

Electronic Supplementary Information (ESI)

Regulating DNA translocation through functionalized soft nanopores

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1. Theoretical modeling, numerical implementation and code validation

The electric field, the ionic concentrations, and the flow field are simultaneously solved to predict the DNA electrokinetic translocation through a functionalized soft nanopore. For convenience, the governing equations, eqns (1)-(4) in the text, are normalized by the following scaling factors: the bulk ionic concentration C_0 as the concentration scale, the radius of dsDNA nanoparticle a as the length scale, the thermal potential RT/F as the potential scale, the Smoluchowski velocity based on RT/F , $U_0 = \varepsilon_f R^2 T^2 / (\mu a F^2)$, as the velocity scale, the reference ionic diffusivity $D_0 = \varepsilon_f R^2 T^2 / \mu F^2$, and the reference pressure $\mu U_0 / a$. Dimensionless form the Poisson-Nernst-Planck (PNP) and the modified Stokes equations can be expressed as

$$-\nabla^{*2} \phi^* = \frac{1}{2} (\kappa a)^2 (z_1 c_1^* + z_2 c_2^*) + h Q^* \quad (\mathbf{R1})$$

$$\nabla^* \cdot \mathbf{N}_j^* = \nabla^* \cdot (\mathbf{u}^* c_j^* - D_j^* \nabla^* c_j^* - z_j D_j^* c_j^* \nabla^* \phi^*) = 0, j=1 \text{ and } 2 \quad (\mathbf{R2})$$

$$-\nabla^* p^* + \nabla^{*2} \mathbf{u}^* - \frac{1}{2}(\kappa a)^2(z_1 c_1^* + z_2 c_2^*)\nabla^* \phi^* - h(\lambda a)^2 \mathbf{u}^* = \mathbf{0} \quad (\text{R3})$$

$$\nabla^* \cdot \mathbf{u}^* = 0 \quad (\text{R4})$$

Here, $\mathbf{N}_j^* = \mathbf{N}_j / C_0 U_0$, $Q^* = \rho_{\text{fix}} a^2 F / (\varepsilon_f RT)$, $\kappa^{-1} = \lambda_D = \sqrt{\varepsilon_f RT / 2F^2 C_0}$, and $\lambda^{-1} = \sqrt{\mu / \gamma}$. κ^{-1} and λ^{-1} represent the Debye screening length and the softness degree of the soft layer, respectively. Using the aforementioned scales, dimensionless form of the dimensional boundary conditions (see the Method part in the text) can be easily derived. The DNA translational velocity U_p is calculated by balancing the z component electrophoretic force, F_E , and the hydrodynamic drag force, F_H , acting on the DNA nanoparticle:¹

$$F_E = \int_{\Omega_p} \varepsilon_f \left[\frac{\partial \phi}{\partial r} \frac{\partial \phi}{\partial z} n_r - \frac{1}{2} \left(\left(\frac{\partial \phi}{\partial r} \right)^2 + \left(\frac{\partial \phi}{\partial z} \right)^2 \right) n_z \right] d\Omega_p, \quad (\text{R5})$$

$$F_H = \int_{\Omega_p} \left[\mu \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right) n_r + n_z \left(-p + 2\mu \frac{\partial u_z}{\partial z} \right) \right] d\Omega_p. \quad (\text{R6})$$

In the above, n_r and n_z are the r and the z components of the unit normal vector, \mathbf{n} , respectively; u_r and u_z are the r and the z components of the fluid velocity, respectively. F_E (F_H) is obtained by integrating the Maxwell (hydrodynamic) stress tensor over the DNA nanoparticle surface, Ω_p .

Equations (R1)-(R4) and the associated boundary conditions are numerically solved by COMSOL (version 3.5a, www.comsol.com), a commercial finite element method based software installed in a high-performance cluster. Mesh independence is checked to ensure that all the results obtained are reliable. Typically, using a total number of ca. 130,000

meshes is sufficient. More details about the implementation of that software can be found in our previous studies.¹⁻² The applicability of the numerical scheme adopted is first examined by solving the problem considered by Liu et al.:³ the electrophoresis of a rigid cylindrical particle along the axis of a long, rigid, uncharged cylindrical pore for the case when the particle length is much larger than its radius ($L_p/a \gg 1$), the pore is much longer than the particle ($L_t/L_p \gg 1$), the surface potential is low, and the applied electric field is weak.³ To simulate their conditions, we assume that the soft layer of the present nanopore is free of fixed charge. Fig. S1a shows the variation of the normalized axial electrophoretic velocity, $u_p^* = U_p/U_r$, with $U_r = \varepsilon_f \zeta_p E / \mu$, as a function of the scaled softness parameter λa at two levels of the scaled double layer thickness κa . This figure reveals that the u_p^* increases with decreasing λa and approaches to that of Liu et al.³ when λa is sufficiently small (ca. 0.5). This is reasonable because the effect of the soft layer becomes insignificant when λa is relatively small. Fig. S1b shows the variation of u_p^* as a function of κa at a very small λa , that is, the presence of the soft layer is unimportant. This figure verifies that the performance of the present numerical scheme is satisfactory. Note that u_p^* is overestimated in Liu et al.³ when κa is small. This is because the effect of double-layer polarization,⁴ which retards the electrophoretic movement of a particle, was neglected in their analysis.

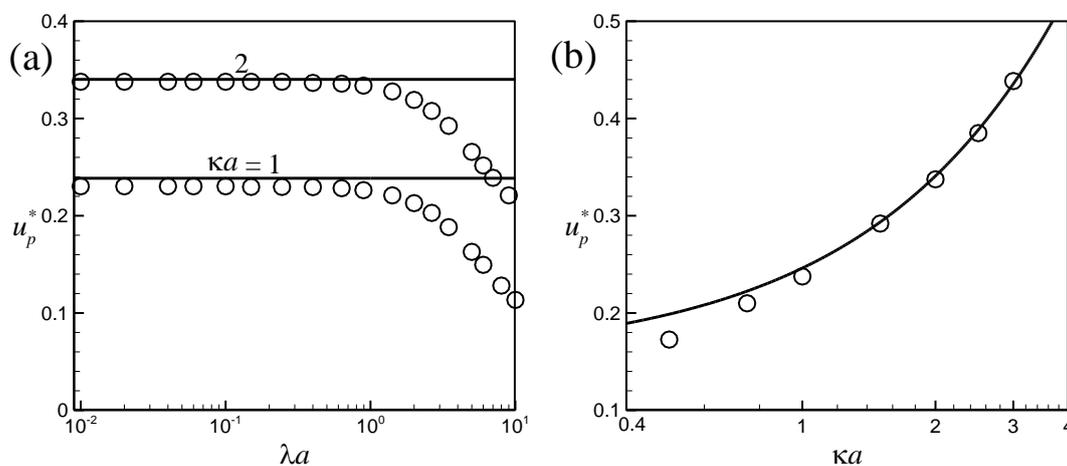


Fig. S1. Normalized axial electrophoretic velocity of a long cylindrical particle of radius a and length L_p translating along the axis of a long, cylindrical tube of radius R_t and length L_t covered with an uniform ion-penetrable soft layer of thickness d as a function of the scaled softness parameter λa at two levels of the scaled double layer thickness κa , (a), and as a function of κa at $\lambda a = 0.1$, (b). The particle is charged with a constant surface potential $\zeta_p = RT/F$ and the tube uncharged, $R_t/a=2$, $d/a=0.5$, $L_p/a=20$, $L_t/L_p=100$, $\rho_{fix} = 0$, and $E=20$ kV/m. Open circles: our numerical results; solid curves: approximate numerical results of Liu et al.³

2. Influences of soft layer properties and bulk salt concentration on the DNA translational velocity

To ensure that a DNA nanoparticle is capable of passing through the soft nanopore in the case of Fig. 5 of the text, the variations of the normalized DNA translational velocity, U_p/U_0 , as a function of the particle location z_p for various combinations of the soft layer properties (ρ_{fix} and λ^{-1}) and the bulk salt concentration C_0 are calculated, and the results are summarized in Fig. S2. Because the electric field inside the nanopore is much higher than that in the fluid compartments (enhanced electric field inside the nanopore, as shown in Fig. 3d of the text), the DNA velocity inside the nanopore is faster than that in the fluid compartments. It is interesting to note that, due to a significant effect of concentration polarization (CP) occurring when the fixed charge density of the soft layer is high (blue dashed curve in Fig. S2a) and/or the bulk salt concentration is high (red dash-dotted and blue dashed curves in Fig. S2b), the DNA velocity profile is highly asymmetric to its location. Under the conditions considered in Fig. S2, the DNA is capable of translocating through the soft nanopore due to consistent positive translation velocity.

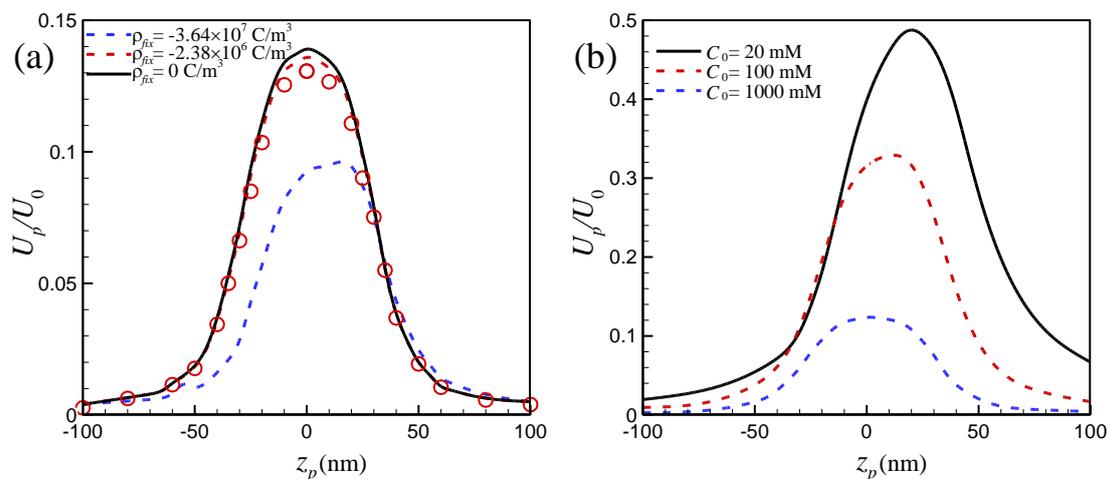


Fig. S2. Variation of the normalized DNA translation velocity U_p/U_0 as a function of the particle location z_p for various values of the fixed charge density ρ_{fix} at $C_0 = 1000 \text{ mM}$, (a), and for various levels of C_0 at $\rho_{fix} = -1.16 \times 10^7 \text{ C/m}^3$ and $\lambda^{-1} = 0.3 \text{ nm}$, (b). Curves in (a): $\lambda^{-1} = 0.3 \text{ nm}$; open circles: $\lambda^{-1} = 0.5 \text{ nm}$ and $\rho_{fix} = -2.38 \times 10^6 \text{ C/m}^3$. The other parameters are the same as those in Fig. 5 of the text.

Notes and references

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3. H. Liu, H. H. Bau and H. H. Hu, *Langmuir*, 2004, **20**, 2628-2639.