tion which is opposite to the applied force. The inset of Fig. 5 illustrates this by showing the total displacement of the chain's center of mass for the salt concentration $\rho_s = 0.05625\sigma^{-3}$ and various slip lengths. In nearly all cases except $\delta_B \approx 0$, the total mobility of the polyelectrolyte is negative.

To summarize this section, both the assumptions and the predictions of section II are supported by our numerical results. The total mobility of the polyelectrolyte can therefore be adequately described by Eqs. (7) and (13).

V. CONCLUSIONS

We have presented mesoscopic DPD simulations of polyelectrolyte electrophoresis in narrow microchannels, taking full account of hydrodynamic and electrostatic interactions. A particular focus was put on studying the effects of the hydrodynamic boundary conditions at the channel walls on the electroosmotic flow and on the net electrophoretic mobility of the polyelectrolyte. We have shown that they can be incorporated into a single dimensionless parameter $(1 + \kappa\,\delta_B)$, where δ_B is the slip length and κ the (local) inverse screening length of the charge distribution at the wall. This was derived analytically and supported by our numerical data. It remained valid even for very narrow channels, where the chain conformations were affected by the confinement.

We have shown that wall slip massively enhances the EOF and hence influences the total mobility of the polyelectrolyte. If the EOF mobility μ_{EOF} and the free draining mobility μ_e oppose each other, *i.e.*, if the effective charges on the polyelectrolyte and the walls have the same sign, the mobility may even become negative. As mentioned in the introduction, this effect has also been observed experimentally[4]. In the other case, where the sign of the charges on the polyelectrolyte and the wall are opposite, the main effect of slip is to enhance the total mobility of the polyelectrolyte.

In summary, the total mobility of polyelectrolytes in microchannels results from an interplay of electroosmotic, electrophoretic, electrostatic and slippage effects. The latter have a particularly strong influence and can be used to design channels with improved properties. For example, the characteristics of the channel walls could be designed to tune effective slip lengths[27] and hence flow velocities, which offers the possibility to optimize the time which is needed for polymer migration or separation techniques. This could be an important aspect for future applications in microchannels or micropumps to accelerate measuring times.

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