Physics of Soft and Biological Matter II: Problem Set 5

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Problem 1 *Mobilities of Various Ions Compared to Colloids, 10 points*

1) Use the Hückel mobility to calculate the mobility of a sodium ion in water:

$$\mu = \frac{Q}{6\pi\eta R} \tag{1}$$

where μ is the mobility, Q is the charge, η is the viscosity of the fluid, and R is the radius of the atom.
2) The Smoluchowski formula is:

$$\mu = \frac{\epsilon\zeta}{\eta} \approx \frac{\sigma}{\eta\kappa} \tag{2}$$

where ϵ is the permittivity and κ is the inverse debye length λ_D^{-1}. Use this formula to calculate the mobility of a colloid of radius 1μm in a solution of ionic strength 0.1M with a charge density of $0.2e/\mathrm{nm}^2$.
3) Calculate the diffusion coefficient of the sodium ion and the colloid using Stokes' law $D = kT/6\pi\eta R$.
4) Recall that the mobility is the ratio of the velocity to the electric field $\mu = v/E =< x > /tE$ and that the diffusion coefficient is $D =< (\Delta x)^2 > /2t$. For both the sodium ion and the colloid calculate the length and time where the mean displacement due to an electric field of 10 V/cm exceeds the mean square displacement caused by thermal fluctuations.

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Problem 2 *Hückel Limit for a Sphere, 5 points*

1) Assuming that the only forces on a charged sphere are an electric force due to an external electric field and Stokes drag, determine the terminal velocity of a charged sphere of radius R and charge Q in a fluid with viscosity η with electric field E. This

is valid in the Hückel limit where the Debye length is much bigger than the particle radius.
2) Use the following Debye-Hückel expression for the potential of a sphere to express this result in terms of the potential (defined as the ζ-potential) at the surface $r = R$:

$$\phi(r) = \frac{Q}{4\pi\epsilon r} \exp -\kappa r \tag{3}$$

Recall we are working in the low salt limit so $\kappa R \ll 1$, use this fact to eliminate the exponential.

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Problem 3 *Electroosmotic Flow over a Flat Plane, 10 points*

1) Use Poisson's equation and assume the ion's take on a Boltzmann distribution obtain a differential equation for the electrostatic potential above a wall of charge density σ in a 1:1 electrolyte:

$$\nabla^2\phi = \frac{-\rho_e}{\epsilon} \tag{4}$$

$$n_i = n_{0i} \exp \frac{-z_i e\phi}{kT} \tag{5}$$

$$\rho_e = \sum_i z_i e n_i \tag{6}$$

Where ϕ is the electrostatic potential, ρ_e is the charge density, ϵ is the permittivity, n_i is the local density of species i and n_{0i} is its bulk density (far from the surface), z_i is the valency, k is Boltzmann's constant, and T is the temperature.
2) The resulting equation is the Poisson-Boltzmann equation. Expand it to first order in order to obtain the Debye-Hückel approximation. This is valid in systems where $z_i e\phi \ll kT$. Show that the right hand side terms of zeroeth order in ϕ are zero when the fluid is electroneutral in the bulk (i.e.$\sum_i n_{0i} z_i e = 0$). The resulting equation should be linear in ϕ resulting in an equation of the form:

$$\nabla^2\phi = \kappa^2\phi \tag{7}$$

where κ is the inverse Debye length. Find the expression for κ.
3) Solve this linear differential equation assuming that the potential goes to zero far from the surface. Use Gauss' law to determine the constant representing the potential at the surface, often referred to as the ζ-potential.
4) Stokes' equation is valid in cases of laminar flow:

$$\eta\nabla^2 v = -f = -E\rho_e \tag{8}$$

where E is the electric field, v is the fluid velocity, and f is the force density on the fluid. Assume this is valid for our system and derive the velocity as a function of the position above the wall, assuming that the velocity at the wall is zero and is finite far from the wall. Find an expression for the velocity far from the wall using the ζ-potential and not the charge density σ, this is the classic Smoluchowski result.

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