

Lecture 15

Electrophoresis

As discussed in Lecture 14, the electrophoresis is a kind of electrokinetic phenomena, that charged particles moving under an external electric field E . The equation of motion for such charged particle, neglecting the gravity and buoyancy, is:

$$\begin{aligned} m \frac{dv}{dt} &= F_{\text{elec}} + F_{\text{friction}} \\ &= qE - \nu f \end{aligned} \quad (15.1)$$

where m is the mass of particle, q is the total charge of the particle, v is the velocity of the particle and f is the friction factor (the direction of friction force is opposite to the velocity). For a spherical object with radius R_s in a fluid with viscosity μ within the low Reynolds number regime, $f = 6\pi\mu R_s$ (Stokes' law¹). At steady state, $dv/dt = 0$, therefore we have:

$$v = \frac{qE}{6\pi\mu R_s} = u_{\text{ep}} E \quad (15.2)$$

where $u_{\text{ep}} = q/(6\pi\mu R_s)$ is the electrophoresis mobility. However, for an unknown kind of particles we know neither q nor R_s . Nevertheless, the macroscopic diffusivity \mathcal{D} of the system is measurable. Using the Einstein equation $u_{\text{ep}} = q\mathcal{D}/k_B T$, we have:

$$\mathcal{D} = \frac{u_{\text{ep}} kT}{q} = \frac{kT}{6\pi\mu R_s} \quad (15.3)$$

which is known as the Stokes-Einstein relation.² This is a handy equation: the microscopic quantity R_s is directly measurable via macroscopic diffusivity \mathcal{D} . To estimate the mobility u_{ep} , knowledge about the charge of particle q , is still required. From the Gauss law, the total charge of a particle equals the surface integral of the displacement field, such that $q = -\int_S \epsilon_0 \epsilon_r \nabla \psi \cdot dn$, therefore to solve the charge of the particle in an electrolyte solution, is equivalently to the problem of the electrical potential (ζ -potential) near the particle. We will show that the ζ -potential indeed determines the electrophoresis mobility of particles. As discussed in Lecture 14, the fluid flow may have a non-negligible influence on the electrostatic potential. Here we will discuss two limiting cases, the Hückel limit where the particle size is much smaller than the Debye length and the Smoluchowski limit where the particle size is much larger than the Debye length, as shown in Figure 15.1.

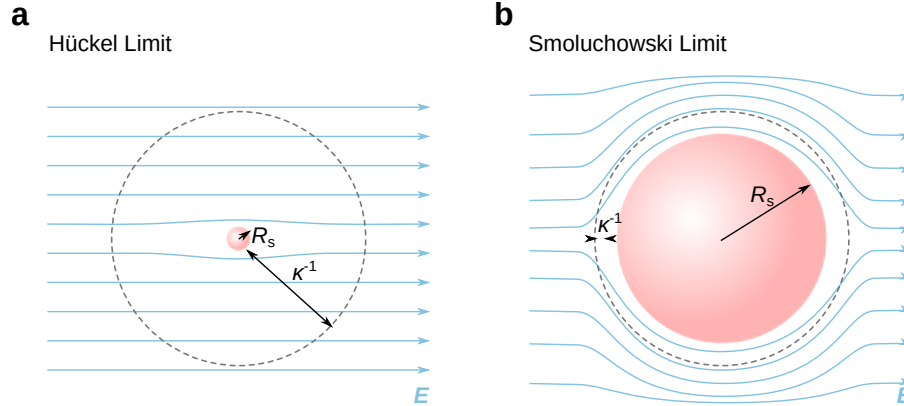


Figure 15.1: Two limiting cases of electrophoresis: (a) Hückel limit (particle size much smaller than Debye length) and (b) Smoluchowski limit (particle size much larger than Debye length).

15.1 The Hückel limit

The Hückel limit is the situation the $R_s \ll \kappa^{-1}$, i.e. the charged particles are considered as point charges, and the potential is solely contributed by equilibrium ion distribution in solution. Assuming a small ζ , the potential distribution is solved by the Debye-Hückel approximation in a spherical coordinate:

$$\begin{aligned}\nabla^2\psi &= \kappa^2\psi \\ \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) &= \kappa^2\psi\end{aligned}\quad (15.4)$$

The differential equation has general solution $\psi(r) = A\frac{e^{-\kappa r}}{r} + B\frac{e^{\kappa r}}{r}$. With the boundary conditions $\psi(\infty) = 0$ we know $B = 0$. From the Gauss's law we know that the total charge within a sphere of radius R_s is:

$$-4\pi R_s^2 \varepsilon_0 \varepsilon_r A \frac{\partial}{\partial r}\left(\frac{e^{-\kappa r}}{r}\right)\Bigg|_{R_s}^{\infty} = 4\pi R_s^2 \varepsilon_0 \varepsilon_r A \frac{e^{-\kappa R_s}(\kappa R_s + 1)}{R_s^2} \approx 4\pi \varepsilon_0 \varepsilon_r A = q \quad (15.5)$$

The last step is derived using $\kappa_s \ll 1$. Therefore we get $A = q/(4\pi\varepsilon_0\varepsilon_r)$. The ζ potential is the value of ψ at $r = R_s$:

$$\zeta = \psi(R_s) = \frac{q}{4\pi\varepsilon_0\varepsilon_r} \frac{e^{-\kappa R_s}}{R_s} \approx \frac{q}{4\pi\varepsilon_0\varepsilon_r R_s} \quad (15.6)$$

Plug this into Equation 15.2, we get the mobility at the Hückel limit:

$$u_H = \frac{2\varepsilon_0\varepsilon_r\zeta}{3\mu} \quad (15.7)$$

which is independent of the particle size (as long as the condition $\kappa R_s \ll 1$ holds).

15.2 The Smoluchowski limit

The Hückel limit is suitable for particles much smaller than the Debye length, i.e. single charge picture. For particles that are much larger than the Debye length, the electrophoresis comes to the Smoluchowski limit, i.e. $\kappa^{-1} \ll R_s$. The influence from the fluid field becomes important for particles at the Smoluchowski limit.³ On the surface of the particle, the thickness of EDL becomes negligible, and is similar to the situation of electroosmosis discussed in Lecture 14. Close to the surface of the particle (but outside the EDL), the particle surface can be regarded as a charged wall with interfacial potential ζ . If we set the particle as the rest frame, the fluid field flows parallel to the surface with a velocity $v_f = (v_x, 0, 0)$. Using the non-slip boundary condition, the fluid velocity far outside the EDL is (see Equation 14.18):

$$v_x = -\frac{\varepsilon_0 \varepsilon_r \zeta}{\mu} E_x \quad (15.8)$$

Since the fluid is macroscopically still, the velocity of the particle relative to the fluid is then:

$$v_p = \frac{\varepsilon_0 \varepsilon_r \zeta}{\mu} E_x = u_s E_x \quad (15.9)$$

with mobility u_E :

$$u_s = \frac{\varepsilon_0 \varepsilon_r \zeta}{\mu} \quad (15.10)$$

As we can see the mobility differs from that in the Hückel limit only by a prefactor. This is an interesting result, since the mobility is again independent of neither the size nor the shape of the particle. In colloidal science, Equations 15.7 and 15.10 are the basis for the instruments called zeta potential analyzers, which measures ζ potential of particles through the electrophoresis mobility. On the other hand, radius R_s (and its distribution) is usually measured by the technique called dynamic light scattering (DLS)⁴.

In summary, the electrophoresis mobility of a particle can be described using the following models:

- Einstein-Stokes relation: $u_{ES} = \frac{q\mathcal{D}}{kT}$

This equation is valid regardless of the particle size.

- Hückel limit: $u_H = \frac{3\varepsilon_0 \varepsilon_r \zeta}{2\mu}$

This is valid when $R_s \ll \kappa^{-1}$, the ζ potential is small compared with $k_B T$ and the particle is spherical

- Smoluchowski limit: $u_S = \frac{\varepsilon_0 \varepsilon_r \zeta}{\mu}$

This is valid when $R_s \gg \kappa^{-1}$, and for any shape of particles.

15.3 Applications of electrophoresis

As we can see in both the Hückel and Smoluchowski limits, the electrophoresis mobility does not depend on the size R_s . If ζ of particles are similar, electrophoresis alone cannot separate them based on the size. This might sound a bit counter-intuitive since we know \mathcal{D} depends on the particle size. However since q is also dependent on R_s and ζ (see Equation 15.6), the influence of R_s is canceled out. In size-separation electrophoresis techniques such as the polyacrylamide gel electrophoresis (PAGE, see Figure 15.2) which separates proteins and nucleic acids, additional resistance comes from nanoscale pores in the polyacrylamide gel. Larger proteins / nucleic acids pass much slower compared with the smaller species and forms bands in the lanes of the gel.

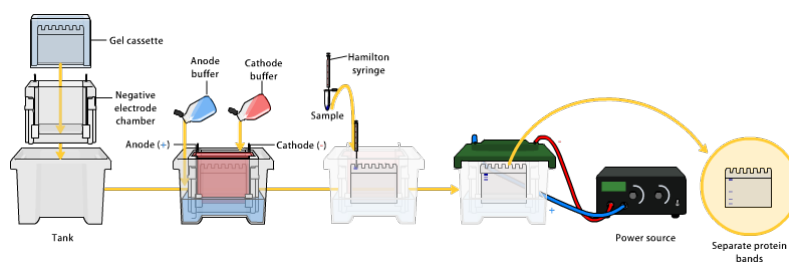


Figure 15.2: Scheme of a typical PAGE separation experiment. Image adapted from wikipedia.

Another recent application is single molecule sensing (such as DNA) based on electrophoresis through nanopores.⁵ In such apparatus, the size of the nanopore is ultra-small that only allows one molecule to pass at the same time. When the nanopore is unoccupied, a baseline current is measured on the electrodes. Once a molecule passes through the nanopore, the flux of current-carrying ions through the nanopore is reduced and the current measured on the electrodes drops (Figure 15.3). Single molecule trans-pore events are thus captured at the low current stages. Depending on the time window Δt and current drop ΔI of the translocation events, the molecule length the folding states can be quantified.

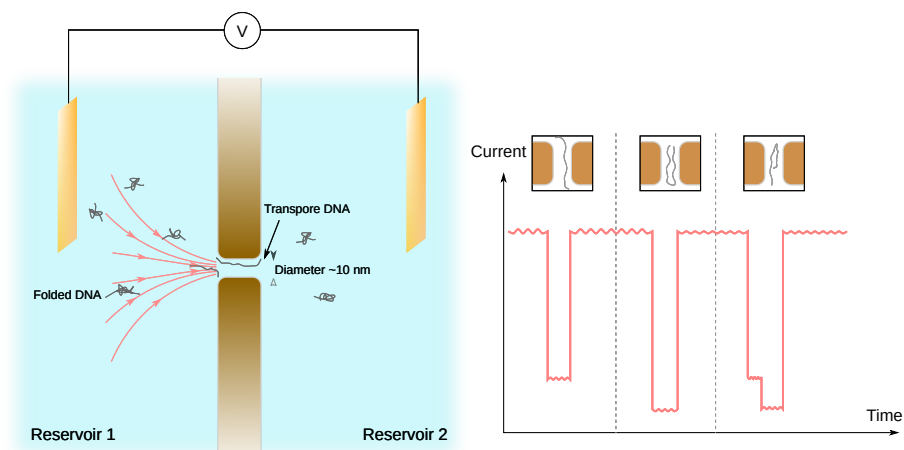


Figure 15.3: Sensing DNA molecules by electrophoresis through nanopores. The current drops when a single molecule passes through the pore. The degree of the drop of current depends on the configuration of molecule inside the pore (i.g. single / double strand).

References

- (1) Stokes, G. G. *Trans. Camb. Phil. Soc* **1850**, 9, 106.
- (2) Einstein, A. *Ann. Phys.* **1905**, 322, 549–560.
- (3) Von Smoluchowski, M. *Bull. Akad. Sci. Cracovie.* **1903**, 8, 182–200.
- (4) Bhattacharjee, S. *J. Control. Release* **2016**, 235, 337–351.
- (5) Clarke, J.; Wu, H.-C.; Jayasinghe, L.; Patel, A.; Reid, S.; Bayley, H. *Nat. Nanotechnol.* **2009**, 4, 265–270.

