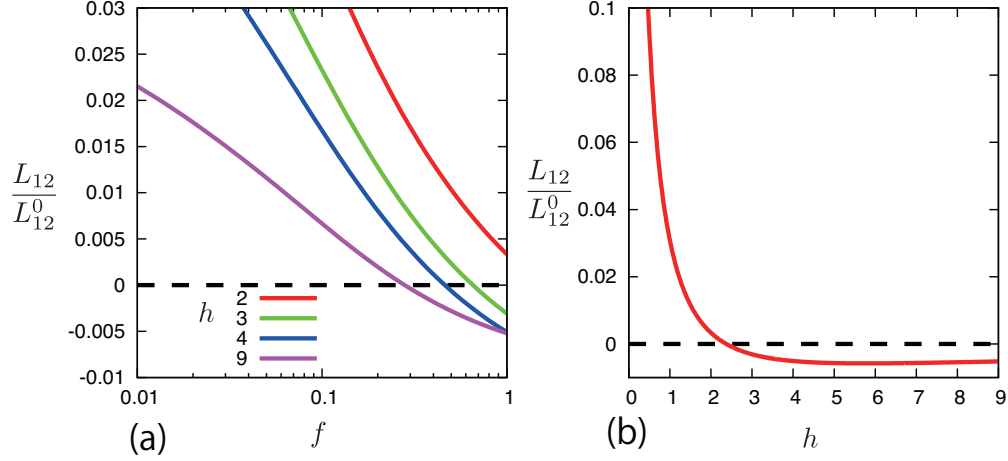


FIG. 21. (a) Electro-osmotic coefficients L_{12} , plotted as functions of the fraction of charged monomers in the polyelectrolytes f . h is varied at fixed salt concentration $c_b^+ = 10^{-6} \text{ mol}/\ell$. (b) Electro-osmotic coefficient L_{12} plotted as a function of h . We set $c_b^+ = 10^{-6} \text{ mol}/\ell$ and $f = 1$. Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. [doi:10.1063/1.4820236](https://doi.org/10.1063/1.4820236)

polyelectrolytes are highly charged. The mechanism of this phenomenon will be discussed later. Fig. 21(a) also shows that electro-osmosis inversion occurs only at sufficiently high h . Fig. 21(b) plots the electro-osmotic coefficient versus h for $c_b^+ = 10^{-6} [\text{mol}/\ell]$ and $f = 1$. As discussed above, the electro-osmotic flow in neutral polymer solutions saturates at L_{12}^b in the low salinity limit, according to eq. (2.21). However, this equation cannot explain the curve in Fig. 21(b).

2.3.1. Relationship between electro-osmosis and static properties

Fig. 22(a) plots the curves of $L_{12} = 0$ and $L_{12} = L_{12}^b$ in a $c_b^+ - f$ plane. As the bulk viscosity parameter h decreases, the region of inverted electro-osmosis ($L_{12} < 0$) shrinks and eventually disappears as h becomes small. On the other hand, the $L_{12} = L_{12}^b$ curves are less sensitive to changes in h . This implies that L_{12} around L_{12}^b depends more on the static than kinetic properties.

To characterize the static properties, we define a quantity Γ as

$$\Gamma = \int_0^L dz (c - c_b). \quad (2.22)$$

Γ measures the amount of excess adsorption of the polyelectrolytes. Fig. 22(b) plots the contour lines of Γ in the $c_b^+ - f$ plane. The $\Gamma = 0$ contour characterizes the adsorption-depletion transition.[80] In the system investigated here, the positively charged polymers are dissolved in the slit between the negatively charged walls. Electrostatic interaction adheres the polymers to the oppositely charged wall surface. On the other hand, intermolecular interaction prevents the polymers from directly contacting the surface (see Fig. 23(a)). When the electrostatic interaction is well screened by high salt content, chemical interaction depletes the polymers from the surface vicinity.

Interestingly, when c_b^+ is fixed, excess adsorption does not continuously increase toward $f = 1$ but instead peaks at an intermediate f . As shown in Fig. 22(b), the polyelectrolytes with $c_b^+ = 10^{-6} \text{ mol}/\ell$ are most strongly adsorbed when $f \approx 5 \times 10^{-3}$. This nonmonotonic behavior is counterintuitive because one expects that highly charged polyelectrolytes will be adsorbed with greatest strength. The adsorption-depletion transition has been intensively studied by Shafir *et al.*[80] Comparing Fig. 22(a) and (b), we find that the curves $L_{12} = L_{12}^b$ roughly coincide with that of $\Gamma = 0$. When the polymers are adsorbed to the surface ($\Gamma > 0$), the electro-osmotic coefficient is smaller than that determined by the surface potential and bulk viscosity L_{12}^b , and *vice versa*.

Fig. 23 shows profiles of the polymer concentration and electrostatic potential at (a) high and (b) low salt concentrations. The fraction of charged monomers is $f = 0.03$. The solution conditions are as indicated in Fig. 22(a). Under low-salinity conditions, where $L_{12} < L_{12}^b$, a peak appears in the concentration profile. Hereafter, the height and the position of the peak are denoted as ϕ_M and z_ϕ , respectively. As shown in Fig. 22(b), the amount of adsorption is positive (*i.e.*, in excess) Hence, we refer to the region of $\phi > \phi_b (= \sqrt{c_b})$ as an adsorption layer, although the polymers themselves do not contact the surface. The electrostatic potential also peaks at $z = z_\psi$. We call this peak an *overcharging potential* and its height is denoted as ψ_M . We should note that the ϕ and ψ peaks appear at different positions, with $z_\psi > z_\phi$. We also define z_0 , which satisfies $\psi(z_0) = 0$. As discussed below, the adsorption layer and the overcharging potential play essential roles in the decrease and inversion of the electro-osmotic coefficient. Conversely, under high-salinity conditions, the profiles monotonically increase to the bulk values without developing peaks. The dependences of ϕ_M and ψ_M on c_b^+ and f are shown in Figs. 24(a) and (b), respectively. The contours of ϕ_M and ψ_M are qualitatively similar to that of L_{12} in Fig. 22(a) but are

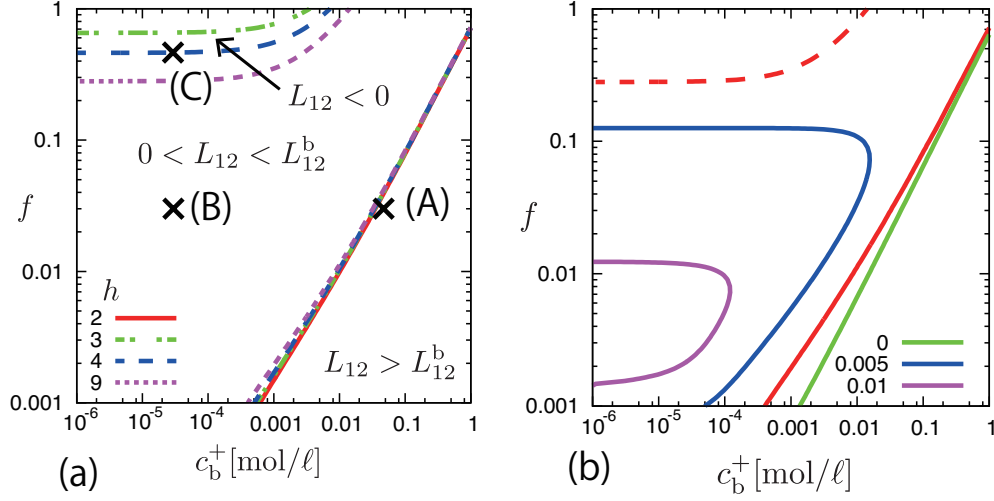


FIG. 22. (a) State diagram of the electro-osmotic flow in the c_b^+ - f plane. Because the polyelectrolyte concentration varies in the slit, the local viscosity depends on the distance from the wall. L_{12}^b is the electro-osmotic coefficient, estimated from the shear viscosity of the bulk solution. (b) Contours of the amount of excess adsorption, Γ , for $\Gamma = 0, 0.005$ and 0.01 . Shown are the contour lines of $L_{12} = 0$ (solid) and $L_{12} = L_{12}^b$ (broken) for $h = 9$. The $\Gamma = 0$ contour behaves similarly to the line $L_{12} = L_{12}^b$ in (a). Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. doi:10.1063/1.4820236

dissimilar from that of the excess adsorption. This implies that the maximum amount of adsorption is not important in the electro-osmotic phenomena.

The uncolored region, in which the profile does not peak, almost coincides with that of $L_{12} > L_{12}^b$. The gradient of the electro-osmotic flow is localized to the range of the Debye screening length from the surface (see Fig. 25(a)). Therefore, the formation of the depletion layer effectively reduces the solvent viscosity. Because the electro-osmotic flow is inversely proportional to the viscosity, depletion enhances the electro-osmosis. At the adsorption-depletion transition, the increase in L_{12} caused by the depletion cancels the decrease caused by adsorption. Then, the $\Gamma = 0$ curve is roughly consistent with that of $L_{12} = L_{12}^b$. Because neutral polymers in solution do not adhere to the surface, electro-osmosis is more strongly suppressed in polyelectrolyte solutions than in neutral polymer solutions.

The uncolored region in Fig. 24(b), where ψ_M develops no peak, is slightly wider than in Fig. 24(a), where ϕ_M develops no peak. This difference is delicate because the Debye screening length becomes comparable to the system size when c_b^+ and f are very small.

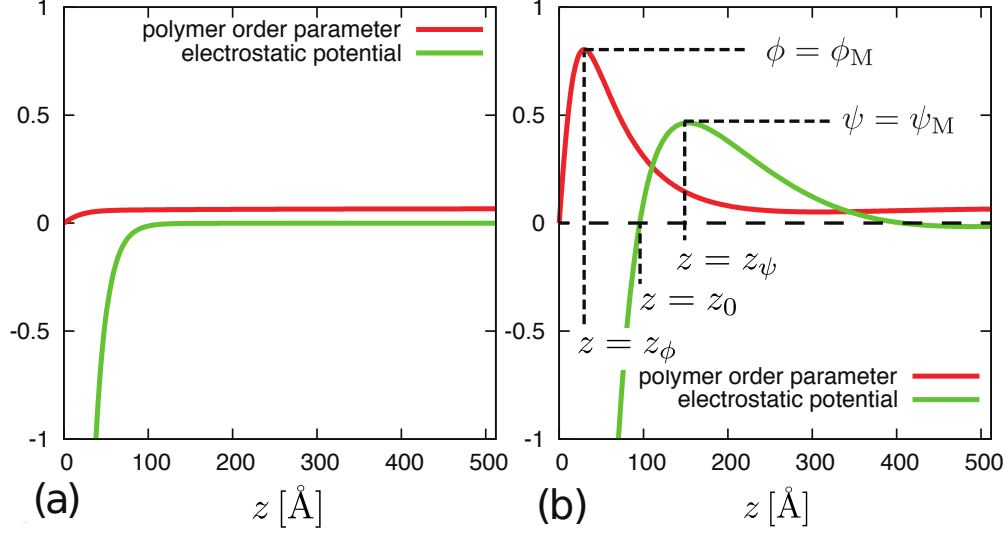


FIG. 23. Profiles of the polymer order parameter ϕ and the electrostatic potential ψ near the surface. The bulk concentrations of the salt are (a) $c_b^+ = 0.0476[\text{mol}/\ell]$ and (b) $c_b^+ = 2.91 \times 10^{-5}[\text{mol}/\ell]$. In both cases, the fraction of charged monomer in the polyelectrolyte is $f = 0.03$. The profiles in (a) and (b) correspond to conditions (A) and (B) in Fig. 22(a). For a clearer representation, we plot $\phi(z)/15\phi_b$ and $15\psi(z)/|\psi_s|$ rather than $\phi(z)$ and $\psi(z)$. Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. doi:10.1063/1.4820236

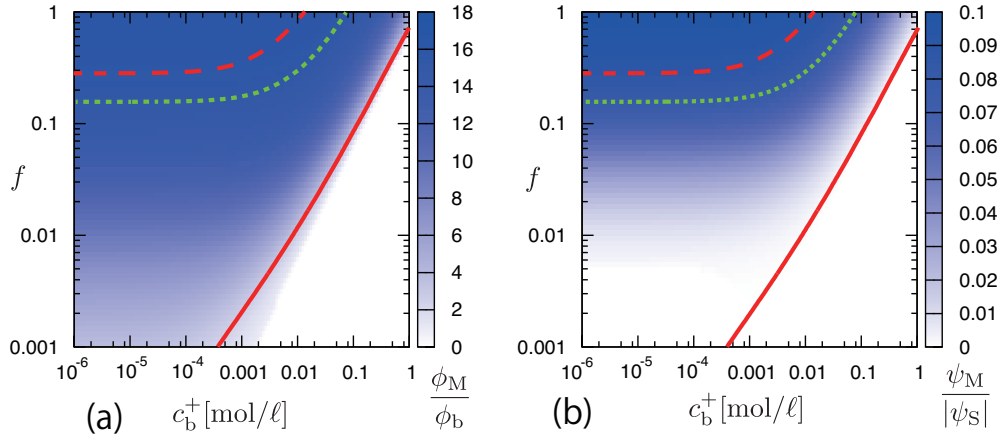


FIG. 24. Effect of c_b^+ and f on the peak heights of (a) concentration profile ϕ_M and (b) electrostatic potential ψ_M . Shown are the contour lines of $L_{12} = 0$ (broken) and $L_{12} = L_{12}^b$ (solid) for $h = 9$. The dotted line is $L_{12} = 0$ estimated by eq. (2.28). Uncolored regions indicate where no peaks appear in ϕ and ψ (*i.e.*, where ϕ_M and ψ_M are undefined). Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. doi:10.1063/1.4820236

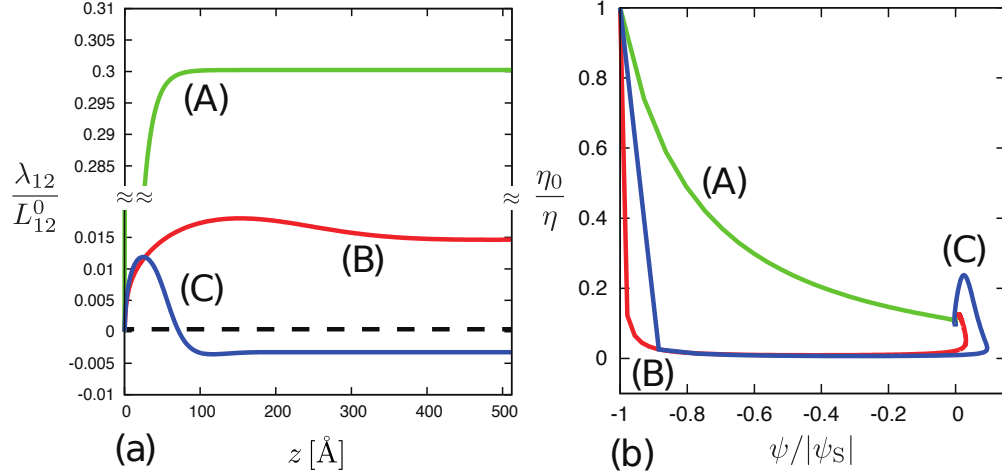


FIG. 25. (a) Profiles of the electro-osmotic flow λ_{12} in three states; (A) depletion state: $c_b^+ = 0.0476 \text{ mol}/\ell$ and $f = 0.03$. (B) adsorption state: $c_b^+ = 2.91 \times 10^{-5} \text{ mol}/\ell$ and $f = 0.03$. (C) flow inversion state: $c_b^+ = 2.91 \times 10^{-5} \text{ mol}/\ell$, and $f = 0.46$. These conditions are marked in Fig. 22(a). In condition (C), the overcharging potential is $\psi_M/|\psi_S| \approx 0.1$. (b) Parametric representations of $\psi(z)$ and $1/\eta(\phi(z))$ for the three states. Points $(\psi/|\psi_S|, \eta_0/\eta) = (-1, 1)$ and $(\psi/|\psi_S|, \eta_0/\eta) = (0, 1/(1+h))$ correspond to the surface ($z = 0$) and bulk ($z = L$), respectively. The bulk viscosity parameter is fixed at $h = 9$. Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. doi:10.1063/1.4820236

2.3.2. Relationship between electro-osmosis and dynamical properties

As shown in Fig. 24, ϕ_M and ψ_M are large in the regime of large f and small c_b^+ , where the electro-osmotic coefficient becomes negative. We emphasize that these large values of ϕ_M and ψ_M are essentially important for the sign reversal of L_{12} .

Fig. 25(a) shows the profiles of the flow field near the surface under three conditions. Here we note that $v_x(z) = \lambda_{12}(z)E$. Conditions (A) and (B) correspond to the adsorption and depletion states, respectively. The global electro-osmotic coefficient L_{12} becomes negative under Condition (C). These conditions are marked in Fig. 22(a). In all cases, the gradient of the flow field is localized to the vicinity of the surface; that is, the flow macroscopically behaves as a plug flow. While curve (A) varies almost monotonically with z , curve (B) is nonmonotonic, and curve (C) is more complex. Under condition (C), the flow direction is positive near the surface, but changes at some distance from the wall, saturating at a negative

value. The saturation value gives the macroscopic electro-osmotic coefficient from eq. (2.13). By contrast, curve (B) remains positive across the range. If the viscosity is homogeneous and independent of the polymer concentration, the flow field is easily calculated from eq. (2.12) as

$$\lambda_{12}(z) = \frac{\varepsilon\varepsilon_0}{\eta} \{\psi(z) - \psi_S\}. \quad (2.23)$$

The overcharging potential is necessary the nonmonotonic variations in (B) and (C). However, because $\psi_S < \psi(z)$ everywhere, the overcharging potential alone cannot explain the negative L_{12} given that η is constant.

If the electrostatic potential monotonically changes with z as in condition (A), $\psi = \psi(z)$ is uniquely expressed by its inverse function $z = z(\psi)$. Then, eq. (2.12) is given by

$$\lambda_{12}(L) = \varepsilon\varepsilon_0 \int_{\psi_S}^0 \eta(\psi')^{-1} d\psi', \quad (2.24)$$

where $\eta(\psi) = \eta(\phi(z(\psi)))$ is also a unique function of ψ . The curves of $\eta(\psi)$ are plotted in Fig. 25(b). Since $\eta(\psi)$ is positive, $\lambda_{12}(L)$ is also positive, indicating that the flow toward E is maintained.

When the overcharging potential arises, as in conditions (B) and (C), z is a multivalued function of ψ , which invalidates eq. (2.24). In this case, eq. (2.12) becomes

$$\begin{aligned} \frac{\lambda_{12}(L)}{\varepsilon\varepsilon_0} &= \int_0^{z_\psi} \frac{dz'}{\eta(z')} \frac{\partial\psi}{\partial z} \Big|_{z'} + \int_{z_\psi}^L \frac{dz'}{\eta(z')} \frac{\partial\psi}{\partial z} \Big|_{z'} \\ &= \int_{\psi_S|z < z_\psi}^{\psi_M} \frac{d\psi'}{\eta(\psi')} - \int_{0|z > z_\psi}^{\psi_M} \frac{d\psi'}{\eta(\psi')}. \end{aligned} \quad (2.25)$$

Here we should note that the paths of the two integrals in eq. (2.25) differ from each other.

According to linear analysis, the electrostatic potential profile may have multiple peaks.[77] The intensities of the peaks decay with increasing distance from the wall. We assume that the highest peak (nearest the wall) plays a dominant role in the electrokinetic flow and ignore the contributions of the remaining peaks.

Fig. 26 is a schematic of eq. (2.25). When the electrostatic potential overcharges, the curve of $1/\eta(\psi)$ is divisible into three segments. These segments delineate three realms, with areas denoted by S_1 , S_2 , and S_3 . Within the slit, the realms correspond to the ranges S_1 : $0 < z < z_0$, S_2 : $z_0 < z < z_\psi$, and S_3 : $z_\psi < z < L$ (see Fig. 23(b)). The first and second terms in eq. (2.25) are given by $S_1 + S_2$ and $S_2 + S_3$, respectively. In terms of these areas,

the electro-osmotic coefficient is given by $L_{12} = (S_1 + S_2) - (S_2 + S_3) = S_1 - S_3$. If $S_1 < S_3$, the macroscopic flow is inverted.

Using eq. (2.25), we devise a simple method for estimating the electro-osmotic coefficient in adsorption states. The viscosity is assumed constant within each realm. More precisely, we assume that polymer concentration is fixed at $\phi = \phi_M$ within the range $0 < z < z_\psi$ and at $\phi = \phi_b$ in $z_\psi < z < L$. These approximations are schematically represented in Fig. 26(b). S_1 and S_3 are then approximated as

$$S_1 \approx -\frac{\varepsilon\varepsilon_0\psi_S}{\eta_S}, \quad (2.26)$$

$$S_3 \approx \varepsilon\varepsilon_0 \left(\frac{1}{\eta_b} - \frac{1}{\eta_S} \right) \psi_M, \quad (2.27)$$

where $\eta_S = \eta_0(1 + h\phi_M/\phi_b)$ and $\eta_b = \eta_0(1 + h)$. Finally, we obtain

$$L_{12} \approx \frac{\eta_b}{\eta_S} L_{12}^b + \left(1 - \frac{\eta_b}{\eta_S} \right) L_{12}^M, \quad (2.28)$$

where $L_{12}^M = -\varepsilon\varepsilon_0\psi_M/\eta_b$ is the electro-osmotic coefficient estimated by the overcharging potential. The $L_{12} = 0$ curve estimated by eq. (2.28) is drawn in Fig. 24. This curve is qualitatively consistent with the numerical solutions. In this estimation, the overcharging potential does not directly cause the inversion of electro-osmotic flow; formation of the highly viscous layer is also important.

2.4. Summary and remarks

Applying a continuum model, we study electro-osmosis in polymer solutions. From numerical calculations and theoretical estimations, we elucidated the behaviors of the electro-osmosis in polymer solutions. The dependence of viscosity on the polymer concentration plays an important role in our model. Our main results are summarized below.

- (i) Even if the polymer solution sandwiched between chemically repulsive walls is electrically neutral, electro-osmosis depends on the salt concentration. Decreasing the salinity suppresses the electro-osmosis.
- (ii) In polyelectrolyte solutions, the formed adsorption layer effectively enlarges the viscosity in the vicinity of the surfaces. Consequently, electro-osmosis is suppressed much more strongly in polyelectrolyte than in neutral polymer solutions. If a sufficiently high

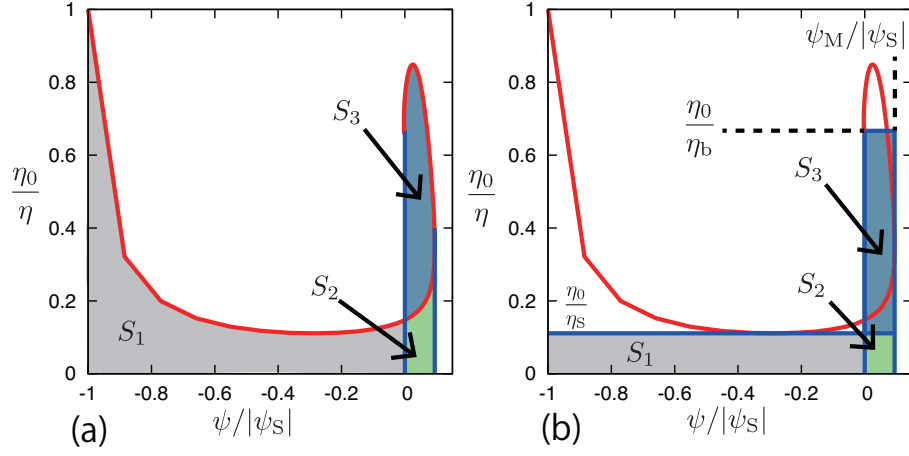


FIG. 26. (a) Schematic for calculating L_{12} in adsorption states from eq. (2.25). ψ and $1/\eta$ are parameterized with respect to z . (b) Approximate representation of $\psi\eta^{-1}$ in (a). This approximation gives a simple form of L_{12} , eq. (2.28). Reprinted with permission from ref. [10]. Copyright 2013, AIP Publishing LLC. doi:10.1063/1.4820236

proportion of the monomers are charged and if the salt concentration is sufficiently low, the electro-osmotic flow can be inverted.

- (iii) We propose a simple equation for estimating the electro-osmotic coefficient in adsorption states (eq. (2.28)). This equation captures the essential features of the inversion of the electro-osmotic coefficient, shown in Fig. 24. According to this expression, inversion is caused by two factors; enhancement of the viscosity by the near-surface adsorption layer and overshoot of the electrostatic potential.

We conclude this section with the following remarks.

- (1) Charge inversion and mobility reversal induced by multivalent electrolytes has been frequently reported.[82] Grosberg *et al.* concluded that such phenomena depend on fluctuation correlations among the multivalent ions, which are excluded in usual Poisson-Boltzmann approaches. Our mean-field approach predicts that similar inversion phenomena occur in polyelectrolyte solutions. According to a molecular dynamics simulation, the phenomena occurs even in monovalent ions solutions confined within nanochannels.[83] The flow profiles obtained in the earlier study are quite similar to

ours; near the surface, the flow is directed toward the electric field, but in the bulk, it is against the field.

- (2) This article considers only limited situations; The surfaces are assumed to chemically and electrostatically repel the polymers. If the surfaces are chemically attractive, the adsorption is much enhanced by chemical forces.[79, 81] The electro-osmotic properties of these surfaces are equally interesting and important.
- (3) From the Onsager reciprocal relations, the electro-osmotic coefficient L_{12} should equal L_{21} in eq. (1.33). The latter represents the electric current due to the mechanical pressure difference. Interestingly, the Onsager coefficient L_{21} is inverted when f is large and c_b^+ is sufficiently small.
- (4) In the above numerical and theoretical analyses, the viscosity parameter h is assumed constant, although in practice it depends on the fraction of charged monomers f and the salt concentration c_b^+ . When f is large and c_b^+ is small, the solution viscosity increases (see Appendix 2.B). Our studies indicate that large f and small c_b favor flow inversion. The same trends were observed for large h . If we set h as a function of f and c_b , more dramatic changes would appear in the curves of L_{12} against f and c_b^+ . Although the L_{12} and the phase diagrams would quantitatively alter, the qualitative trends, *i.e.*, suppression of the electro-osmotic flow and inversion at large f and a small c_b^+ , should remain intact.

Appendix 2.A Local equilibrium conditions for the components

Because we apply an external field E along the x direction (see Fig. 18), the total electrostatic potential is not $\psi(z)$ in eq. (2.4), but instead is $\psi_{\text{total}}(x, z) = \psi(z) - Ex$. Assuming the local equilibrium condition, the chemical potential of the cation and anion is given by eqs. (1.44) and (1.44) replaced ψ_{total} instead of ψ . In the geometry of the investigated system, the diffusion flux of the ion, given by

$$\mathbf{j}^i = -\frac{c^i}{\zeta^i} \nabla \mu^i, \quad (2.29)$$

is divided into two components:

$$\mathbf{j}^i = j_x^i \hat{\mathbf{x}} + j_z^i \hat{\mathbf{z}}, \quad (2.30)$$

$$j_x^i = \pm \frac{c^i}{\zeta^i} E, \quad (2.31)$$

$$j_z^i = -\frac{c^i}{\zeta^i} \frac{\partial}{\partial z} [k_B T \ln(c^i a_i^3) \pm e\psi(z)]. \quad (2.32)$$

Here $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ are the unit vectors along the x and z axes, respectively. Because the system is confined by the walls at $z = 0$ and $2L$, the diffusion flux along the z direction vanishes at steady state. Thus, we obtain the Boltzmann distribution along the z axis. On the other hand, the diffusion flux remains along the x axis. Because the applied electric field is sufficiently weak and orthogonal to $-\nabla\psi$, it influences neither the concentration fields nor the polymer conformation.

Appendix 2.B Scaling behaviors in polyelectrolyte solutions

The scaling behaviors of polyelectrolyte solutions are known to widely differ from those of uncharged polymer solutions. At the overlap concentration c^* in a polyelectrolyte solution, the monomer density inside the coil equals the overall monomer density in the solution.^[75] In our notation, the overlap concentration in a theta solvent is determined by $c^*(1 + 2c_b^+/c^*f)^{-3/2} \approx N^{-2}a^{-2}\ell_B^{-1}f^{-2}$.

In the low-salt or salt-free regime, the overlap concentration becomes $c^* \approx (a^2\ell_B N f)^{-1}$. Conversely, it approaches $c^* \cong \{8(c_b^+)^3 a^{-4}\ell_B^{-2} f^{-7} N^{-4}\}^{1/5}$ in the high-salt regime. Between these two extremes, the overlap concentration decreases as f increases. Given the same polymer length N , polyelectrolyte chains expand more than their uncharged counterparts.

The viscosity of polyelectrolyte solutions also obeys scaling behaviors, which depend on the solvent quality and the polymer concentration regime. For example, the viscosity of a semidilute solution in a theta solvent is given by $\eta \approx \eta_0 N a \ell_B^{1/2} f c^{1/2} (1 + 2c_b^+/fc)^{-3/4}$. If the salt is not dissolved or is insufficiently dilute, this expression approaches $\eta \approx \eta_0 N a \ell_B^{1/2} f c^{1/2}$; that is, the viscosity is proportional to $c^{1/2}$ (Fuoss law). On the other hand, in highly saline conditions the viscosity behaves as $\eta \approx \eta_0 N a \ell_B^{1/2} (c_b^+)^{-3/4} f^{7/4} c^{5/4}$. The viscosity depends on the polymer concentration as $c^{5/4}$, identical to that of an uncharged polymer solution in a theta solvent, namely $\eta \approx \eta_0 N (ca^3)^{1/(3\nu-1)}$ with $\nu = 3/5$. Physically, this result implies that electrostatic interactions in a polyelectrolyte solution are well screened by the salt.

3. NONLINEAR ELECTRO-OSMOSIS OF UNCHARGED POLYMER SOLUTIONS WITH LOW IONIC STRENGTH

In previous section, we consider linear behavior with respect to small electric field. However, when we apply a strong electric field, the structure of double layer may change and it would make electro-osmosis nonlinear. In this section, we investigate such a nonlinear behavior. Unfortunately, we restrict discussion about neutral polymer at low salinity. Main part of this section is published in ref. [84].

3.1. Toy model

First, we propose a toy model for electro-osmosis of polymer solutions. A dilute solution of non-adsorbing polymers is considered. The viscosity of the solution is given by

$$\eta = \eta_0(1 + \eta_{\text{sp}}), \quad (3.1)$$

where η_0 is the viscosity of the pure solvent, and η_{sp} is the specific viscosity of the solution. The gyration length of the polymers is defined as δ_0 , which is of the same order of the equilibrium depletion length. It is assumed that the polymers have $\delta_0 \approx 100$ nm. Ions are also dissolved in the solution with the Debye length λ . When a well deionized water is considered, the Debye length is of the order of $\lambda \approx 10^3$ nm although such a salt-free water is hardly realized owing spontaneous dissolutions of carbon dioxides. The interfacial structure near a charged surface is characterized by λ and δ_0 . When an external electric field is applied, a shear flow is locally imposed within the distance λ from the wall, and the resultant shear rate is

$$\dot{\gamma} \approx \frac{\mu_0 E}{\lambda}, \quad (3.2)$$

where μ_0 is the electro-osmotic mobility for the pure solvent and is estimated typically as $\mu_0 \approx 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$. According to the studies of the cross-stream migration in the uniform shear flow,[34] the depletion layer thickness depends on the shear rate,

$$\delta \approx \delta_0(\tau \dot{\gamma})^2, \quad (3.3)$$

where τ is the characteristic relaxation time of the polymers,

$$\tau \approx \frac{\eta_0 \delta_0^3}{k_B T}, \quad (3.4)$$

where $k_B T$ is the thermal energy and is typically 10^{-4} s at room temperature. Using eqs.(3.2) and (3.3), the depletion length in the presence of the applied electric field E can be expressed by

$$\delta \approx \begin{cases} \delta_0 & \text{for } E < E_0, \\ \left(\frac{E}{E_0}\right)^2 \delta_0 & \text{for } E_0 \leq E \leq E_1, \\ \lambda & \text{for } E_1 < E, \end{cases} \quad (3.5)$$

where $E_0 = \lambda/\tau\mu_0$, and $E_1 = E_0\sqrt{\lambda/\delta_0}$. Here, for simplicity, we assume that the depletion length does not exceed the Debye length. The effective viscosity in the double layer is given by

$$\eta_{\text{eff}} \approx \eta_0 \left[1 + \eta_{\text{sp}} \left(1 - \frac{\delta}{\lambda} \right) \right], \quad (3.6)$$

and the nonlinear mobility can be estimated by $\mu \approx \mu_0(\eta_0/\eta_{\text{eff}})$. Therefore, the mobility is obtained as

$$\mu \approx \begin{cases} \frac{\mu_0}{1 + \eta_{\text{sp}}(1 - (\delta_0/\lambda))} & \text{for } E < E_0, \\ \frac{\mu_0}{1 + \eta_{\text{sp}}(1 - (E/E_1)^2)} & \text{for } E_0 \leq E \leq E_1, \\ \mu_0 & \text{for } E_1 < E. \end{cases} \quad (3.7)$$

Fig. 27 (a) shows schematically the thickness of a depletion layer as a function of electric field strength. Fig. 27 (b) is the nonlinear electro-osmotic mobility. The mobility increases and is saturated with increasing electric field. The threshold electric field E_0 is typically 10^3 V/m that is experimentally accessible.

3.2. Model for simulation

In this section, our method of Brownian dynamics simulation is described. As shown in Fig. 28(a), a dumbbell is simulated in a electrolyte solution with a no-slip boundary at $z = 0$. The dumbbell shows a dilute solution behavior. The solvent is described by a continuum fluid with the viscosity η_0 and fills up the upper half of space ($z > 0$). Electrolytes are also treated implicitly with the Debye length $\lambda = \kappa^{-1}$. The dumbbell has two beads whose

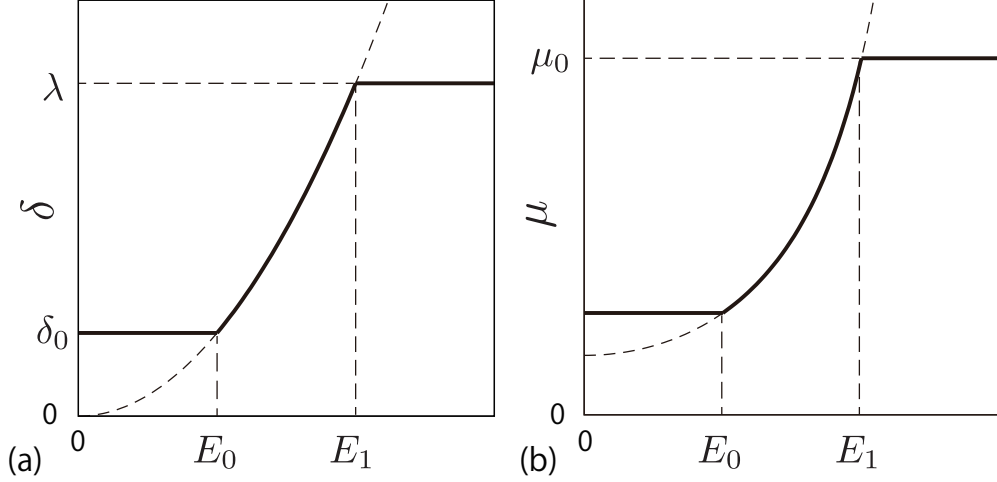


FIG. 27. (a) The depletion length as a function of the applied electric field. (b) The electro-osmotic mobility as a function of the applied electric field. Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

hydrodynamic radii are a , and actually the bead consists of many monomeric units of the polymer (see Fig. 28(c)). The positions of the beads are represented by $\mathbf{x}_1$ and $\mathbf{x}_2$ (see Fig. 28). Then we solve overdamped Langevin equations[85] given by

$$\frac{dx_{n\alpha}}{dt} = u_0(z_n)\delta_{\alpha x} + \sum_{m,\beta} (G_{\alpha\beta}^{nm}F_{m\beta} + k_B T \nabla_{m\beta} G_{\alpha\beta}^{nm}) + \sqrt{2k_B T} \left(\sqrt{\mathbf{G}} \right)_{\alpha\beta}^{nm} \cdot \xi_{m\beta},$$

for $n = 1, 2$, $\alpha = x, y, z$, (3.8)

where $X_{n\alpha}$ is the α component of a vector $\mathbf{X}_n$. $u_0(z)$ is the external plug flow, $\nabla_{n\alpha} = \partial/\partial x_{n\alpha}$, $\mathbf{G}$ is the mobility tensor, $\mathbf{F}_n = -\nabla_n U$ is the force exerted on the n th bead, U is the interaction energy given as a function of $\mathbf{x}_n$, and $k_B T$ is the thermal energy. $\sqrt{\mathbf{G}}$ is the square root of $\mathbf{G}$ such that $\left(\sqrt{\mathbf{G}} \right)_{\alpha\gamma}^{nl} \left(\sqrt{\mathbf{G}} \right)_{\beta\gamma}^{ml} = G_{\alpha\beta}^{nm}$, whereas $\cdot$ denotes the Itô multiplication,[86] and ξ_n is the Gaussian white noise which satisfies the relation as

$$\langle \xi_{n\alpha}(t) \xi_{m\beta}(t') \rangle = \delta_{nm} \delta_{\alpha\beta} \delta(t - t'). \quad (3.9)$$

To include the effects of the no-slip boundary, Rotne-Prager approximation for Blake tensor[87] is used for the mobility tensor for distinct particles ($n \neq m$), [88, 89] although it is valid only for particles separated far away. In this study, we neglect lubrication corrections for nearby particles.[90] The Blake tensor for the velocity at $\mathbf{x}_2$ induced by a point force at $\mathbf{x}_1$ with the no-slip boundary at $z = 0$ is given by the Oseen tensor and the coupling

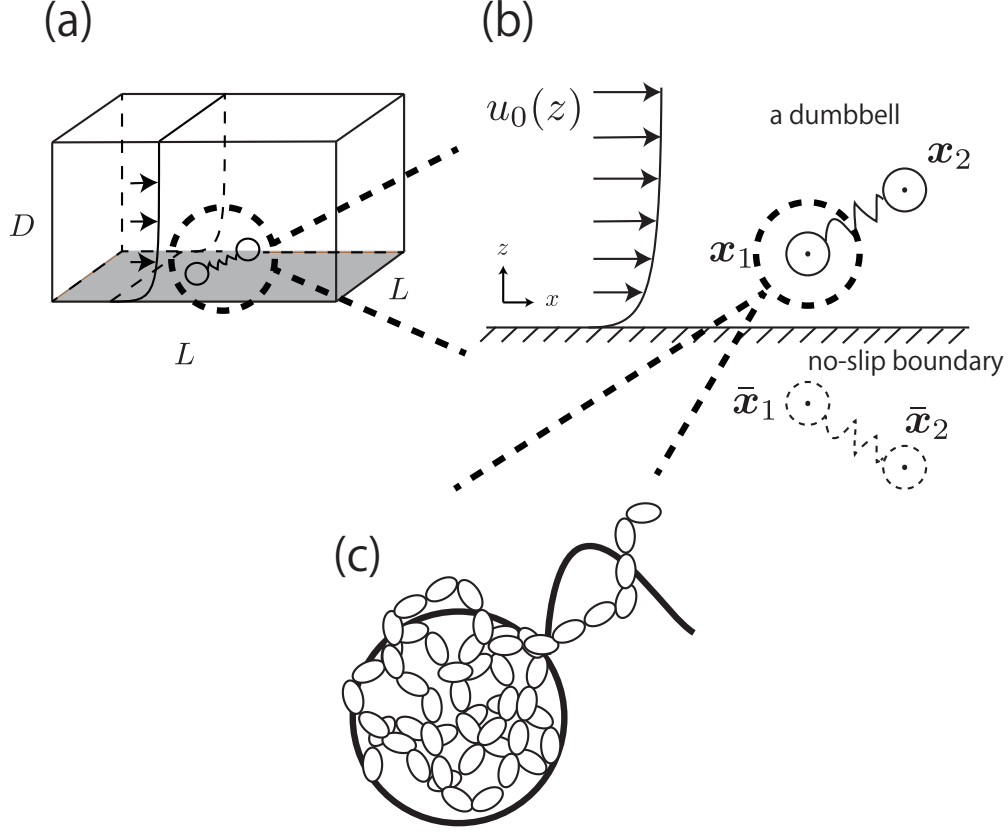


FIG. 28. (a) A dumbbell in the simulated box with $L \times L \times D$. Periodic boundary condition has imposed at x - y plane. (b) A x - z projection of the dumbbell in the electro-osmotic flow. (c) An enlarged illustration of the bead in the dumbbell. It is composed of a large number of monomeric units of the polymers. Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

fluid-wall tensor as,[87]

$$G_{\alpha\beta}^B(\mathbf{x}_2, \mathbf{x}_1) = S_{\alpha\beta}(\mathbf{q}) + G_{\alpha\beta}^W(\mathbf{x}_2, \mathbf{x}_1), \quad (3.10)$$

where $\mathbf{q} = \mathbf{x}_2 - \mathbf{x}_1$, $\mathbf{R} = \mathbf{x}_2 - \bar{\mathbf{x}}_1$, and $\bar{\mathbf{x}}_1$ is the mirror image of $\mathbf{x}_1$ with respect to the plane $z = 0$ (see Fig. 28(b)). The Oseen tensor given by

$$S_{\alpha\beta}(\mathbf{q}) = \frac{1}{8\pi\eta_0} \left(\frac{\delta_{\alpha\beta}}{q} + \frac{q_\alpha q_\beta}{q^3} \right), \quad (3.11)$$

where q is the magnitude of $\mathbf{q}$, and the second term in eq. (3.10) is

$$\begin{aligned} G_{\alpha\beta}^W(\mathbf{x}_2, \mathbf{x}_1) = & -S_{\alpha\beta}(\mathbf{R}) + z_1^2(1 - 2\delta_{\beta z})\nabla_R^2 S_{\alpha\beta}(\mathbf{R}) \\ & - 2z_1(1 - 2\delta_{\beta z})S_{\alpha z, \beta}(\mathbf{R}), \end{aligned} \quad (3.12)$$

where

$$S_{\alpha\beta,\gamma}(\mathbf{q}) = \nabla_{q\gamma} S_{\alpha\beta}(\mathbf{q}), \quad (3.13)$$

and $\nabla_{q\gamma} = \partial/\partial q_\gamma$. The Rotne-Prager approximation of the Blake tensor is given by [9, 88–91]

$$G_{\alpha\beta}^{\text{RPB}}(\mathbf{x}_2, \mathbf{x}_1) = \begin{cases} \left(1 + \frac{a^2}{6}\nabla_1^2 + \frac{a^2}{6}\nabla_2^2\right) G_{\alpha\beta}^{\text{B}}(\mathbf{x}_2, \mathbf{x}_1) + \mathcal{O}(a^4) \\ \text{for } q > 2a, \\ \\ \frac{1}{6\pi\eta_0 a} \left[\delta_{\alpha\beta} - \frac{9q}{32a} \left(\delta_{\alpha\beta} - \frac{q_\alpha q_\beta}{3q^2} \right) \right] \\ + \left(1 + \frac{a^2}{6}\nabla_1^2 + \frac{a^2}{6}\nabla_2^2\right) G_{\alpha\beta}^{\text{W}}(\mathbf{x}_2, \mathbf{x}_1) + \mathcal{O}(a^4) \\ \text{for } q \leq 2a. \end{cases} \quad (3.14)$$

The mobility tensor for the self part is given by [9, 88–91]

$$G_{\alpha\beta}^{\text{self}}(z) = \lim_{\mathbf{x} \rightarrow \mathbf{x}_1} G_{\alpha\beta}^{\text{RPB}}(\mathbf{x}, \mathbf{x}_1) = \begin{pmatrix} \mu_{\parallel}(z) & 0 & 0 \\ 0 & \mu_{\parallel}(z) & 0 \\ 0 & 0 & \mu_{\perp}(z) \end{pmatrix}, \quad (3.15)$$

where

$$\mu_{\parallel}(z) = \frac{1}{6\pi\eta_0 a} \left[1 - \frac{9a}{16z} + \frac{1}{8} \left(\frac{a}{z} \right)^3 \right] + \mathcal{O}(a^4), \quad (3.16)$$

$$\mu_{\perp}(z) = \frac{1}{6\pi\eta_0 a} \left[1 - \frac{9a}{8z} + \frac{1}{2} \left(\frac{a}{z} \right)^3 \right] + \mathcal{O}(a^4). \quad (3.17)$$

Finally we obtain the mobility tensor as

$$G_{\alpha\beta}^{nm} = \delta_{nm} G_{\alpha\beta}^{\text{self}}(z_n) + (1 - \delta_{nm}) G_{\alpha\beta}^{\text{RPB}}(\mathbf{x}_n, \mathbf{x}_m). \quad (3.18)$$

The non-uniform mobility term in eq. (3.8) can be simplified within using the Rotne-Prager approximation of the Blake tensor because the relation

$$\sum_{\beta=x,y,z} \nabla_{m\beta} G_{\alpha\beta}^{\text{RPB}}(\mathbf{x}_n, \mathbf{x}_m) = 0, \quad (3.19)$$

is hold. Thus, the non-uniform mobility term is rewritten by

$$\sum_{m,\beta} \nabla_{m\beta} G_{\alpha\beta}^{nm} = \delta_{\alpha z} \nabla_{nz} \mu_{\perp}(z_n). \quad (3.20)$$

The interaction energy includes spring and bead-wall interaction given by

$$U = U^s(q) + \sum_{n=1,2} U^w(z_n), \quad (3.21)$$

where U^s is the spring energy as

$$U^s(q) = \begin{cases} \frac{H}{2}q^2, & \text{Hookian dumbbells,} \\ -\frac{H}{2}q_0^2 \ln \left[1 - \left(\frac{q}{q_0} \right)^2 \right], & \text{FENE dumbbells,} \end{cases} \quad (3.22)$$

where a FENE dumbbell stands for a finitely extensible nonlinear elastic dumbbell, and a parameter $b = Hq_0^2/k_B T$ is defined for convenience. U^w is the bead-wall interaction,^[92] which is purely repulsive as

$$U^w(z) = \begin{cases} w \left[\frac{2}{5} \left(\frac{a}{z} \right)^{10} - \left(\frac{a}{z} \right)^4 + \frac{3}{5} \right] & \text{for } z \leq a, \\ 0 & \text{for } z > a. \end{cases} \quad (3.23)$$

Eq. (3.8) is numerically solved. Reflection boundary condition is set at $z = D$. When the center of the dumbbell goes across the boundary, the z -coordinate of each beads are transformed from z to $2D - z$. For the lateral directions, the periodic boundary conditions are imposed. The size of the lateral directions is $L \times L$.

3.3. Results of simulation

The concentration and velocity profiles are calculated by

$$c(z) = \frac{1}{L^2} \left\langle \delta \left(z - \frac{z_1 + z_2}{2} \right) \right\rangle, \quad (3.24)$$

and

$$\delta u(z) = \frac{1}{\eta_0 L^2} \left\langle \sum_{n=1,2} \min(z, z_n) F_{nx} \right\rangle, \quad (3.25)$$

where $\delta(z)$ is the delta function, $\delta u(z) = u(z) - u_0(z)$ is the velocity increment due to the polymeric stress, and $\langle \dots \rangle$ means a statistical average in steady states. The derivation of eq. (3.25) is written in Appendix 3.A.

TABLE 2. Simulation parameters. N_t is the number of total steps, N_i is the number of interval steps for observation, N_m is the number of the sampling for each parameter set, and $\Delta\tau$ is the time increment. Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

	Hookian FENE $b = 600$ FENE $b = 50$		
N_t	5×10^{10}	5×10^{10}	25×10^{10}
N_i	5×10^3	5×10^3	25×10^3
N_m	3	3	5
$\Delta\tau$	0.01	0.0025	0.0001

For the surface with small zeta potential compared to $k_B T/e$ where e is the elementary charge, the imposed electro-osmotic flow $u_0(z)$ is given by

$$u_0(z) = \mu_0 E (1 - e^{-\kappa z}), \quad (3.26)$$

where μ_0 is the electro-osmotic mobility in the pure solvent, and E is the applied electric field.[2] Eq. (3.8) is rewritten in a dimensionless form with the length scale $\delta_0 = \sqrt{k_B T/H}$ and time scale $\tau = 6\pi\eta_0 a/4H$. The different types of dumbbells are simulated with the parameters noted in Table 2. It should be noted that the simulated systems are treated as dilute systems and the linearity with respect to the bulk polymer concentration is preserved. After sample averaging, we obtain the concentration at the upper boundary $c(D)$, which slightly deviates from $(L^2 D)^{-1}$ because of the inhomogeneity near the surface. Hereafter, we define the normalized concentration as,

$$C(z) = \frac{c(z)}{c(D)}. \quad (3.27)$$

As well as the concentration profile, the velocity increment $\delta u(z)$ has the linearity with respect to $c(D)$. For convenience, we set a characteristic concentration $c_b = 0.1\delta_0^{-3}$, and the nonlinear electro-osmotic mobility is defined by

$$\mu(E) = \mu_0 + \frac{c_b}{c(D)} \frac{\delta u(D)}{E}. \quad (3.28)$$

The top boundary is placed at $D = 100\delta_0$, the lateral size is set to $L = 1000\delta_0$, and the Debye length is set to $\lambda = \kappa^{-1} = 10\delta_0$. We also set $w = 3k_B T$, and a hydrodynamic parameter h^*

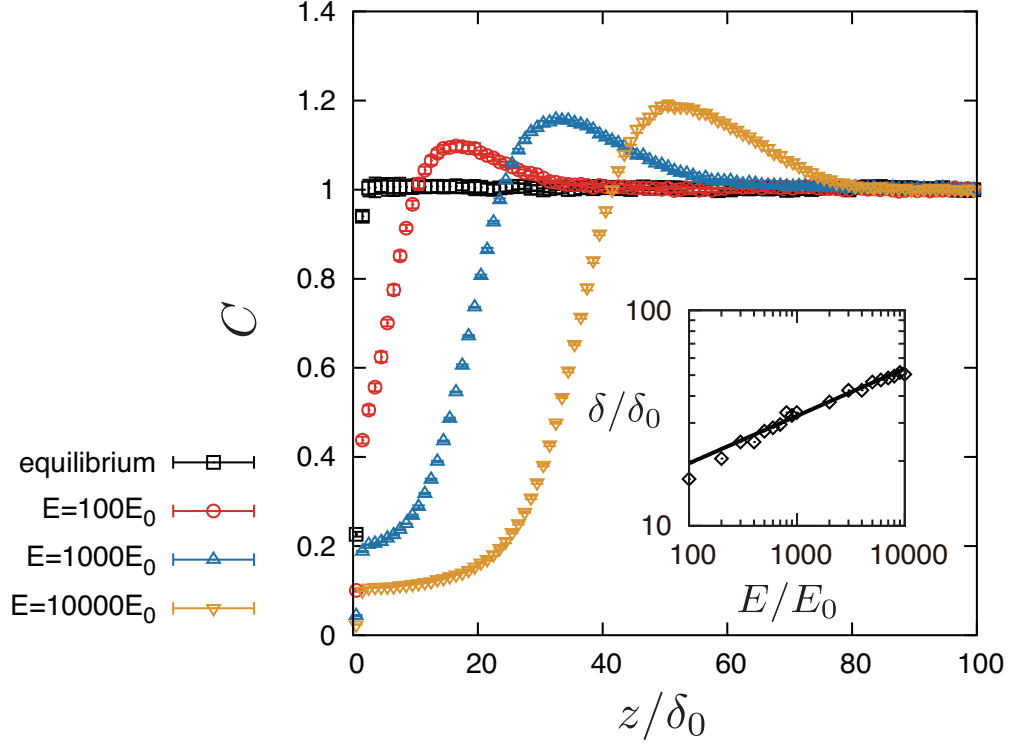


FIG. 29. The concentration profiles of the Hookian dumbbells with varied applied electric fields. The inset shows the depletion length as a function of the applied field. The points are obtained by the Brownian dynamics simulation and the line is fitted by $\delta/\delta_0 = A(E/E_0)^B$, where $A = 7.08$ and $B = 0.22$. Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

as[34]

$$h^* = \frac{a}{\sqrt{\pi}\delta_0} = 0.25. \quad (3.29)$$

Fig. 29 shows the steady state profiles of the Hookian-dumbbell concentration as functions of the distance from the wall. In the equilibrium state of $E = 0$, the profile shows the depletion layer whose thickness is of the same order as the gyration length δ_0 . When the applied electric field is increased stronger, the depletion layer becomes larger than the equilibrium one and a peak is formed. The inset in Fig. 29 shows the depletion length as a function of the applied field. The depletion length is defined by the position of the concentration peak. It shows a power-law behavior and its exponent is 0.22, which is much smaller than 2.0 in the case of a uniform shear flow.[34] The value of the concentration at the peak also increases as the electric field is enlarged.

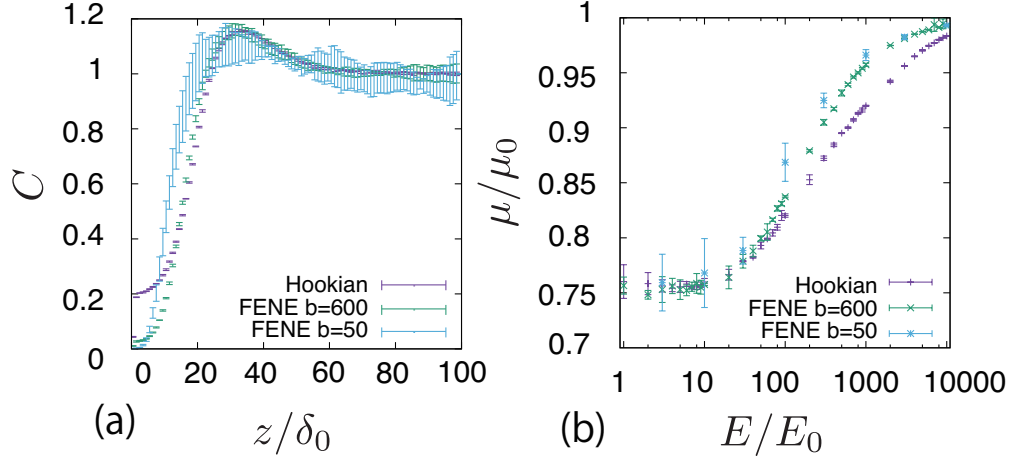


FIG. 30. (a) The concentration profiles of the polymers at $E = 1000E_0$ in the different types of dumbbells. (b) Plots of the nonlinear electro-osmotic mobilities with respect to E . Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

The results mentioned above are for the Hookian dumbbell which is infinitely extensible with the shear deformation. To consider more realistic polymers, the finitely extensible nonlinear elastic dumbbell is simulated. Fig. 30 (a) shows the concentration profiles at $E = 1000E_0$. Interestingly, the one-peak behaviors are also observed in the FENE dumbbells. In the case of the Hookian dumbbell, the concentration near the surface remains finite. On the other hand, in the case of the FENE dumbbells, the concentrations near the surface are negligibly small. Fig. 30 (b) plots the electro-osmotic mobilities with respect to the applied electric field. It is clearly shown the resultant electro-osmosis grows nonlinearly with respect to applied electric field. When the applied field gets stronger, the mobility increases and is saturated similarly to that in the toy model. The two types of the dumbbells have different rheological properties from each other at the bulk,[93–95] so that this nonlinearity is not owing to the rheological properties of the dumbbells. On the other hand, the mobility is almost constant for $E \lesssim 10E_0$, and this threshold of the linearity is larger than E_0 , that is predicted by the toy model. Likewise the saturation is observed when $E \approx 10^4E_0$, which is larger than E_1 .

To clarify the difference of the profiles near the surface, $\langle q^2 \rangle$ and $\langle q_z^2/q^2 \rangle$ are plotted with respect to the distance from the surface. Fig. 31 (a) shows the profiles of $\langle q_z^2/q^2 \rangle$. In the bulk, they approach to $1/3$, which means the dumbbells are distributed isotropically. Near the surface, the polymers are inclined by the shear flow. Concerning the angles between

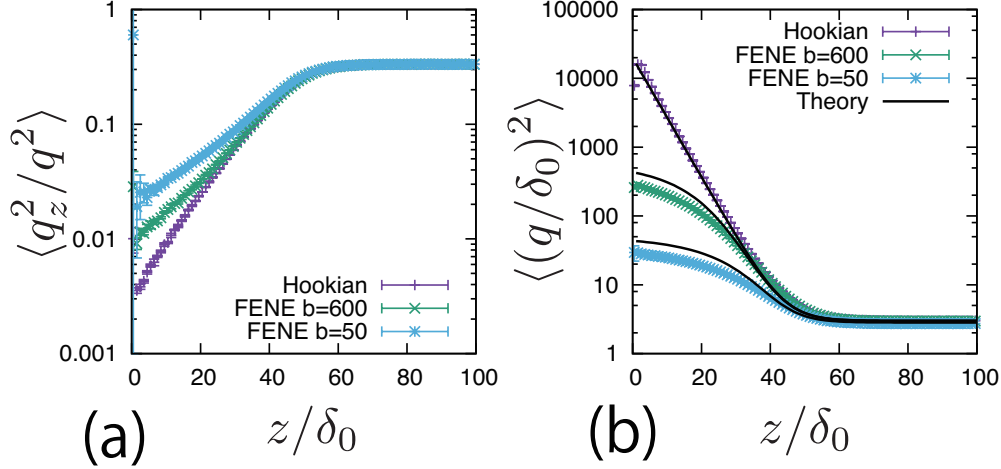


FIG. 31. (a) The profiles of $\langle q_z^2/q^2 \rangle$ at $E = 1000E_0$ in the different types of the dumbbells. (b) The profiles of $\langle (q/\delta_0)^2 \rangle$ at $E = 1000E_0$ in the different types of the dumbbells. The curved lines are calculated by eqs. (3.62) and (3.71). Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

the z -axis and the dumbbell direction, that of the Hookian dumbbell is the largest among them. Fig. 31 (b) plots the profiles of $\langle q^2 \rangle$. In the bulk, they approach to $3\delta_0$ which is the equilibrium value of them. Near the surface, they become larger since the polymers are elongated by the shear flow. In the case of FENE dumbbells, the saturations of the dumbbell length are observed. These behaviors are largely different from the minor difference in the concentration profiles.

3.4. Kinetic theory

In this section, a kinetic theory for a dumbbell is developed based on Ma-Graham theory.[34] The probability function $\Psi(\mathbf{x}_1, \mathbf{x}_2, t)$ obeys the continuity equation

$$\frac{\partial \Psi}{\partial t} = -\nabla_1 \cdot (\dot{\mathbf{x}}_1 \Psi) - \nabla_2 \cdot (\dot{\mathbf{x}}_2 \Psi), \quad (3.30)$$

where $\dot{\mathbf{x}}_n$ is the flux velocity being given by[57]

$$\dot{x}_{n\alpha} = u_0(z_n)\delta_{x\alpha} - \sum_{m,\beta} G_{\alpha\beta}^{nm} \nabla_{m\beta} (U + k_B T \ln \Psi). \quad (3.31)$$

In the kinetic model, the beads are treated as point-like particles. Thus, the mobility tensor is obtained by using $\mathbf{G}^B$ instead of $\mathbf{G}^{RPB}$ for both the self and distinct parts. The continuity

equation can be rewritten with $\mathbf{q}$ and $\mathbf{r}$ as

$$\frac{\partial \Psi}{\partial t} = -\nabla_{\mathbf{r}} \cdot (\dot{\mathbf{r}} \Psi) - \nabla_{\mathbf{q}} \cdot (\dot{\mathbf{q}} \Psi), \quad (3.32)$$

where $\mathbf{r} = (\mathbf{x}_1 + \mathbf{x}_2)/2$ is the center of the mass of the dumbbell. We also define ∇_1 and ∇_2 as

$$\nabla_1 = \frac{1}{2} \nabla_{\mathbf{r}} - \nabla_{\mathbf{q}}, \quad (3.33)$$

$$\nabla_2 = \frac{1}{2} \nabla_{\mathbf{r}} + \nabla_{\mathbf{q}}. \quad (3.34)$$

Then, the probability function is also regarded as a function of $\mathbf{r}$ and $\mathbf{q}$. Here we neglect the interaction between the wall and beads. The flux velocities for $\mathbf{r}$ and $\mathbf{q}$ are obtained by

$$\begin{aligned} \dot{r}_\alpha &= \frac{1}{2} [u_0(z_1) + u_0(z_2)] \delta_{x\alpha} + \frac{1}{2} \bar{G}_{\alpha\beta} F_\beta^s \\ &\quad + \frac{k_B T}{2} \bar{G}_{\alpha\beta} \nabla_{q\beta} \ln \Psi - D_{\alpha\beta}^K \nabla_{r\beta} \ln \Psi, \end{aligned} \quad (3.35)$$

$$\begin{aligned} \dot{q}_\alpha &= [u_0(z_2) - u_0(z_1)] \delta_{x\alpha} - \hat{G}_{\alpha\beta} F_\beta^s \\ &\quad + \frac{k_B T}{2} \bar{G}_{\alpha\beta} \nabla_{r\beta} \ln \Psi - k_B T \hat{G}_{\alpha\beta} \nabla_{q\beta} \ln \Psi, \end{aligned} \quad (3.36)$$

where $\mathbf{F}^s = -\nabla_1 U^s$ is the spring force, and $\mathbf{D}^K$ is the Kirkwood diffusion tensor which characterizes the diffusivity of macromolecules, given by

$$\mathbf{D}^K = \frac{k_B T (\mathbf{G}^{11} + \mathbf{G}^{12} + \mathbf{G}^{21} + \mathbf{G}^{22})}{4}. \quad (3.37)$$

$\bar{\mathbf{G}}$ and $\hat{\mathbf{G}}$ are a variation of the mobility tensors defined by

$$\bar{\mathbf{G}} = \mathbf{G}^{11} - \mathbf{G}^{12} + \mathbf{G}^{21} - \mathbf{G}^{22}, \quad (3.38)$$

$$\hat{\mathbf{G}} = \mathbf{G}^{11} - \mathbf{G}^{12} - \mathbf{G}^{21} + \mathbf{G}^{22}. \quad (3.39)$$

The concentration field $c(\mathbf{r}, t)$ can be obtained by integrating the probability function with respect to the spring coordinate. It is given by

$$c(\mathbf{r}, t) = \int \Psi(\mathbf{r}, \mathbf{q}, t) d\mathbf{q}. \quad (3.40)$$

We also define the probability function only for the spring coordinate as

$$\hat{\Psi}(\mathbf{q}, t; \mathbf{r}) = \frac{\Psi(\mathbf{r}, \mathbf{q}, t)}{c(\mathbf{r}, t)}. \quad (3.41)$$

These new fields satisfy the continuity conditions, such that

$$\frac{\partial c}{\partial t} = -\nabla_r \cdot (c\langle \dot{\mathbf{r}} \rangle_q), \quad (3.42)$$

$$\frac{\partial \hat{\Psi}}{\partial t} = -\nabla_q \cdot (\hat{\Psi} \dot{\mathbf{q}}), \quad (3.43)$$

where $\langle \dots \rangle_q$ means the average with the spring coordinate, as

$$\langle \dots \rangle_q = \frac{\int \dots \Psi(\mathbf{r}, \mathbf{q}, t) d\mathbf{q}}{c(\mathbf{r}, t)} = \int \dots \hat{\Psi}(\mathbf{r}, \mathbf{q}, t) d\mathbf{q}. \quad (3.44)$$

For the limit of $q \ll r$, $\bar{\mathbf{G}}$ and $\mathbf{D}^K$ can be expanded with $\mathbf{r}$. With keeping only the leading term, we obtain

$$\bar{\mathbf{G}} = \frac{3}{32\pi\eta_0 z^2} \begin{pmatrix} -q_z & 0 & -\omega q_x \\ 0 & -q_z & -\omega q_y \\ \omega q_x & \omega q_y & -2q_z \end{pmatrix} + \dots, \quad (3.45)$$

$$\mathbf{D}^K = \frac{k_B T}{12\pi\eta_0 a} \left[\mathbf{I} + \frac{3a}{4} \mathbf{S}(\mathbf{q}) \right] + \dots, \quad (3.46)$$

where

$$\omega = \left[1 + \frac{q_x^2 + q_y^2}{4z^2} \right]^{-5/2}. \quad (3.47)$$

It should be noted that the approximation is more accurate than that in a previous study[34] since they considered only $\omega \approx 1$, which is not satisfied near the surface. With the approximation, eq. (3.36) is averaged by $\hat{\Psi}$, and finally we obtain the concentration flux for z direction as

$$c\langle \dot{r}_z \rangle_q = cu_{\text{mig}}(z) - \frac{d}{dz} [c\langle D_{zz}^K \rangle_q], \quad (3.48)$$

where

$$\begin{aligned} u_{\text{mig}}(z) &= \frac{1}{2} \langle \bar{G}_{z\beta} F_\beta^s - k_B T \nabla_{q\beta} \bar{G}_{z\beta} \rangle_q \\ &= \frac{3}{64\pi\eta_0 z^2} \\ &\quad \times \langle \omega(q_x F_x^s + q_y F_y^s) - 2q_z F_z^s - 2k_B T(\omega - 1) \rangle_q. \end{aligned} \quad (3.49)$$

Eq. (3.48) indicates two opposite fluxes of the polymers due to the external flow field. One is the migration flux from the wall toward the bulk and originates from the hydrodynamic interaction between the wall and the force dipoles.[34] The other is the diffusion flux from

the bulk to the surface wall and is not found in the case of polymers in uniform shear flows.[34] It should be noted that the second flux includes not only the ordinary diffusion flux $\langle D_{zz}^K \rangle_q \nabla_{r,z} c$, but also the diffusion flux due to the q -inhomogeneity, $c \nabla_{r,z} \langle D_{zz}^K \rangle_q$. When the external shear flow is uniform, the second flux vanishes, and the depletion length is proportional to the square of the shear rate since the migration velocity is proportional to the normal stress difference.[34] In the case of a plug flow, the diffusion flux suppresses the growth of the depletion layer and it may answer why the exponent of the depletion length is much smaller than 2.0 in the uniform shear flow. In steady states of the electro-osmosis, the total flux in eq. (3.48) becomes zero, and thus,

$$\frac{dc}{dz} = \frac{c}{\langle D_{zz}^K \rangle_q} \left(u_{\text{mig}} - \frac{d\langle D_{zz}^K \rangle_q}{dz} \right). \quad (3.50)$$

This equation shows the migration flux and the diffusion flux are balanced at the peak of the concentration profiles. Finally the concentration profile is calculated by

$$c = c_b \exp \left[\int_D^z \frac{1}{\langle D_{zz}^K \rangle_q} \left(u_{\text{mig}}(z') - \frac{d\langle D_{zz}^K \rangle_q}{dz} \right) dz' \right]. \quad (3.51)$$

The resultant flow profile can be calculated by

$$\delta u(z) = -\frac{1}{\eta_0} \int_0^z \sigma_{xz}^p(z') dz', \quad (3.52)$$

where σ^p is the polymeric part of the stress tensor as

$$\sigma^p = c \langle \mathbf{q} \otimes \mathbf{F}^s \rangle_q - ck_B T \mathbf{I}. \quad (3.53)$$

To obtain explicit expressions of c and δu , it is necessary to estimate u_{mig} , $\langle D_{zz}^K \rangle_q$, and σ^p . For this purpose, eq. (3.43) should be analyzed. However, eq. (3.43) is highly complicated. Even without the wall effects, it cannot be solved exactly, so that several approximation methods have been proposed.[96] For simplicity, all the hydrodynamic interactions are ignored, and thus, the continuity equation is given

$$\frac{\partial \hat{\Psi}}{\partial t} = -\nabla_{q\alpha} \left[\left(\frac{du_0}{dz} q_z \delta_{z\alpha} - \frac{2F_\alpha^s}{6\pi\eta_0 a} \right) \hat{\Psi} - \frac{2k_B T}{6\pi\eta_0 a} \nabla_{q\alpha} \hat{\Psi} \right]. \quad (3.54)$$

For the Hookian dumbbell eq. (3.54) can be solved for the second moment of $\mathbf{q}$, and for the FENE dumbbell pre-averaged approximation[94, 95] is employed. The curved lines in Fig. 31 are calculated with these approximations, and they agree quantitatively well with

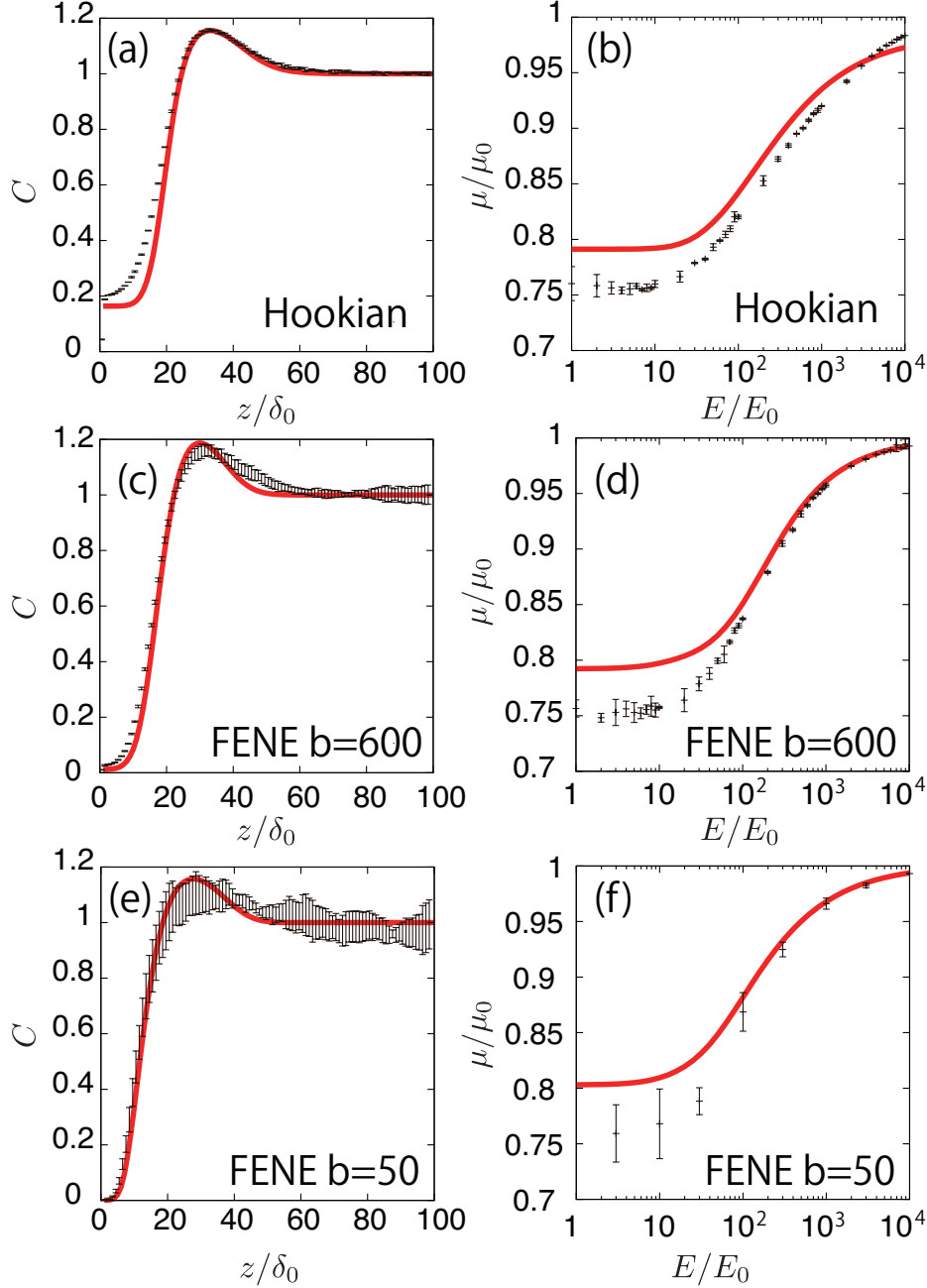


FIG. 32. (a) The concentration profiles of the Hookian dumbbell as a function of the distance from the surface. The points show the simulation results and the curved line is calculated by the kinetic theory. (b) The nonlinear electro-osmotic mobilities of the Hookian dumbbell as a function of a applied electric field. (c) and (d) Those for the FENE dumbbell with $b = 600$. (e) and (f) Those for the FENE dumbbell with $b = 50$. Reproduced from ref. [84] with permission of The Royal Society of Chemistry. [doi:10.1039/C5SM01507C](https://doi.org/10.1039/C5SM01507C)

the simulation results. In Appendix 3.B, approximated expressions for these quantities of the Hookian and FENE dumbbells are written.

Fig. 32 (a), (c) and (e) show the concentration profiles for the applied field $E = 1000E_0$. The points are obtained by the Brownian dynamics simulation and the curved lines are obtained by the kinetic theory. The theoretical calculations quantitatively cover well the simulations. Moreover, they reproduce the differences in the concentration near the surface between the Hookian and FENE dumbbells, since the migration velocities can be approximately proportional to $\langle\omega\rangle_q$ (see Appendix 3.B), and it is much suppressed in the case of the Hookian dumbbells. Fig. 32 (b), (d), and (f) show the nonlinear electro-osmotic mobilities with respect to the applied field. The theoretical curved lines also have an acceptable tendency with the simulation results. However, they are not so consistent with the simulation results in weak applied electric fields since the equilibrium depletion layer is not considered in the kinetic theory.

3.5. Summary and remarks

With Brownian dynamics simulations, nonlinear behaviors of electro-osmosis of dilute polymer solutions are studied. The simulation results agree with a toy-model and analytical calculations of a kinetic theory. The main results are summarized below.

- (i) Under an external plug flow, the polymer migrates toward the bulk. The concentration profile of the polymer shows a depletion layer and a single peak. The thickness of the depletion layer depends on the electric field. At the peak, the migration flux is balanced to the diffusion flux.
- (ii) The growth of depletion layer leads to increment and saturation in the electro-osmotic mobility. Qualitatively this behavior does not depend on the rheological properties of the dumbbells.
- (iii) Analytical calculation of the concentration and the nonlinear mobility by the kinetic theory is in agreement with the Brownian dynamics simulation. The threshold of the electric field for the nonlinear growth and saturation of the mobility is much larger than the prediction of the toy model, since the diffuse flux suppresses the migration toward the bulk due to the inhomogeneous shear flow.

We conclude this study with the following remarks.

- (1) Nonlinear electro-osmosis with $\lambda \ll \delta_0$ has already been observed experimentally.[29, 30] They reported the mobility is increased with increasing the electric field. However, the nonlinear electro-osmosis with $\lambda \gg \delta_0$ has not been reported experimentally, and therefore, experimental verification of our findings is highly desired.
- (2) It would be a future problem whether the hydrodynamic interaction between the polymers and the surface plays an important role in electro-osmosis in polymer solutions even though $\lambda \ll \delta_0$ or not. In this case the elongation of the polymers is strongly inhomogeneous under the plug flow with a short Debye length, and thus, more realistic chain models should be considered.
- (3) Addition of charged polymers into solutions can change the direction of the linear electro-osmotic flow.[10, 26] When a sufficiently strong electric field is applied to this system, the direction of the flow might recover its original one. It needs to be investigated theoretically and experimentally.

Appendix 3.A Derivation of the velocity for Brownian dynamics simulation

In this appendix, the derivation of eq. (3.25) is explained. The velocity field induced by the polymer is given by

$$\delta u(z) = -\frac{1}{\eta_0} \int_0^z \sigma_{xz}^p(z) dz, \quad (3.55)$$

and the polymeric part of the stress tensor is obtained by averaging those of the microscopic expression in the lateral directions as

$$\sigma_{\alpha\beta}^p = \frac{1}{L^2} \int dx dy \hat{\sigma}_{\alpha\beta}^p(\mathbf{x}). \quad (3.56)$$

Here the microscopic expression of the stress tensor is given by

$$\hat{\sigma}_{\alpha\beta}^p(\mathbf{x}) = -\frac{1}{2} \sum_n \sum_{m \neq n} F_{nm,\alpha} x_{nm,\beta} \delta_{nm}^s(\mathbf{x}), \quad (3.57)$$

where $\mathbf{F}_{nm}$ is the force exerted on the n -th bead from the m -th bead and $\delta_{nm}^s(\mathbf{x})$ is the symmetrized delta function given by

$$\delta_{nm}^s(\mathbf{x}) = \int_0^1 ds \delta(\mathbf{x} - s\mathbf{x}_n - (1-s)\mathbf{x}_m). \quad (3.58)$$

The symmetrized delta function is integrated in the lateral directions as

$$\begin{aligned}\bar{\delta}_{nm}^s(z) &= \int dx dy \delta_{nm}^s(\mathbf{x}) = \int_0^1 ds \delta(z - sz_n - (1-s)z_m) \\ &= \frac{\theta(z - z_m) - \theta(z - z_n)}{z_n - z_m},\end{aligned}\tag{3.59}$$

where $\theta(z_n - z) = 1 - \theta(z - z_n)$. Then we obtain

$$\begin{aligned}\int_0^z dz' \bar{\delta}_S^{nm}(z') &= \frac{(z - z_n)\theta(z - z_n) - (z - z_m)\theta(z - z_m)}{z_m - z_n} \\ &= \frac{\min(z, z_n) - \min(z, z_m)}{z_n - z_m},\end{aligned}\tag{3.60}$$

where $\min(z, z_n) = z\theta(z) - (z - z_n)\theta(z - z_n)$. Finally, the velocity increment is expressed by

$$\begin{aligned}\delta u(z) &= \frac{1}{2\eta_0 L^2} \sum_{n,m} F_{nm,1}(z_n - z_m) \int_0^z dz' \bar{\delta}_{nm}^s(z') \\ &= \frac{1}{2\eta_0 L^2} \sum_{nm} F_{nm,1} [\min(z, z_n) - \min(z, z_m)] \\ &= \frac{1}{\eta_0 L^2} \sum_n \min(z, z_n) F_{n,1}.\end{aligned}\tag{3.61}$$

Appendix 3.B Approximated expressions for kinetic theory

3.B.1 Hookian dumbbell

Eq. (3.54) can be rewritten in a closed form for the second moment of the spring coordinates in a steady state with an imposed plug flow. The solution is given by[95]

$$\langle \mathbf{q} \otimes \mathbf{q} \rangle_q = \frac{k_B T}{H} \begin{pmatrix} 1 + 2\theta^2 & 0 & \theta \\ 0 & 1 & 0 \\ \theta & 0 & 1 \end{pmatrix},\tag{3.62}$$

where

$$\theta = \tau \frac{du_0}{dz} = \tau \kappa \mu_0 E e^{-\kappa z}.\tag{3.63}$$

Therefore, we have

$$\langle \mathbf{q} \otimes \mathbf{F}^s \rangle_q = H \langle \mathbf{q} \otimes \mathbf{q} \rangle_q,\tag{3.64}$$

and the polymeric stress tensor is

$$\begin{aligned}\boldsymbol{\sigma}^p &= c\langle \mathbf{q} \otimes \mathbf{F}^s \rangle_q - ck_B T \mathbf{I} \\ &= ck_B T \begin{pmatrix} 2\theta^2 & 0 & \theta \\ 0 & 0 & 0 \\ \theta & 0 & 0 \end{pmatrix}.\end{aligned}\quad (3.65)$$

The Kirkwood diffusion constant can be estimated by

$$\begin{aligned}\langle D_{zz}^K \rangle_q &= \frac{k_B T}{12\pi\eta_0 a} \left[1 + \frac{3a}{4} \left\langle \frac{1}{q} \left(1 + \frac{q_z^2}{q^2} \right) \right\rangle_q \right] \\ &\approx \frac{k_B T}{12\pi\eta_0 a} \left[1 + \frac{3a}{4} \frac{\langle q^2 + q_z^2 \rangle_q}{\langle q^2 \rangle_q^{3/2}} \right],\end{aligned}\quad (3.66)$$

where the second term is split into the second order moments, and thus, we obtain

$$\langle D_{zz}^K \rangle_q = \frac{k_B T}{12\pi\eta_0 a} \left[1 + \frac{3a}{4\delta} \frac{2(\theta^2 + 2)}{(2\theta^2 + 3)^{3/2}} \right]. \quad (3.67)$$

It is differentiated with z as

$$\frac{d}{dz} \langle D_{zz}^K \rangle_q = \frac{k_B T}{12\pi\eta_0 a} \frac{3a}{4\delta} \frac{4\kappa\theta^2(\theta^2 + 3)}{(2\theta^2 + 3)^{5/2}}. \quad (3.68)$$

The migration velocity can be estimated using the splitting approximation of the averages as

$$\begin{aligned}u_{\text{mig}}(z) &= \frac{3k_B T}{64\pi\eta_0 z^2} \langle \omega(q_x^2 + q_y^2) - 2\omega \rangle_q \\ &\approx \frac{3k_B T}{32\pi\eta_0 z^2} \langle \omega \rangle_q \langle q_x^2 + q_y^2 - 2 \rangle_q \\ &= \frac{3k_B T}{32\pi\eta_0 z^2} \langle \omega \rangle_q \theta^2,\end{aligned}\quad (3.69)$$

where

$$\begin{aligned}\langle \omega \rangle_q &= \left\langle \left(1 + \frac{q_x^2 + q_y^2}{4z^2} \right)^{-5/2} \right\rangle_q \\ &\approx \left(1 + \frac{\theta^2 + 1}{2z^2} \right)^{-5/2}.\end{aligned}\quad (3.70)$$

3.B.2 FENE dumbbell

The second moment of the spring coordinate for a FENE dumbbell can be obtained by pre-averaged closures of p-FENE model.[94, 95] It is given by

$$\langle \mathbf{q} \otimes \mathbf{q} \rangle_q = \frac{k_B T}{H} \frac{\Theta}{\theta} \begin{pmatrix} 1 + 2\Theta^2 & 0 & \Theta \\ 0 & 1 & 0 \\ \Theta & 0 & 1 \end{pmatrix}, \quad (3.71)$$

and

$$\langle \mathbf{q} \otimes \mathbf{F} \rangle_q = k_B T \begin{pmatrix} 1 + 2\Theta^2 & 0 & \Theta \\ 0 & 1 & 0 \\ \Theta & 0 & 1 \end{pmatrix}, \quad (3.72)$$

where

$$\Theta = 6\sqrt{\frac{3+b}{54}} \sinh \left\{ \frac{1}{3} \operatorname{arcsinh} \left[\frac{b\theta}{108} \left(\frac{3+b}{54} \right)^{-3/2} \right] \right\}. \quad (3.73)$$

The polymer stress tensor is

$$\boldsymbol{\sigma}^p = ck_B T \begin{pmatrix} 2\Theta^2 & 0 & \Theta \\ 0 & 0 & 0 \\ \Theta & 0 & 0 \end{pmatrix}. \quad (3.74)$$

The Kirkwood diffusion constant is

$$\langle D_{zz}^K \rangle_q = \frac{k_B T}{12\pi\eta_0 a} \left[1 + \frac{3a}{4\delta} \sqrt{\frac{\theta}{\Theta}} \frac{2(\Theta^2 + 2)}{(2\Theta^2 + 3)^{3/2}} \right], \quad (3.75)$$

and its derivative is

$$\begin{aligned} \frac{d}{dz} \langle D_{zz}^K \rangle_q &= \frac{k_B T}{12\pi\eta_0 a} \frac{3a}{4\delta} \times \kappa \sqrt{\frac{\theta}{\Theta}} \\ &\times \left[\theta \frac{d\Theta}{d\theta} \frac{4\Theta(\Theta^2 + 3)}{(2\Theta^2 + 3)^{5/2}} + \left(\frac{\theta}{\Theta} \frac{d\Theta}{d\theta} - 1 \right) \frac{2(\Theta^2 + 2)}{(2\Theta^2 + 3)^{3/2}} \right], \end{aligned} \quad (3.76)$$

where

$$\begin{aligned} \frac{d\Theta}{d\theta} &= 2\sqrt{\frac{b+3}{54}} \cosh \left\{ \frac{1}{3} \operatorname{arcsinh} \left[\frac{b\theta}{108} \left(\frac{3+b}{54} \right)^{-3/2} \right] \right\} \\ &\times \frac{b}{108} \left[\left(\frac{b\theta}{108} \right)^2 + \left(\frac{b+3}{54} \right)^3 \right]^{-1/2}. \end{aligned} \quad (3.77)$$

Finally the migration velocity is obtained as

$$u_{\text{mig}} \approx \frac{3k_{\text{B}}T}{32\pi\eta_0 z^2} \langle \omega \rangle_q \Theta^2, \quad (3.78)$$

where

$$\langle \omega \rangle_q \approx \left(1 + \frac{\Theta}{\theta} \frac{\Theta^2 + 1}{2z^2} \right)^{-5/2}. \quad (3.79)$$

4. SUMMARY

4.1. Conclusion

Electro-osmotic flow of charged and uncharged polymer solutions is studied by theories and simulations. We close this thesis with the following conclusion.

- (i) In the linear regime, charged and uncharged polymer solutions are treated within the framework of self-consistent field theory. When the polymer is uncharged and non-adsorbing, the structure of the electric double layer is characterized by the two lengths: the Debye length and the depletion length of the polymer. The electro-osmotic mobility varies according to the equilibrium structure of the double layers. When the salinity is low enough that the Debye length exceeds larger than the depletion length, the mobility is suppressed by the polymeric stress. On the other hand, when the salinity is large, the mobility is as large as that without the polymer.
- (ii) When the polymer is charged and chemically non-adsorbing to surfaces but electrically attractive, the depletion-adsorption transition occurs at a specific salt concentration. The transition is quite sharp, and the electro-osmotic mobility also varies sharply near the transition point. Furthermore, in the strong adsorption state, the linear mobility changes its sign. Flow reversal is induced by a combination of a high-viscosity adsorption layer and the overcharging potential.
- (iii) In the nonlinear regime, a neutral non-adsorbing polymer solution is studied using a Brownian dynamics simulation and theoretical calculation of the Fokker-Planck equation. The profile of the polymer concentration in a strong electric field shows a dynamic depletion layer that is ten times as thick as the equilibrium one. The mobility reflects the structure near the surface and become larger with increasing external electric field. When the depletion length equals the Debye length, the magnitude of the mobility is saturated and is nearly equal to that without the polymer. Theoretical calculation reproduces these results quantitatively.

4.2. Future works

Finally, we remark on the prospects. We have already given specific remarks in each section, so here we present remarks relevant to the entire thesis.

- (a) To verify our theory, it is desirable that more experimental studies to be reported. Our theory assumes that the complex molecular force between the surface and the polymer is treated by a simple boundary condition, and the individual properties of the polymers are totally neglected. Therefore, our prediction is only qualitatively meaningful. To make the theory more accurate and quantitative, experimental data are indispensable.
- (b) In sections 2 and 3, we totally ignored the dielectric nonuniformity induced by polymer adsorption and depletion. Most polymers have a dielectric constant of ~ 5 which is much smaller than that of water; thus, it seems to be important to consider the effect on the distribution of ions and the electrokinetic properties.
- (c) Using our results, we can control the electro-osmotic mobility by changing the salinity, charge fraction, and applied electric field. However, the magnitude of the mobility does not exceed the mobility without the polymer. To exceed it, it seems to be crucial that the added polymer reduce the original viscosity. One idea is adsorption to the surface with strongly hydrophobic polymers. This will create a pseudo-boundary, and the water molecules will be repelled from it to form the water depletion layer.
- (d) In this thesis, our study is limited to fundamental research to clarify the characteristic behaviour of the electrokinetics in polymer solutions. To promote and encourage experimental research, we should investigate more practical problems such as the efficiency of energy conversion. Another consideration is the entrance and exit effect on the electrokinetics, which is unavoidable in experiments. Around the entrance and exit of the channel or capillary, a concentration polarization is induced by the charge neutrality condition. This effect on the electrokinetics in the middle of channels or capillaries seems to be severe.

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