Evaluation of Ion Binding to DNA Duplexes Using a Size-Modified Poisson-Boltzmann Theory (Supporting Information)

Vincent B. Chu, Yu Bai, Jan Lipfert, Daniel Herschlag, and Sebastian Doniach

May 17, 2007

Grand Free Energy Density of the Lattice Gas

The grand free energy density $\mathcal{A}$ of the lattice gas, now with an explicit treatment of excluded volume effects is:

$$\mathcal{A} = -k_B T \log \mathcal{Z} = U - TS \tag{7}$$

where:

$$\begin{aligned} U &= c^1(z_1 e\psi - \mu_1) + c^2(z_2 e\psi - \mu_2) + c^3(z_3 e\psi - \mu_3) \\ -TS &= \frac{k_B T}{a^3}\{c^1 a^3 \ln(c^1 a^3/k) + c^2 a^3 \ln(c^2 a^3) + c^3 a^3 \ln(c^3 a^3) \\ &\quad + k[1 - (c^1 a^3/k) - c^2 a^3 - c^3 a^3] \ln[1 - (c^1 a^3/k) - c^2 a^3 - c^3 a^3] \\ &\quad - (k-1)(1 - c^2 a^3 - c^3 a^3) \ln(1 - c^2 a^3 - c^3 a^3) \end{aligned} \tag{8}$$

The size-modified free energy density is the size-modified version of the free energy density for the PB equation derived by Sharp and Honig from variational

principles [1]. In fact, their result can be obtained formally in the limit $k \to 1$ and $a \to 0$. Borukhov's free energy expression fpr equal-size ions can be obtained similarly in the limit $k \to 1$[2].

Parameters used in the Poisson-Boltzmann Calculation

We employed the Adaptive Poisson-Boltzmann Solver (APBS) to obtain solutions to the Poisson-Boltzmann equations. The parameter set presented below refers to the parameters of the software. For more information, please refer to the APBS documentation (`http://apbs.sourceforge.net/`).

```
mg-auto
cglen 250 250 400
fglen 192 192 336
dime 129 129 225
npbe
bcfl mdh
pdie 2.0
sdie 78.54
srfm smol
chgm spl2
srad 1.4
swin 0.3
temp 298.1
gamma 0.105
calcenergy total
calcforce no
```

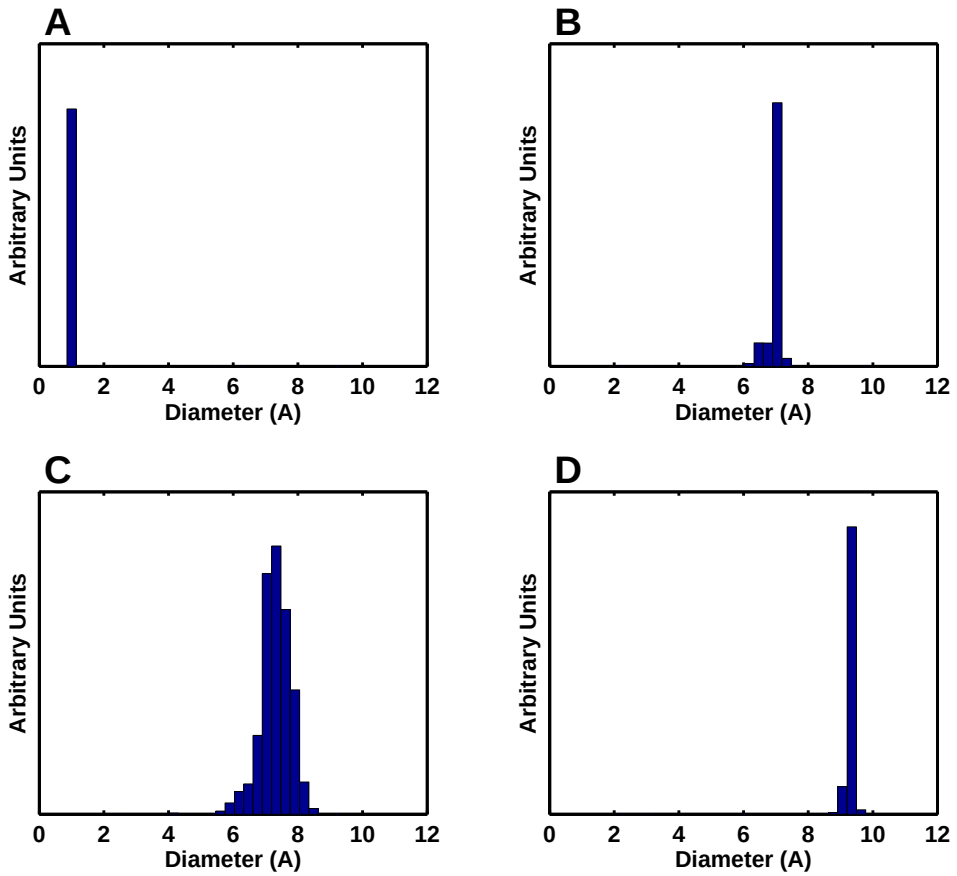

Figure 7: Distribution of fitted ionic size parameters obtained from bootstrap analysis of 2000 simulated datasets for Li^+ (A), Na^+ (B), K^+ (C), and Rb^+ (D).

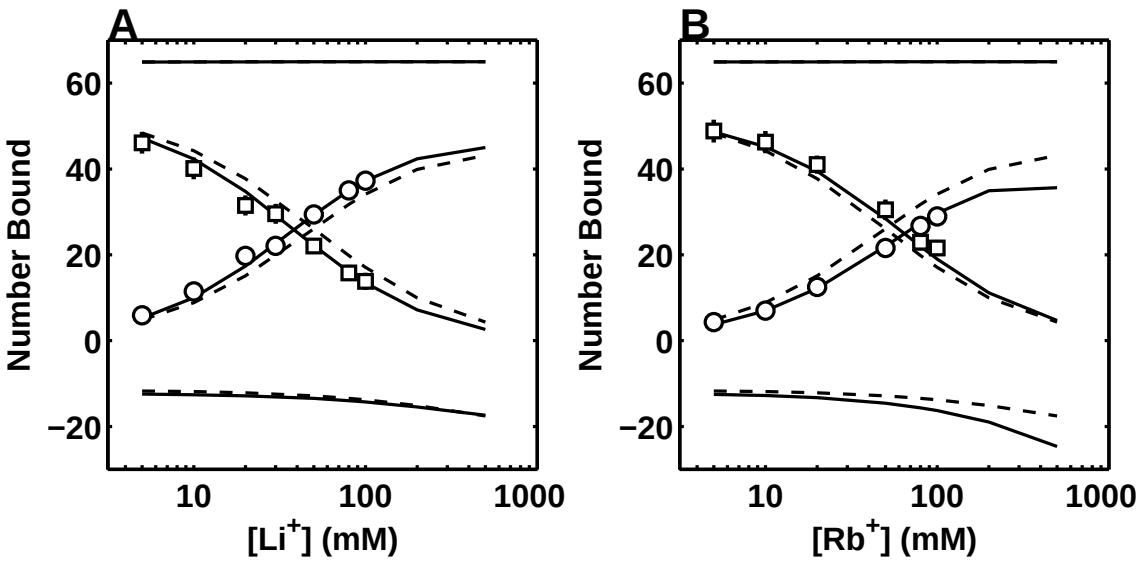

Figure 8: SMPB (solid) and PB (dashed) prediction for BC=Li^+ (A) or Rb^+ (B) competing against BC=50 mM Na^+ around a 24 bp DNA triplex. CC plotted with squares (□) and fixed BC with circles (◯). SMPB curves were computed using size parameters obtained from fitting against 50 mM Na^+ 24 bp duplex competition data.

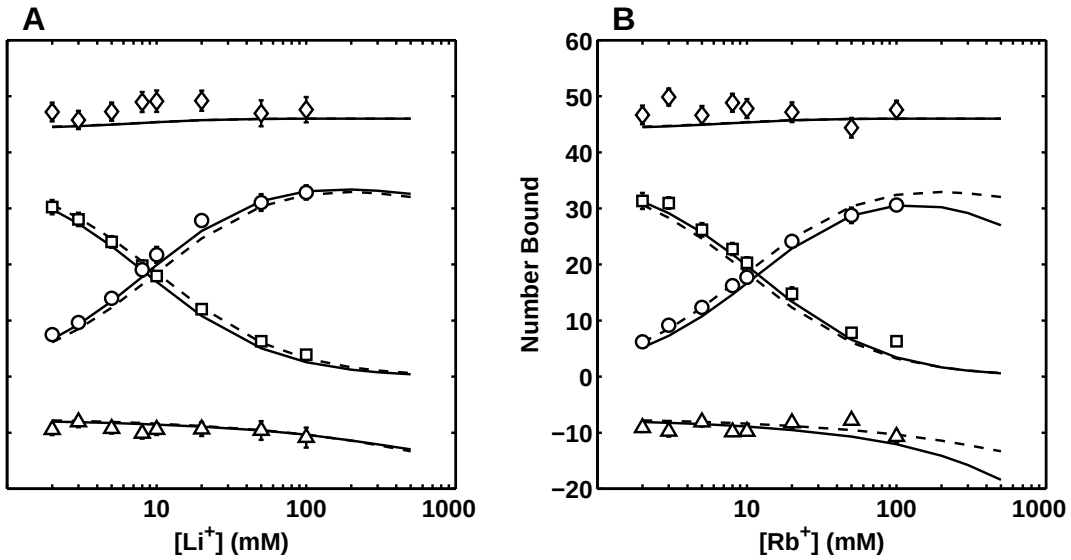

Figure 9: SMPB (solid) and PB (dashed) prediction for CC=Li^+ (A) or Rb^+ (B) competing against fixed 10 mM Na^+ around a 24bp DNA duplex. Net charge plotted with diamonds (◊), CC with squares (□), fixed BC with circles (◯), and co-ion with trianges (△). SMPB curves were computed using size parameters obtained from fitting against 50 mM Na^+ 24bp duplex competition data.

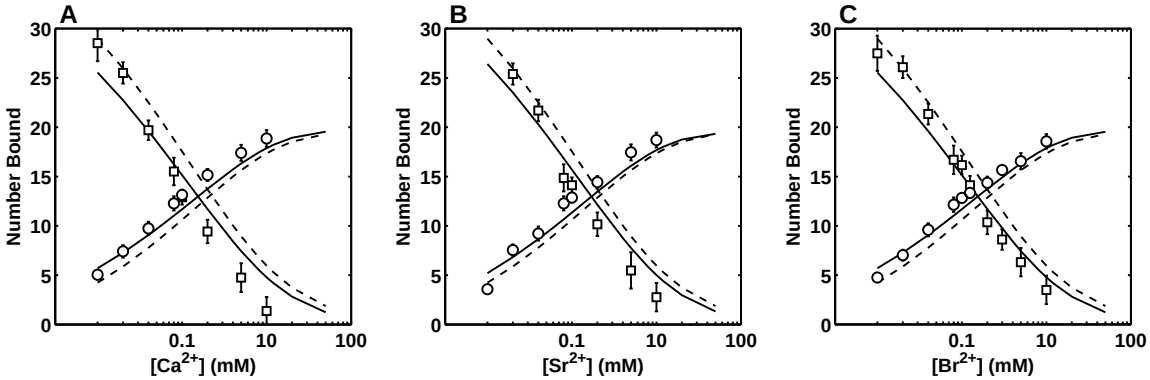

Figure 10: Global best-fit ion-binding curves for Ca^{2+} (A), Sr^{2+} (B), Br^{2+} (C). Net charge plotted with diamonds (◊), CC with squares (□), fixed BC with circles (◯), and co-ion with trianges (△). SMPB is plotted with solid lines while PB theory is plotted with dashed lines.

References

[1] Sharp, K. A., and B. Honig. 1990. Calculating total electrostatic energies with the nonlinear Poisson-Boltzmann equation. *J. Phys. Chem.* 94:7684–7692.

[2] Borukhov, I., D. Andelman, and H. Orland. 1997. Steric effects in electrolytes: A modified Poisson-Boltzmann equation. *Phys. Rev. Lett.* 79:435–438.