

Diffusion of a dipolar tracer in a salty surface

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The two dimensional translational and rotational diffusion coefficients of a dipolar tracer in a charged surface are determined with the generalized Langevin equation approach. The electrolyte friction effect on the translational brownian movement displays a maximum as a function of ionic strength showing similar trends to its three dimensional counterpart. However, its effect on the rotational motion is important only at low and moderate salt concentration and negligible at high ionic concentration.

Keywords: Transport properties; lateral diffusion.

Se determinaron los coeficientes de difusión en dos dimensiones de una trazadora dipolar en una superficie cargada con el enfoque de la ecuación de Langevin generalizada. la fricción de electrolito en el movimiento browniano traslacional presenta un máximo como función de la intensidad iónica mostrando un comportamiento similar a su contraparte tridimensional. Sin embargo, el efecto de la fricción de electrolito en el movimiento rotacional es importante sólo a concentraciones bajas o moderadas y es despreciable a alta concentración iónica.

Descriptores: Difusión; electrolito; coloide; membrana.

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1. Introduction

Diffusion properties of biopolymers and colloidal particles with anisotropic interactions in charged interfaces and membranes are of much current interest [1–7]. Due to the spatial constraint on the particles to lie in a quasi bidimensional film, the long range nature of the electrostatic interactions among charged particles leads to unusual structural properties: imperfect shielding of the electric field in the normal direction to the plane, and non-exponential screening by the supporting electrolyte solution, to the field in the lateral direction, in contrast to what occurs in a three dimensional environment [8]. The diffusion coefficient of a particle in concentrated solutions confined to a bidimensional geometry is currently measured with the methods of fluorescence recovery after photobleaching, and single particle tracking [2, 3]. These techniques allow to determine the effect of direct interactions on tracer diffusion properties. In this work we study the longtime translational and rotational diffusion of a bidimensional dipolar tracer in an electrolyte solution of several point like ionic species (brownian multicomponent plasma, BMP) in a membrane, and determine the effect of the electrostatic interaction between the tracer and its electrical double layer. We use the generalized Langevin equation approach to calculate the friction contribution on the tracer $\Delta\zeta$ due to direct interactions among particles [9]. This quantity is given in terms of the dipole-ion pair correlation function obtained at the Debye-Hückel (DH) level from a solution of the corresponding Poisson-Boltzmann equation for the BMP in the anisotropic electric field of the dipolar particle. In this approach, the correlation function is the static property that embodies the non-exponential screening of ions confined to planes. At this level of approximation our model system is

analytically soluble and we obtain explicit analytic expressions for both the pair correlation function, and of the translational and rotational diffusion coefficients in terms of ionic strength and dipole moment. The electrolyte friction effect makes the translational friction on the tracer to display a maximum in terms of the ionic strength similar to the diffusion in a bulk solution. However, for the rotational two dimensional friction this effect is only important at low and moderate salt concentration, and it is completely negligible at high salt concentration, where the tracer diffuses with its free rotational diffusion constant value.

2. Debye-Hückel theory of structural properties

In this section we define the model potential of the tracer, and the charged membrane by a multicomponent electrolyte solution at surface charge density \bar{n}_α in an aqueous continuous solvent of dielectric constant ϵ . The two dimensional electrostatic potentials of an α -species point like ion of charge q_α in the plane is

$$u_\alpha(r) = \frac{q_\alpha \ln(r)}{\epsilon}, \quad (1)$$

and we model the electrical dipolar tracer as a hard disc of diameter σ :

$$\phi(\mathbf{r}) = \frac{\mu \hat{\mu} \cdot \hat{\mathbf{r}}}{\epsilon r} + \phi^{HC}(\mathbf{r}), \quad (2)$$

where $\phi^{HC}(\mathbf{r})$ is infinite within the disc core that contains the dipole and zero otherwise.

The unit vector $\hat{\mu}$ determines the orientation of the dipole of magnitude μ by an angle ϕ with respect to the field vector position \mathbf{r} , where $\hat{\mathbf{r}} = \mathbf{r}/r$ and $\hat{\mu} \cdot \hat{\mathbf{r}} = \cos\phi$. We consider a Boltzmann's probability distribution of ions

$$n_\alpha(\mathbf{r}) = \bar{n}_\alpha e^{-\beta q_\alpha \psi(\mathbf{r})}, \quad (3)$$

where $\beta = 1/k_B T$, k_B the Boltzmann's constant, T the temperature and

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \sum_\alpha \int d^2 r' n_\alpha(\mathbf{r}') u_\alpha(|\mathbf{r} - \mathbf{r}'|). \quad (4)$$

The Poisson-Boltzmann equation corresponding to the source fields of Eqs. (1) and (2) is given by

$$\epsilon \nabla^2 \psi(\mathbf{r}) = -2\pi \sum_\alpha q_\alpha n_\alpha(\mathbf{r}) - 2\pi \nabla \cdot \mathbf{P}(\mathbf{r}), \quad (5)$$

with $\mathbf{P}(\mathbf{r}) = \bar{\mu} \delta(\mathbf{r})$, $\bar{\mu} = \mu \hat{\mu}$, $\delta(\mathbf{r})$ the Dirac's delta function in two dimensions. For a low charged surface we approximate the profile concentration Eq. (3) by its Debye-Hückel limit $n_\alpha(\mathbf{r}) = \bar{n}_\alpha [1 - \beta q_\alpha \psi(\mathbf{r})] \theta(r - \sigma)$, with $\theta(r - \sigma)$ the Heaviside step function, and therefore Eq. (5) reduces to

$$\nabla^2 \psi(\mathbf{r}) = e^{-\beta \phi^{HC}(\mathbf{r})} \kappa^2 \psi(\mathbf{r}) - \frac{2\pi}{\epsilon} \nabla \cdot \mathbf{P}(\mathbf{r}), \quad (6)$$

where the electroneutrality condition $\sum_\alpha n_\alpha q_\alpha = 0$ was used and $\kappa^2 = 2\pi\beta \sum_\alpha \bar{n}_\alpha q_\alpha^2 / \epsilon$. The solution to this equation is given in Appendix A, and leads to the effective potential

$$\psi(\mathbf{r}) = \begin{cases} \frac{\mu\kappa}{\epsilon} \frac{K_1(\kappa r) \hat{\mu} \cdot \hat{\mathbf{r}}}{[\kappa\sigma K_1(\kappa\sigma) + \frac{1}{2}(\kappa\sigma)^2 K_0(\kappa\sigma)]}, & r > \sigma \\ \left[-\frac{\mu\kappa}{\epsilon\sigma} \frac{K_0(\kappa\sigma)r}{[\kappa\sigma K_0(\kappa\sigma) + 2K_1(\kappa\sigma)]} + \frac{\mu}{\epsilon r} \right] \hat{\mu} \cdot \hat{\mathbf{r}}, & r \leq \sigma, \end{cases} \quad (7)$$

with K_ν the modified Bessel function of order ν . The pair correlation function $g(\mathbf{r})$ of ions in the field of the dipolar tracer is $n_\alpha(\mathbf{r}) = \bar{n}_\alpha g(\mathbf{r})$, and the two dimensional Fourier transform of the total correlation function, is given by

$$h(\mathbf{k}) = g(\mathbf{k}) - 1 = \frac{2\pi i \beta \mu \kappa}{\epsilon} \frac{\hat{\mu} \cdot \hat{\mathbf{k}}}{[\kappa\sigma K_1(\kappa\sigma) + \frac{1}{2}(\kappa\sigma)^2 K_0(\kappa\sigma)]} \times \left[-\frac{\kappa\sigma}{k^2 + \kappa^2} J_1(k\sigma) K_1(\kappa\sigma) + \frac{\kappa\sigma}{k^2 + \kappa^2} J_1(k\sigma) K_2(\kappa\sigma) \right], \quad (8)$$

where $i = \sqrt{-1}$, $\hat{\mathbf{k}} = \mathbf{k}/k$ (with the wave vector \mathbf{k} of magnitude $k = |\mathbf{k}|$), and J_ν the Bessel function of order ν . These structural quantities will be used in the next section to determine the electrolyte friction effect on the diffusion of the tracer in the plane.

3. Longtime tracer diffusion

In this section we calculate the effect of the friction of the electrolyte solution on the diffusion of the dipolar tracer. This time-dependent friction $\Delta \overset{\leftrightarrow}{\zeta}(t)$ derives from the direct interactions of the ions with the dipolar particle and leads to a contribution to its bare friction $\zeta^{\overset{\leftrightarrow}{0}}$ at infinite dilution of the supporting electrolyte, that is, in the absence of interactions. The total direct force $\mathbf{F}(t)$ and torque $\mathbf{T}(t)$ on the tracer particle, exerted by the ions are, respectively

$$\mathbf{F}(t) = \sum_\alpha \int d\mathbf{r} [\nabla \psi_\alpha(\mathbf{r})] n_\alpha(\mathbf{r}; t), \quad (9)$$

and

$$\mathbf{T}(t) = \sum_\alpha \int d\mathbf{r} [\mathbf{r} \times \nabla \psi_\alpha(\mathbf{r})] n_\alpha(\mathbf{r}; t), \quad (10)$$

where $n_\alpha(\mathbf{r}; t)$ is the instantaneous local concentration of ions with the equilibrium ensemble average $n_\alpha^{eq}(\mathbf{r}) \equiv \langle n_\alpha(\mathbf{r}; t) \rangle$, and $\psi_\alpha(\mathbf{r}) = q_\alpha \psi(\mathbf{r})$.

The translational and rotational motion of the tracer is determined by its linear and angular velocities $\mathbf{V}(t)$, $\mathbf{W}(t)$, respectively, as observed from a laboratory frame with origin at the center of mass of the tracer particle. The cartesian components of the velocities coincide with the orientation of the principal axis of the particle. Thus, the Langevin equation describing the diffusion of the tracer in solution can be written exactly as a linear function of the instantaneous fluctuations in the concentration $\delta n_\alpha(\mathbf{r}; t) = n_\alpha(\mathbf{r}; t) - n_\alpha^{eq}(\mathbf{r})$ as:

$$\overset{\leftrightarrow}{\mathbf{M}} \cdot \frac{d \overset{\leftrightarrow}{\mathbf{V}}(t)}{dt} = -\overset{\leftrightarrow}{\zeta}^{\overset{\leftrightarrow}{0}} \cdot \overset{\leftrightarrow}{\mathbf{V}}(t) + \mathbf{f}^{\overset{\leftrightarrow}{0}}(t) + \sum_\alpha \int d\mathbf{r} [\overset{\leftrightarrow}{\nabla} \psi_\alpha(\mathbf{r})] \delta \mathbf{n}_\alpha(\mathbf{r}; t). \quad (11)$$

This equation couples the dynamical quantities $d \overset{\leftrightarrow}{\mathbf{V}}(t)/dt$ and $\delta n_\alpha(\mathbf{r}; t)$. $\overset{\leftrightarrow}{\mathbf{M}}_{ij} = M \delta_{ij}$ ($i, j = 1, 2$), $\overset{\leftrightarrow}{\mathbf{M}}_{ij} = \delta_{ij} I_{i-2}$ ($i, j = 3$), with M, I_1 being the mass and principal moment of inertia of the tracer. The diffusion tensor $D^{\overset{\leftrightarrow}{0}} \equiv k_B T / \overset{\leftrightarrow}{\zeta}^{\overset{\leftrightarrow}{0}}$, with $\zeta_{ij}^{\overset{\leftrightarrow}{0}}$ ($i, j = 1, 2, 3$), that turns out to be diagonal with the nonzero components $\zeta_{11}^{\overset{\leftrightarrow}{0}} = \zeta_{\perp}^{\overset{\leftrightarrow}{0}}$, $\zeta_{22}^{\overset{\leftrightarrow}{0}} = \zeta_{\parallel}^{\overset{\leftrightarrow}{0}}$, $\zeta_{33}^{\overset{\leftrightarrow}{0}} = \zeta_{\text{R}}^{\overset{\leftrightarrow}{0}}$, being the free friction coefficients coupling the random white force and torque, grouped in $\mathbf{f}^{\overset{\leftrightarrow}{0}}(t)$, with the generalized velocity $\overset{\leftrightarrow}{\mathbf{V}}(t) = (\mathbf{V}(t), \mathbf{W}(t))$, $\overset{\leftrightarrow}{\nabla} = (\nabla, \mathbf{r} \times \nabla)$. The theory of fluctuations of linear irreversible thermodynamics, leads to the general evolution equation for $\delta n_\alpha(\mathbf{r}; t)$ as:

$$\begin{aligned} \frac{\partial \delta n_\alpha(\mathbf{r}; t)}{\partial t} &= [\vec{\nabla} n_\alpha^{eq}(\mathbf{r})] \cdot \vec{\nabla}(t) \\ &- \sum_{\gamma\beta} \int_0^t dt' \int d\mathbf{r}' \int d\mathbf{r}'' L_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'; t-t') \\ &\quad \times \sigma_{\gamma\beta}^{-1}(\mathbf{r}', \mathbf{r}'') \delta n_\beta(\mathbf{r}''; t') + h_\alpha(\mathbf{r}; t), \end{aligned} \quad (12)$$

with $h_\alpha(\mathbf{r}; t)$ being a fluctuation term with zero mean that satisfies the fluctuation dissipation relationship $L(\mathbf{r}, \mathbf{r}'; t) = \langle h(\mathbf{r}; t)h(\mathbf{r}'; 0) \rangle$. In Eq. (12), σ^{-1} is the inverse of the static correlation function of $\delta n_\alpha(\mathbf{r}; 0)$: $\sigma_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \langle \delta n_\alpha(\mathbf{r}; 0)\delta n_\beta(\mathbf{r}'; 0) \rangle$.

The solution of Eq. (12) can be written as

$$\begin{aligned} \delta n_\alpha(\mathbf{r}; t) &= \sum_\beta \int d\mathbf{r}' \chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t) \delta n_\beta(\mathbf{r}'; 0) \\ &+ \sum_\beta \int_0^t dt' \int d\mathbf{r}' \chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t-t') [\vec{\nabla} n_\beta^{eq}(\mathbf{r}') \cdot \vec{\nabla}(t')] \\ &+ \sum_\beta \int_0^t dt' \int d\mathbf{r}' \chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t-t') h_\beta(\mathbf{r}'; t'), \end{aligned} \quad (13)$$

with $\chi(t)$ being the propagator of Eq. (13) that satisfies

$$\begin{aligned} \frac{\partial \chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t)}{\partial t} &= - \sum_{\gamma\delta} \int_0^t dt' \int d\mathbf{r}'' \mathbf{r}'' L_{\alpha\gamma}(\mathbf{r}, \mathbf{r}''; t-t') \\ &\quad \times \sigma_{\gamma\delta}^{-1}(\mathbf{r}'', \mathbf{r}''') \chi_{\delta\beta}(\mathbf{r}''', \mathbf{r}'; t'), \end{aligned} \quad (14)$$

with the initial condition $\chi(0) = 1$. By using Eq. (13) we eliminate the variable $\delta n_\alpha(\mathbf{r}'; t)$ in Eq. (11) and we obtain the generalized Langevin equation [9]

$$\begin{aligned} \hat{\mathbf{M}} \cdot \frac{d\vec{\mathbf{V}}(t)}{dt} &= -\zeta^{\vec{0}} \cdot \vec{\mathbf{V}}(t) + \mathbf{f}^{\vec{0}}(t) \\ &- \int_0^t dt' \Delta \zeta^{\vec{0}}(t-t') \cdot \vec{\mathbf{V}}(t') + \vec{\mathbf{F}}(t). \end{aligned} \quad (15)$$

In Eq. (15), $\vec{\mathbf{F}}(t)$ is a fluctuating generalized force deriving from the spontaneous departures from zero of the net direct force exerted by the other particles on the tracer. It groups a random force and torque on the tracer with zero mean value, and time dependent correlation function given by $\langle \vec{\mathbf{F}}(t) \vec{\mathbf{F}}^\dagger(0) \rangle = k_B T \Delta \zeta^{\vec{0}}(t)$, with the time dependent friction contribution

$$\begin{aligned} \Delta \zeta^{\vec{0}}(t) &= \beta \sum_{\alpha\beta\gamma} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' [\vec{\nabla} \psi_\alpha(\mathbf{r})] \chi_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; t) \\ &\quad \sigma_{\beta\gamma}(\mathbf{r}', \mathbf{r}'') [\vec{\nabla} \psi_\gamma(\mathbf{r}'')]. \end{aligned} \quad (16)$$

Equation (16) is an exact result for the dynamical friction on a nonspherical tracer diffusing in a host suspension of particles of radially symmetric interactions, which for our case in this manuscript, it is constituted by the BMP. We are interested in the longtime friction coefficient obtained at the diffusive regime

$$\Delta \zeta^{\vec{0}} = \int_0^\infty dt \Delta \zeta^{\vec{0}}(t). \quad (17)$$

In order to apply Eq. (17) we introduce an approximation for $\chi(t) = \exp[\int d\mathbf{r}'' L(\mathbf{r}, \mathbf{r}'') \sigma^{-1}(\mathbf{r}'', \mathbf{r}') t]$ given by the homogeneous Fick's diffusion approximation $L_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \delta_{\alpha\beta} \vec{\nabla} \cdot \mathbf{D}_\alpha^{\vec{0}} \cdot \mathbf{n}_\alpha^{eq}(\mathbf{r}) \cdot \vec{\nabla} \delta(\mathbf{r} - \mathbf{r}')$, for the instantaneous relaxation of the concentration of the spherical particles in the external tracer's electric field. Therefore, the Fourier transform of $\chi_{\alpha\beta}(k, t) = \exp[-k^2 D_\alpha^{\vec{0}} \bar{n}_\alpha \sigma_{\alpha\beta}^{-1}(k) t]$. The general expressions for the static friction coefficients within the so-called homogeneous modified Fick's approximation for the relaxation of ions in the tracer's field [9] gives the static translational friction

$$\Delta \zeta = \frac{k_B T}{(2\pi)^2} \sum_\alpha \frac{\bar{n}_\alpha}{D_\alpha^0} \int d^2 k \hat{\mathbf{k}} \hat{\mathbf{k}} h(\mathbf{k}) h(-\mathbf{k}), \quad (18)$$

and for the rotational motion

$$\Delta \zeta_R = \frac{k_B T}{(2\pi)^2} \sum_\alpha \frac{\bar{n}_\alpha}{D_R^0} \int d^2 k [\hat{\mathbf{k}} \times \nabla_{\mathbf{k}} h(\mathbf{k})] [\hat{\mathbf{k}} \times \nabla_{\mathbf{k}} h(-\mathbf{k})], \quad (19)$$

where $\nabla_{\mathbf{k}}$ is the gradient operator, $\bar{D}^0 = D^0 + D_{CM}^0$, $D_{CM}^0 = (D_{||}^0 + D_{\perp}^0)/2$ for the tracer and we assumed $D^0 \equiv D_\alpha^0$ for all ions. The modified diffusion constant due to charge fluctuations is $D_\gamma = k_B T / (\zeta_\gamma^0 + \Delta \zeta_\gamma)$, where $\gamma = ||, \perp, R$. Substitution of Eq. (8) into Eqs. (18) and (19) lead to the total translational friction $\Delta \zeta = (\Delta \zeta_{||} + \Delta \zeta_{\perp})/2$:

$$\Delta \zeta = \frac{\mu^2}{4\epsilon\sigma^2 \bar{D}^0} TRANS�(x) Z(\kappa\sigma), \quad (20)$$

with

$$\begin{aligned} TRANS�(x) &= \\ &[I_2(x)K_2(x) + \frac{xI_2'(x)K_2(x)}{2} + \frac{xI_2(x)K_2'(x)}{2}] \\ &\quad \times K_1^2(x) - \frac{xK_1^2(x)}{2} [I_1'(x)K_1(x) + I_1(x)K_1'(x)] \\ &\quad + 2K_1(x)K_2(x) [I_1'(x)K_1(x) + I_1(x)K_1'(x)] \\ &\quad + \frac{K_1(x)K_2(x)}{2} [xI_0''(x)K_0(x) + I_0'(x)K_0(x) \\ &\quad + 2xI_0'(x)K_0'(x) + xI_0(x)K_0''(x) + I_0(x)K_0'(x)], \end{aligned} \quad (21)$$

and

$$\Delta\zeta_R = \frac{\mu^2}{2\epsilon D^0} \text{ROT}(\kappa\sigma)Z(\kappa\sigma), \quad (22)$$

with

$$\begin{aligned} \text{ROT}(x) = & \frac{-K_1^2(x)}{2x} [I_1'(x)K_1(x) + I_1(x)K_1'(x)] \\ & + (K_1(x)K_2(x) - \frac{xK_2^2(x)}{4}) \\ & \times [\frac{-I_2(x)K_1(x)}{x^2} + \frac{I_2'(x)K_1(x)}{x} + \frac{I_2(x)K_1'(x)}{x}] \\ & - \frac{xK_2^2(x)}{4} \frac{d}{dx} (\frac{I_1(x)K_0(x)}{x}), \quad (23) \end{aligned}$$

where $x = \kappa\sigma$. I_ν is a modified Bessel function of order ν . $I_\nu'(x) = dI_\nu(x)/dx$, $I_\nu''(x) = d^2I_\nu(x)/dx^2$, and similarly for the other Bessel functions. Also $Z(\kappa\sigma) = (\kappa\sigma)^4 / [\kappa\sigma K_1(\kappa\sigma) + \frac{1}{2}(\kappa\sigma)^2 K_0(\kappa\sigma)]$. In Fig. 1 the functions $\text{TRANSL}(\kappa\sigma)Z(\kappa\sigma)$ and $\text{ROT}(\kappa\sigma)Z(\kappa\sigma)$ are plotted in terms of $\kappa\sigma$. Fig. 1a shows that $\Delta\zeta$ has a maximum at about $\kappa\sigma \approx 4.8$ which leads to a minimum in the translational diffusion coefficient $D = k_B T / (\zeta^0 + \Delta\zeta)$ due to electrolyte friction, a feature also noticed in the three dimensional version of this system [9]. Fig. 1b depicts $\Delta\zeta_R$ as an increasingly damped function for increasing values of the ionic strength, such that at a high ionic concentration the static rotational friction $\Delta\zeta_R$ becomes zero. That is, for sufficiently high ionic concentration $\kappa\sigma \geq 2$ the rotational diffusion coefficient $D_R = k_B T / (\zeta_R^0 + \Delta\zeta_R)$ of the dipolar tracer is exactly the same as its free diffusion coefficient $D_R^0 = k_B T / \zeta_R^0$. Thus, electrolyte friction becomes an important effect on the two dimensional rotational brownian motion only at small and moderate salt concentration. In the three dimensional version of this model, *i.e.*, in the rotational brownian movement of an electric dipolar tracer in a BMP, the longtime rotational diffusion constant shows a minimum for a given salt concentration, in the same way as for the translational diffusion property [9]. Therefore, the electrolyte friction effect at high salt concentration on the two dimensional rotational diffusion of the dipolar tracer is less effective than in its three dimensional counterpart.

4. Conclusion

In this manuscript we presented an analytically soluble model of the electrolyte friction effect on the longtime rotational and translational diffusion coefficients of a dipolar tracer particle diffusing in a charged membrane. For the translational brownian motion we found that the friction contribution due to direct interactions between the tracer and the surrounding ions displays a non-monotonous behavior, with a maximum at an intermediate ionic strength, a behavior also found for this property in the three dimensional version of this

model. However, the two dimensional rotational friction contribution (contrary to what occurs in three dimensions) is a monotonous decreasing function of salt concentration such that it is zero at high ionic content where the tracer diffuses with its free rotational friction value.

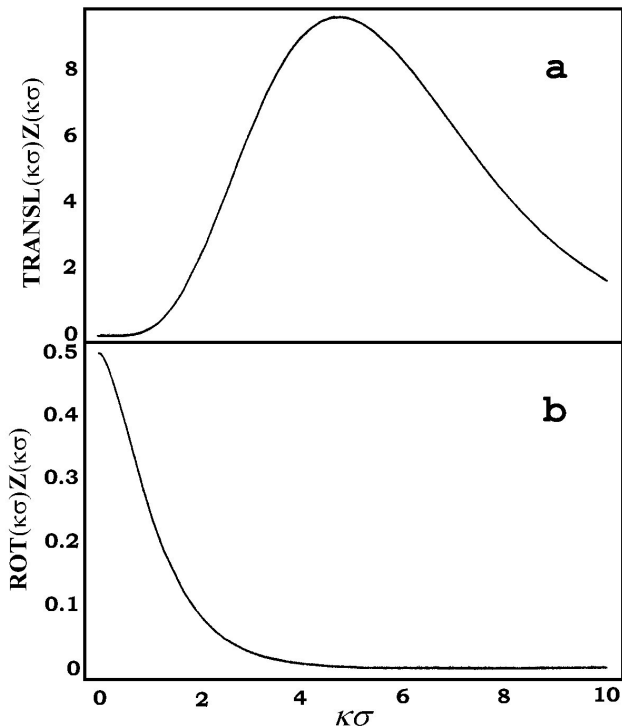


FIGURE 1. (a) plot of $\text{TRANSL}(\kappa\sigma)Z(\kappa\sigma)$ as a function of ionic strength $\kappa\sigma$; (b) same plot for $\text{ROT}(\kappa\sigma)Z(\kappa\sigma)$

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Appendix A

The general solution of the Poisson-Boltzmann equation (6) of Section II reads

$$\psi(\mathbf{r}) = \begin{cases} A_0 + B_0 \ln r + \sum_{l=1}^{\infty} [A_l r^l + \frac{B_l}{r^l}] \cos(l\theta), & r > \sigma \\ \sum_{l=0}^{\infty} [C_l K_l(\kappa r) r + D_l I_l(\kappa r)] \cos(l\theta), & 0 < r \leq \sigma \end{cases} \quad (\text{A1})$$

where K_l and I_l are modified Bessel functions of order l . The boundary conditions on the field $\psi(\mathbf{r})$ are: (a) $\psi(\mathbf{r}) \rightarrow \frac{\mu\hat{\mu}}{\epsilon r}$ for $r \rightarrow 0$, (b) $\psi(\mathbf{r}) \rightarrow 0$ for $r \rightarrow \infty$, (c) $\psi(\sigma^+) = \psi(\sigma^-)$, (d) $d\psi(\mathbf{r})/dr|_{\sigma^+} = d\psi(\mathbf{r})/dr|_{\sigma^-}$. From condition (a), and the general solution Eq. (A1) for $0 < r \leq \sigma$ one gets

$\psi(\mathbf{r}) = (A_1 r + \frac{B_1}{r}) \cos(\theta)$ with $B_1 = \mu/\epsilon$. Using the second part of the solution, for $r > \sigma$ and condition (b) we get $D_l = 0$ since $I_l(\kappa r)$ diverges when $r \rightarrow \infty$ and in order to get a converged solution $\psi(\mathbf{r}) = C_1 K_1(\kappa r) \cos(\theta)$ with $l = 1$. Finally from (c) and (d) it is found that

$$A_1 \sigma + \frac{\mu}{\epsilon \sigma} = C_1 K_1(\kappa \sigma) \quad (\text{A2})$$

and

$$A_1 - \frac{\mu}{\epsilon \sigma^2} = -C_1 \kappa [K_0(\kappa \sigma) + \frac{K_1(\kappa \sigma)}{\kappa \sigma}]. \quad (\text{A3})$$

From Eqs. (A2) and (A3) it follows that:

$$A_1 = -\frac{\mu \kappa}{\epsilon \sigma} \frac{K_0(\kappa \sigma)}{[\kappa \sigma K_0(\kappa \sigma) + 2K_1(\kappa \sigma)]} \quad (\text{A4})$$

$$C_1 = \frac{2\mu}{\epsilon \sigma} \frac{1}{[\kappa \sigma K_0(\kappa \sigma) + 2K_1(\kappa \sigma)]}. \quad (\text{A5})$$

Substitution of A_1 and C_1 into the expression for $\psi(\mathbf{r})$ given above leads to Eq. (7) of Section II.

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1. R. Lipowsky and E. Sackmann, *Handbook of Biological Physics*, Vol.1 (Elsevier Science B.V, 1995)
 2. B. Maier and J.O. Radler, *Phys.Rev.Lett.* **82** (1999) 1911.
 3. M.J. Saxton and K. Jacobson, *Ann. Rev. Biophys. Biomol.Struct.* **26** (1997) 373.
 4. T. Ala-Nissila, S. Herminghaus, T. Hjelt and P. Leiderer, *Phys.Rev.Lett.* **76** (1996) 4003.
 5. M.L. Kurnaz and D.K. Schwartz, *J. Rheol.* **41** (1997) 1173.
 6. E. Lomba, F. Lado and J.J. Weis, *Phys. Rev. E* **61** (2000) 3838.
 7. B. Cichocki and B.U. Felderhof, *J. Phys: Condens. Matter* **6** (1994) 7287.
 8. E.S. Velázquez and L. Blum, *Physica A* **244** (1997) 453.
 9. M. Hernández-Contreras and M. Medina-Noyola, *Phys. Rev. E* **53** (1996) R4306.