

Scaling for selectivity in uniformly charged selective nanopores

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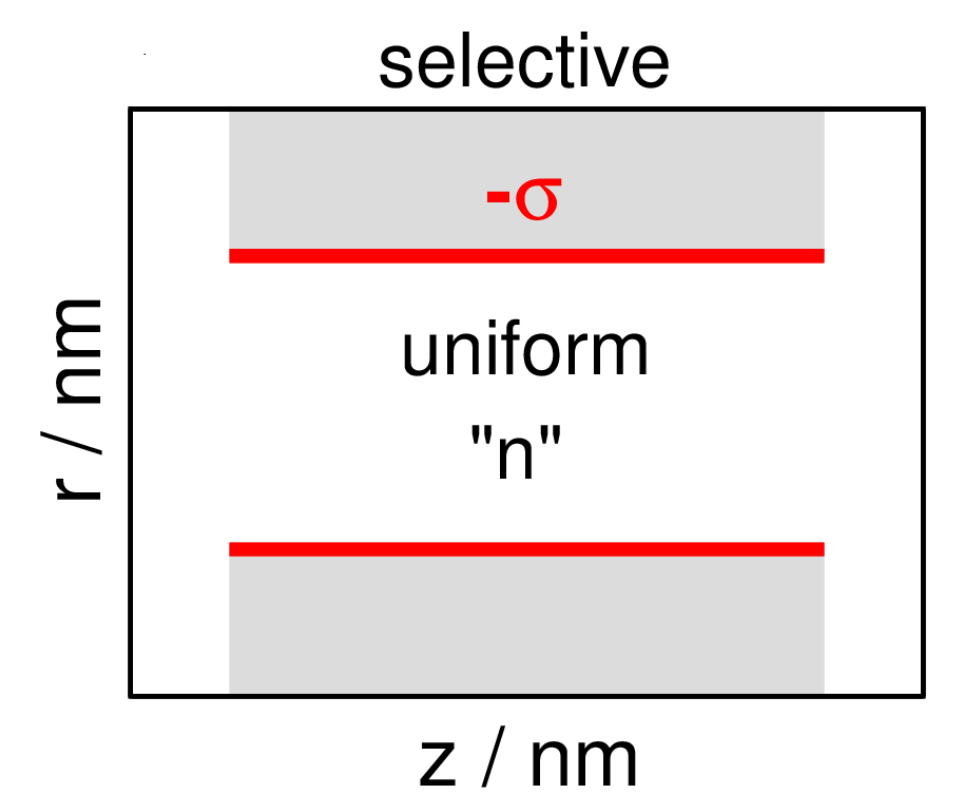
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Introduction

Nanopores are nanoscale channels embedded in a membrane, which provide controlled transport of ions between the bulk phases on either side of a membrane. A charge pattern is chemically deposited on the inner wall of the engineered nanopores, which gives different output functions for different input parameters, from which a device function can be generated. Such a device function for uniformly charged nanopores is selectivity. The selectivity determines which ions (cations or anions) are more likely to pass through the channel. Scaling means that the device function is a unique function of a scaling parameter that can be generated from the system parameters by a simple analytical function. The Dukhin number is a parameter traditionally used in the literature to give the ratio of surface to volume conductivity for a charged wall (Bikerman, Lyklema, Dukhin). Using simple simulation models, we show that scaling operates on selectivity and that the scaling parameter is the Dukhin number and its various extensions for finite nanopores and multivalent electrolytes, respectively. This allows us to predict the output property associated with different combinations of input parameters, which is useful for the design of nanodevices.

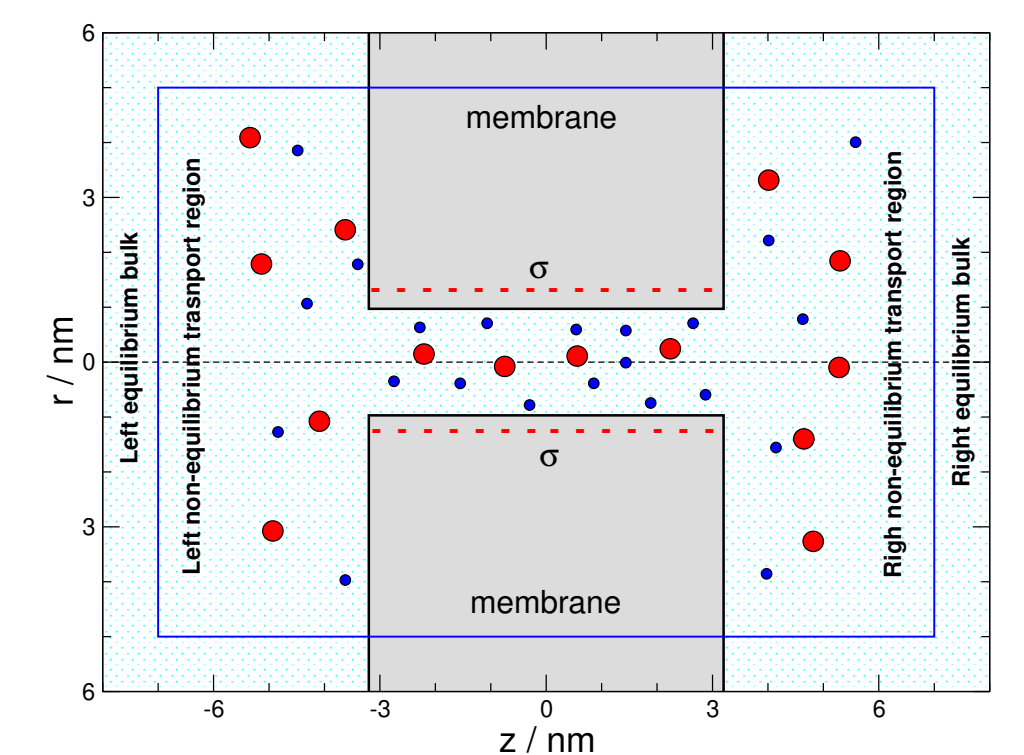


Nanopores

- Natural (ion channels) and artificial pores in a membrane
- Input parameters:**
 - Nanopore fabrication:** radius (R), length (H), surface charge (σ)
 - Experimentally controllable:** electrolyte concentration in bulk (c), voltage (U), ionic valences (z_i)
- Output (measurable) parameters:** electric currents (I_+ , I_-), particle currents (J_+ , J_-), $I_i = z_i e J_i$
- Device function** is selectivity in uniformly charged pores: $S_+ = \frac{|J_+| - |J_-|}{|J_+| + |J_-|}$

Model and method

- Nernst-Planck equation:** $\mathbf{j}_i(\mathbf{r}) = -\frac{1}{kT} D_i(\mathbf{r}) c_i(\mathbf{r}) \nabla \mu_i(\mathbf{r})$
- Relationship between *concentration profile* ($c_i(\mathbf{r})$) and *chemical potential profile* ($\mu_i(\mathbf{r})$) is computed with
 - Local Equilibrium Monte Carlo [1]** → LEMC+NP
 - Poisson-Boltzmann theory** → PNP
- Water:** implicit (response functions: ϵ , D_i)



What is scaling?

- Scaling means that the device function, F , is an analytical function of a (dimensionless) scaling parameter, ξ , that is an analytical function of the input parameters $\{a_i\}$:

$$F = f[\xi(a_1, a_2, a_3 \dots)]$$

- Practical importance:** if we have a scaling parameter, ξ , for a given combination of a_1, a_2, \dots , we can predict the device function for another combination, a'_1, a'_2, \dots , giving the same ξ → **nanopore design**
- For a nanopore, the input parameters (a_i) are $R, H, c, \sigma, U, z_+, z_-$
- But what is the scaling parameter, ξ ?

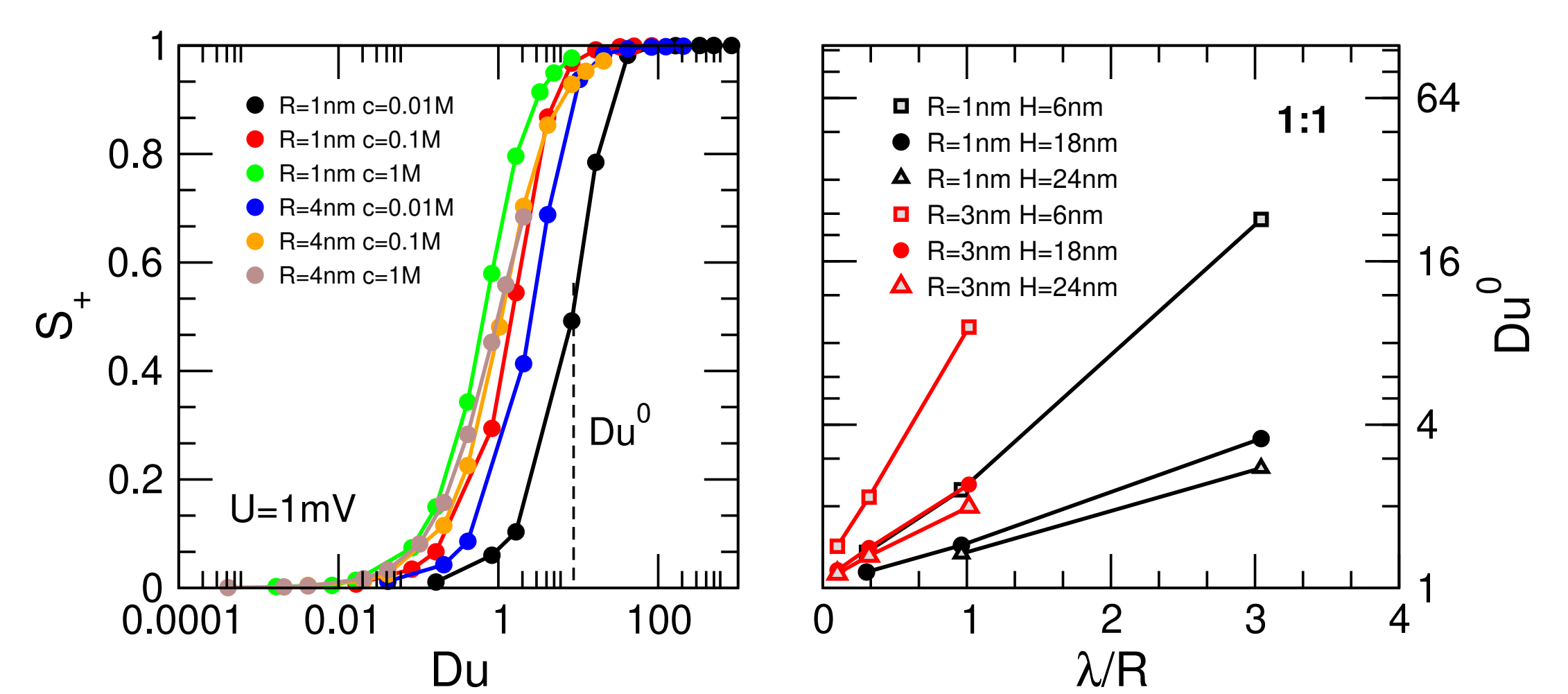
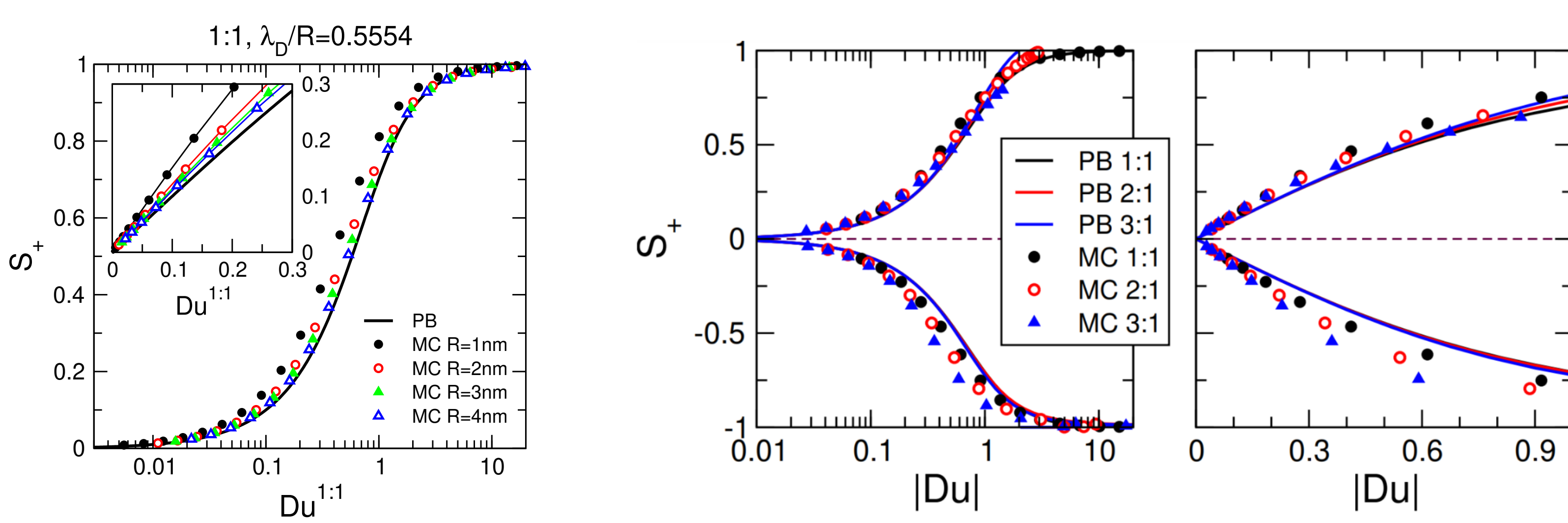
Dukhin number and its variants

- Bocquet's definition [2]** for 1:1 electrolyte: $Du^{1:1} = \frac{|\sigma|}{e c R}$ rewritten as $Du = \frac{|\sigma| 8 \pi l_B \lambda_D^2}{e R}$
- $l_B = \frac{e^2}{4 \pi \epsilon_0 \epsilon k T}$ is the **Bjerrum-length** and $\lambda_D = \left(\frac{c e^2}{\epsilon_0 \epsilon k T \sum_i z_i^2 \nu_i} \right)^{-1/2}$ is the **Debye-length**
- Extension to multivalent electrolytes³:** $Du^{z_+:z_-} = \frac{(z_+ + |z_-|) Du}{2 + (z_+ - |z_-|) Du}$
- Modified Dukhin number⁴:** $mDu = \frac{H}{\lambda_D} Du = \frac{|\sigma| 8 \pi l_B \lambda_D H}{e R}$

Results

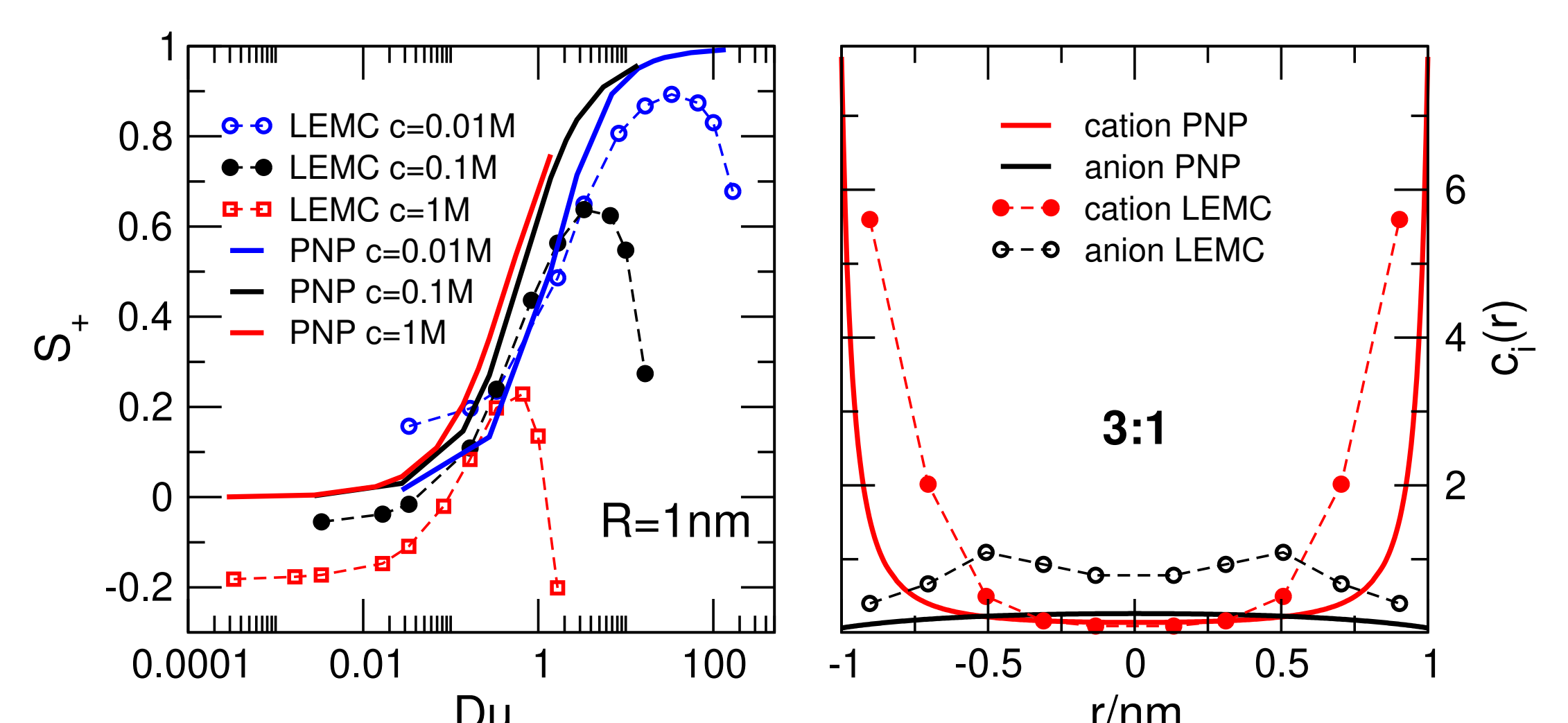
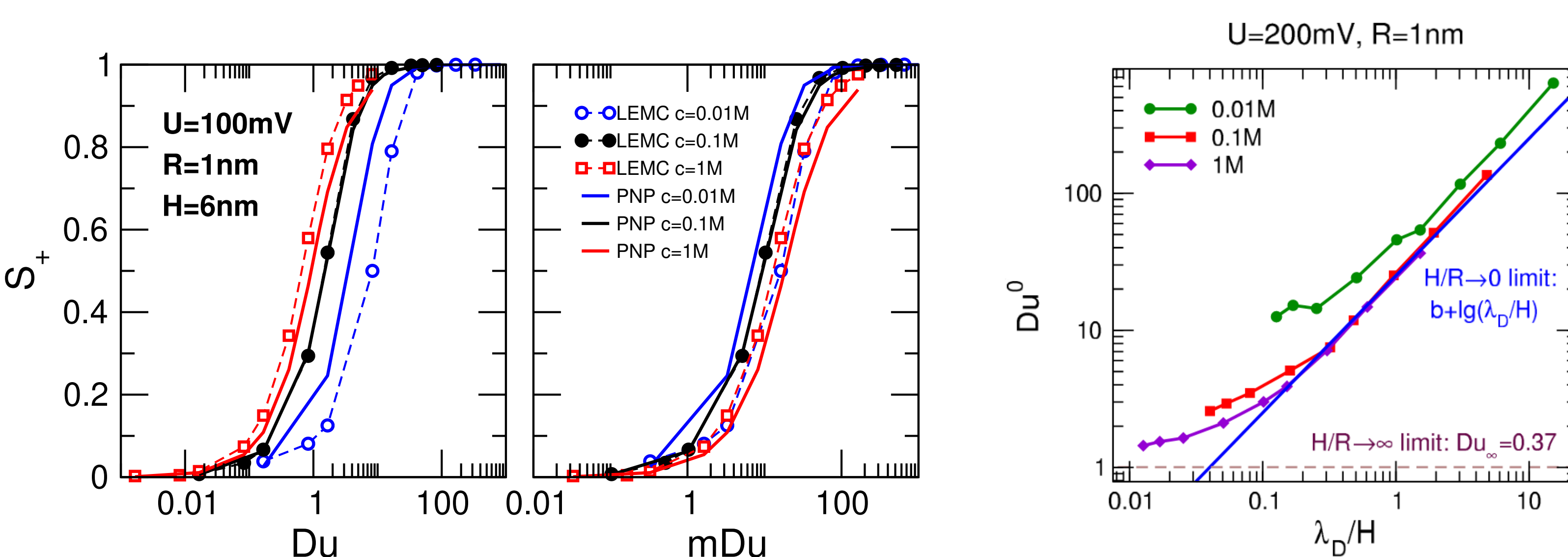
In the limit of $H \rightarrow \infty$ and $U \rightarrow 0$, the scaling parameter is Du or $Du^{z_+:z_-}$. Reference: [3]

Du is getting better scaling parameter as H increases, U decreases, or λ_D/R decreases.



If λ_D/R is large (R small), U is large, and H is small, mDu is a promising scaling parameter. Reference: [4]

For 3:1 electrolytes, strong ionic correlations cause charge inversion and disagreement between mean-field PNP and computer simulations (NP+LEMC).



Conclusion

- Scaling works well if an analytical theory is available for the system: linearized Poisson-Boltzmann for $H \rightarrow \infty$. It is reasonable if a mean-field theory is applicable for the system: PNP
- The Dukhin number is no longer a good scaling parameter when axial effects are strong (small H , large U). Deviation from scaling occurs when ionic correlations are strong: NP+LEMC.

References

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- (3) Zs. Sarkadi, D. Fertig, M. Valiskó, D. Boda. *J. Mol. Liq.* **357**, 119072, 2022.
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