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The Electrophoretic Mobility of a Polyelectrolyte within a Radially Confining Potential Well TYLER SHENDRUK, MARTIN BERTRAND, GARY W. SLATER, University of Ottawa — We demonstrate that a polyelectrolyte electrophoresing while radially confined by a mechanical force has a conformationally dependent electrophoretic mobility that differs from its free-draining value. The mobility increases as a function of the confining harmonic potential and in the absence of solid walls. Mesoscale MPCD-MD hybrid simulations that include electro-hydrodynamics through a mean-field Debye Hückel approximation will be presented for a variety of well widths and contour lengths, demonstrating that mobility increases with confinement after a critical point but remains independent of polymerization. For this reason, models based on a change of monomer friction coefficient at the confinement boundary (such as those recently put forward to explain experimentally measured mobility polyelectrolytes confined within nano- and microfluidic channels) are not sufficient to explain our observations. Since the potential acts perpendicular to the electric field and only on the monomers, the Electro-Hydrodynamic Equivalence Principle does not predict the mobility to differ. We present a course-grained theory explaining these findings in terms of hydrodynamic coupling within overlapping diffuse layers.

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