Supplementary Material for "Dynamics and Limitations of Spontaneous Polyelectrolyte Intrusion into a Charged Nanocavity"

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DYNAMICS AND CONCENTRATION OF POLYELECTROLYTE AND COUNTERIONS

Figure S4 shows the dynamic changes of the number of anionic polyelectrolyte (PE) counterions and cationic cavity counterions inside and near the cavity with radius $R_{\rm in} = 7\sigma$ during PE intrusion for three different surface charge concentrations at the inner shell of the capsid, $\alpha = 0.1$ (absolute number: $N_c = 59$), 0.3 ($N_c = 180$), and 0.8 ($N_c = 481$), from left to right.

Comparing with the inset in Fig. 1(b) in the main text, the only partially intruded and packed fragment of the flexible PE already overcharges it negatively, which makes it locally unfavorable for further segments of the chain to intrude. The process stops. Only very few anions accompany the PE into the capsid, but cannot compensate for the overcharging. In Fig. S5, we plot the equilibrium distributions of the PE monomers and the anionic and cationic counterions for the same surface charge densities. For $\alpha = 0.1$ (left figure), no particular counterion accumulation inside or near the capsid hull is observed.

Slightly above the charge inversion threshold ($\alpha = 0.3$, Fig. S4 center), cationic cavity counterions initially located inside the capsid are released while the PE moves in. For the reasons discussed in the main text, the PE cannot enter the capsid completely. The positive overcharge of the capsid is not sufficient to pull the PE into the capsid. The counterions do not noticeably contribute to charge inversion, as can be seen in Fig S5 (center).

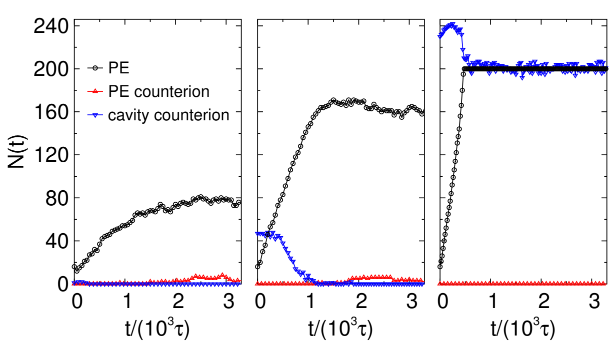

FIG. S4. Time evolution of the number of charges of the flexible polyelectrolyte and the counterions inside the cavity with radius $R_{\rm in} = 7\sigma$ and adsorbed to it from the outside. The figures from left to right correspond to $\alpha = 0.1$, 0.3, and 0.8, respectively.

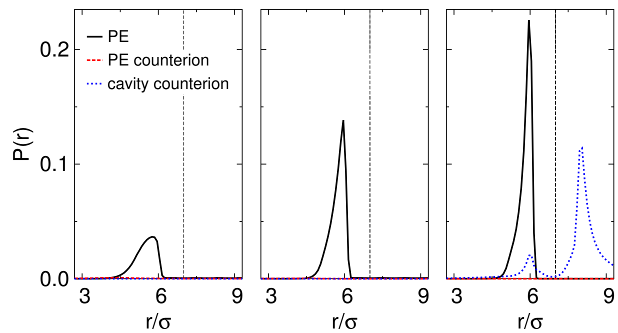

FIG. S5. Distribution of monomers of the flexible polyelectrolyte and counterions from the center of the cavity. The figures from left to right correspond to $\alpha = 0.1$, 0.3, and 0.8 at the interior capsid radius $R_{\rm in} = 7\sigma$, which is marked by the dashed vertical line.

The scenario is entirely different for high surface charge density concentration $\alpha = 0.8$ (Fig. S4 right). Not only the entire PE chain is accommodated inside, a similar number of cationic counterions adsorbs inside and outside the capsid as well (see Fig. S5 right). Despite this, the capsid remains strongly positively overcharged. This is necessary, but also sufficient, to enable the tight packing of the polyelectrolyte inside the capsid. Since no anionic counterions follow the polyelectrolyte into the capsid, electrostatic repulsion between like-charged monomers is not balanced by counterion condensation in this case. It is exclusively handled by the positive surface charges.

ENERGIES AND FORCES

For the successful intrusion event shown in Fig. 2 and discussed in the main text, Fig. S6(a) shows the time evolution of components of the potential energy of the hybrid system. Not surprisingly, the bending energy of the semiflexible PE increases while it enters the capsid and coils up. After the polymer intrusion process is fin-

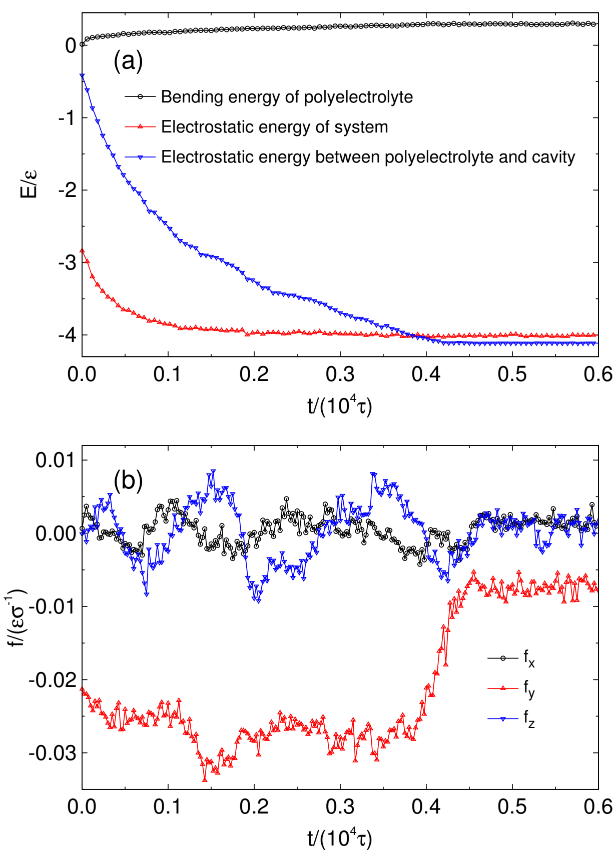

FIG. S6. (a) Electrostatic and bending energies and (b) electrostatic force components parallel ($f_{x,y}$) and perpendicular (f_z) to the portal tube axis as functions of time for the successful intrusion event shown in Fig. 2 and discussed in the main text.

ished at about $t \approx 4300\tau$, the bending energy remains widely constant. The electrostatic energy of the system, which includes all charged components (counterions, PE, cavity surface charges), decreases initially, but saturates quickly, when electrostatic equilibrium is reached. However, also shown in Fig. S6(a), the electrostatic interaction energy between the surface charges inside the cavity and the PE decreases more slowly, which means that in the early stage of the intrusion process, counterions balance most of the PE and surface charges. Later in the process, the counterions are repulsed by the capsid and the polyelectrolyte takes over their role. From the moment on when the PE has fully intruded into the capsid, the total electrostatic energy and the PE-cavity contribution to it are almost identical.

The components of the force parallel and perpendicular to the tube axis that are exerted on the PE by the cavity charges are plotted in Fig. S6(b). Whereas the force components perpendicular to the tube axis ($f_{x,y}$) randomly fluctuate about zero, there is clearly a directed force that acts along the tube axis in $-y$ direction and pulls the polyelectrolyte into the cavity. After complete polymer intrusion ($t \approx 4300\tau$), this pulling force diminishes quickly. Except for small statistical fluctuations, all residual forces effectively disappear in the long term and the system reaches stationary equilibrium.