Electrophoretic Mobility within a Confining Well

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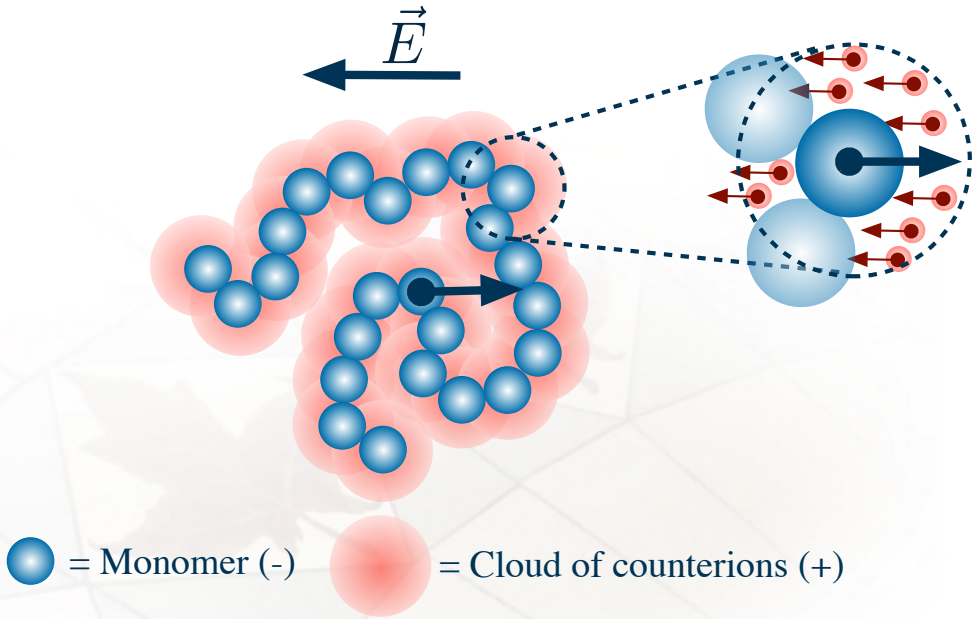
Free-Solution Electrophoresis:
free-draining polyelectrolytes

Free-Draining

- Free-solution electrophoretic mobility ($\mu_0 = Q/\xi$) is *independent* of *length* and *conformation*



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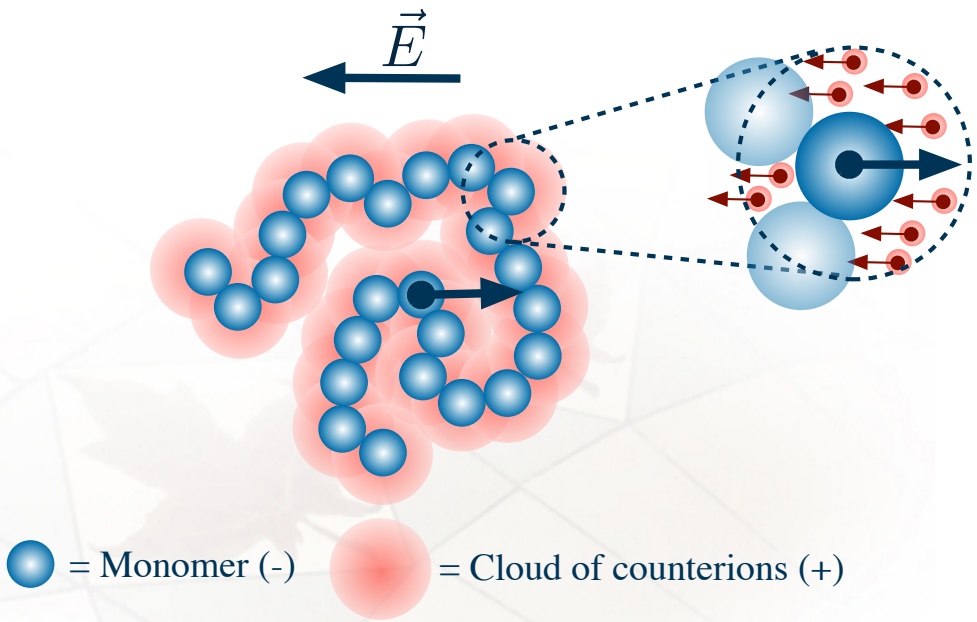

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- Drag is local and effective friction (ξ) increases with length (N), just like effective charge (Q)

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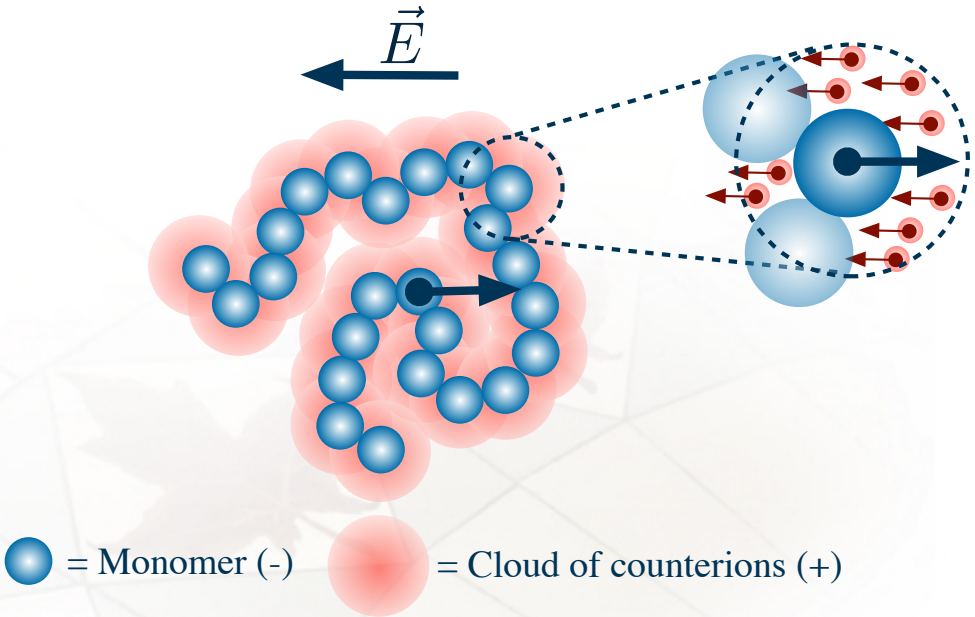

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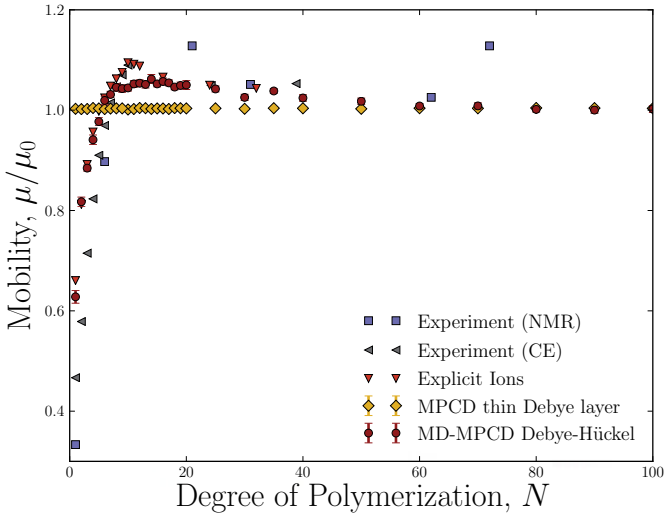
  - electrostatic
  - and hydrodynamic interactions.



Separation via electrophoresis:
breaking friction's *extensivity*

- Many systems subvert mobility's size independence by *simultaneously* applying both an electric field $\vec{E}$ and a mechanical force $\vec{f}$
  Examples: Gels, end-labeled free-solution electrophoresis, collisions with posts, translocation through nanopores, *etc.*

[a] Balducci, Mao, Han and Doyle, Macromolecules, 39(18), 2006. Cross, Strychalski and Craighead, J. Appl. Phys., 102(2), 2007. Salieb-Beugelaar, *et.al.*, Nano Letters, 8(7), 2008.
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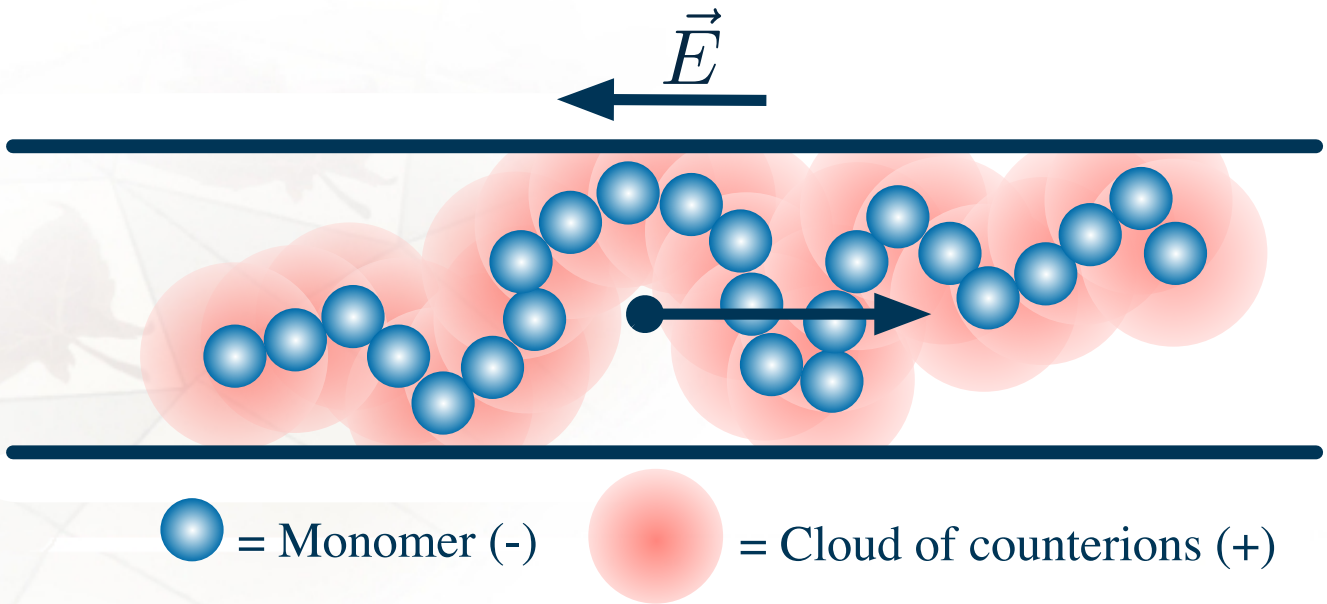

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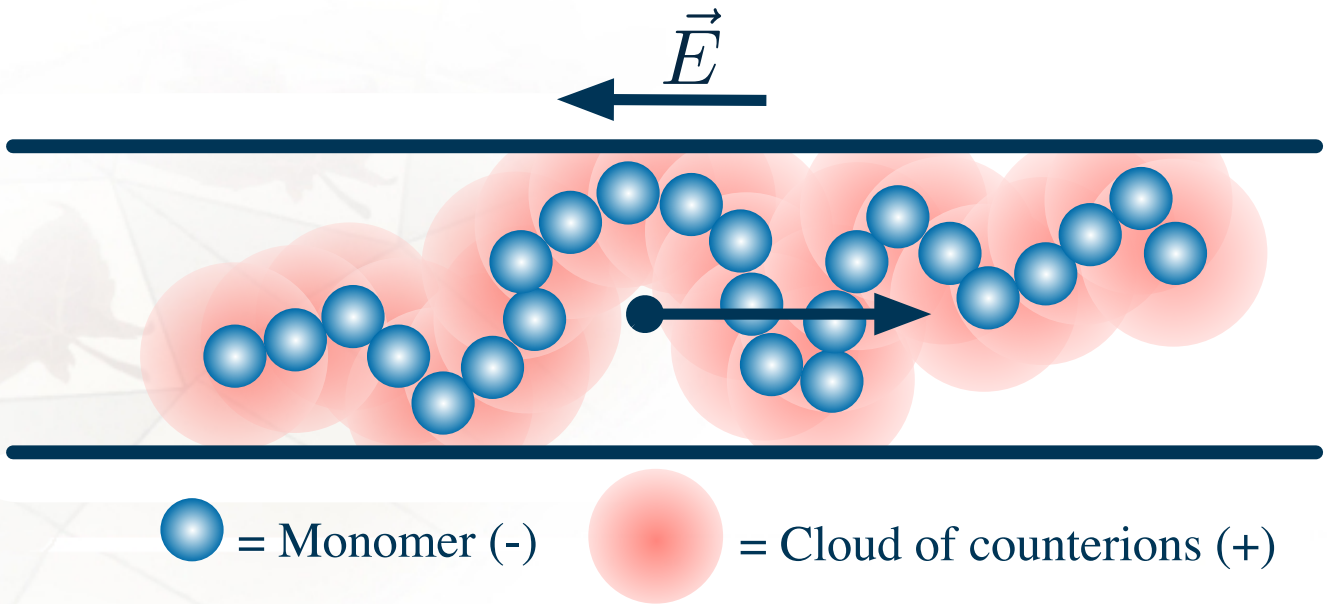

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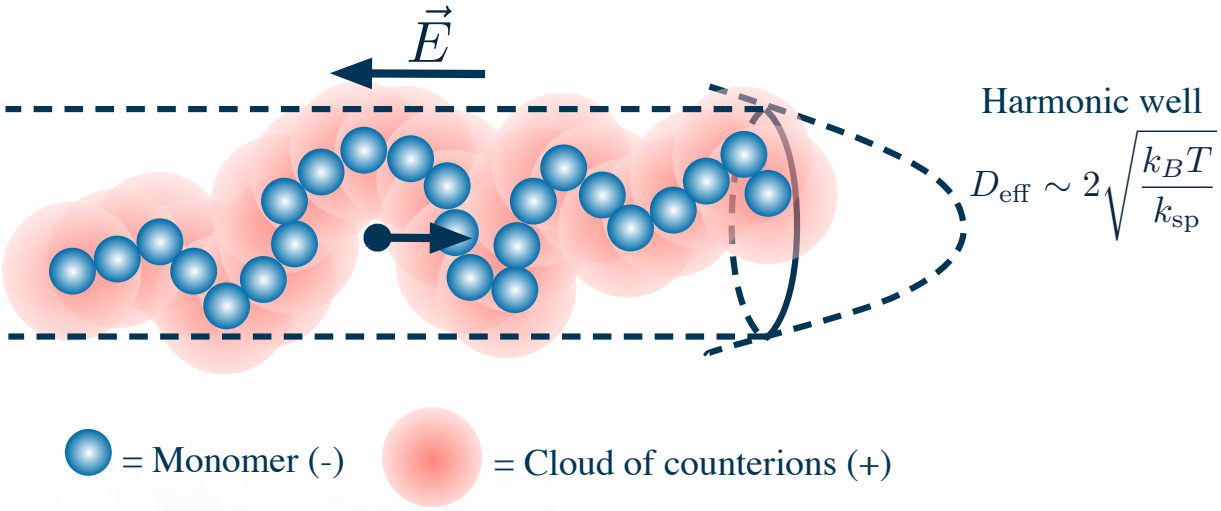
Simulate a Simple System:
remove walls entirely!



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  - no walls
  - harmonic well (spring constant k) acts on monomers
  - transparent to fluid

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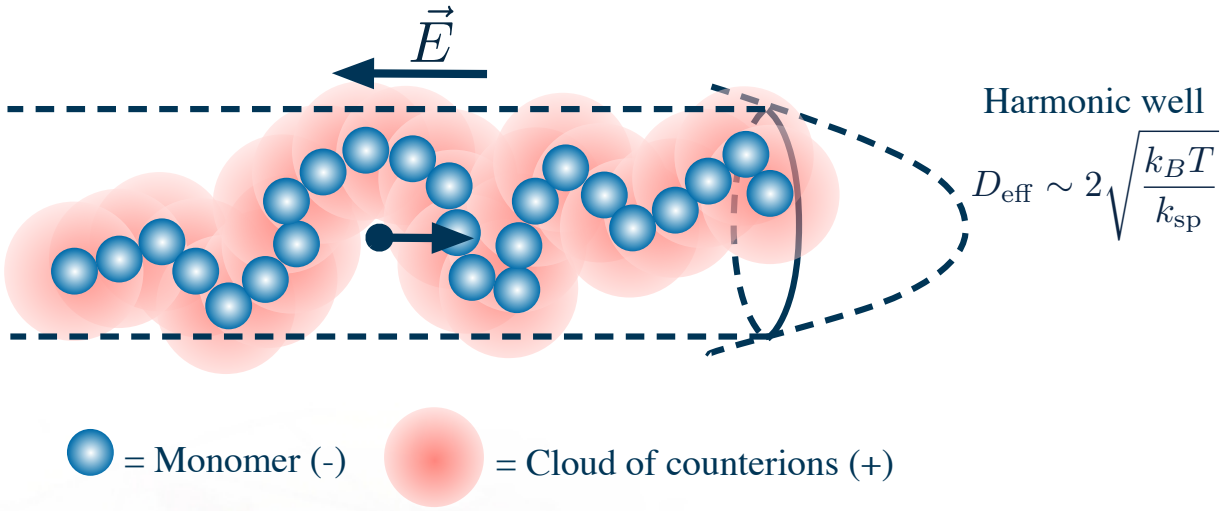

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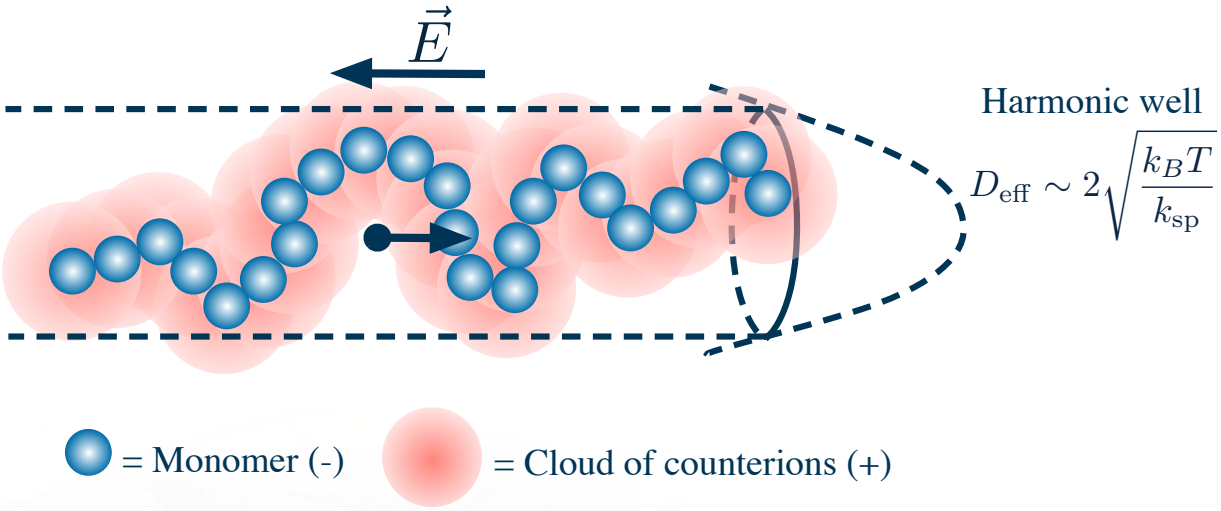

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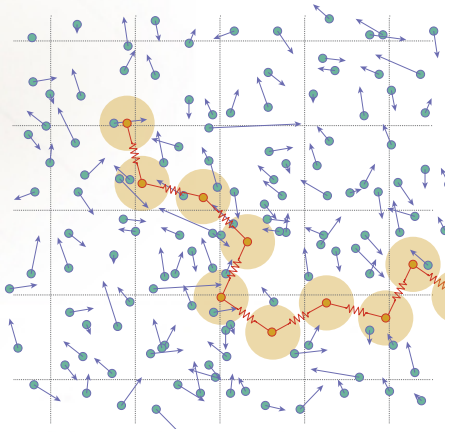
Coarse-Grained Electrohydrodynamics:
Mean-Field MPCD-MD Debye-Hückel Algorithm



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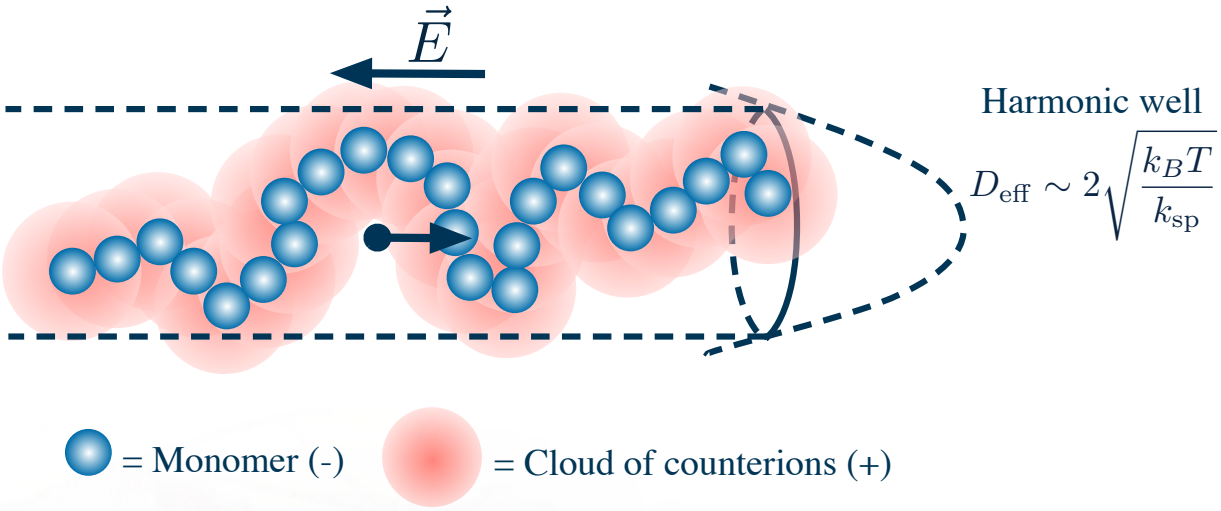

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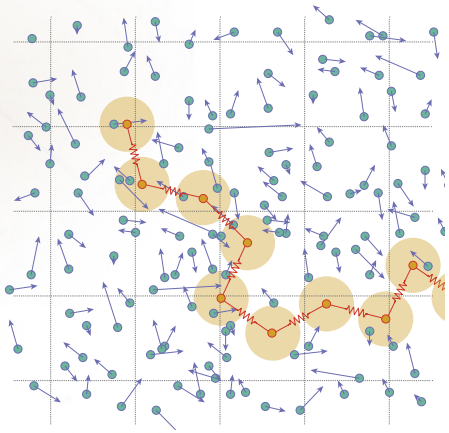
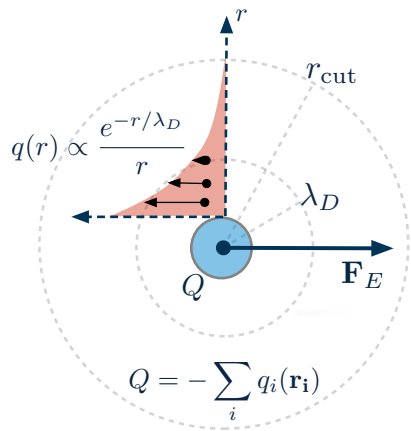
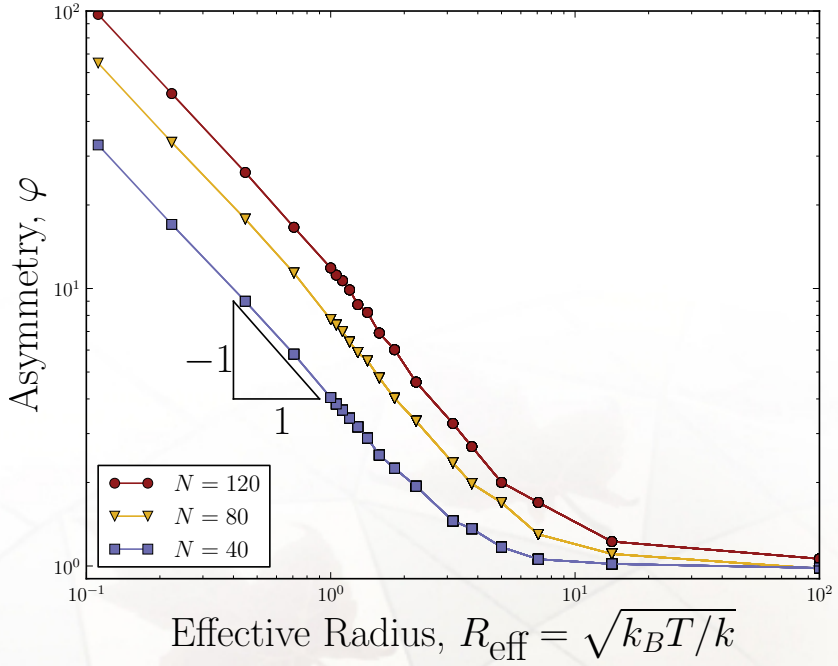




Mobility:
of confined and deformed polyelectrolytes

Asymmetry ratio



where $\varphi = R_{g,x}/R_{g,r}$

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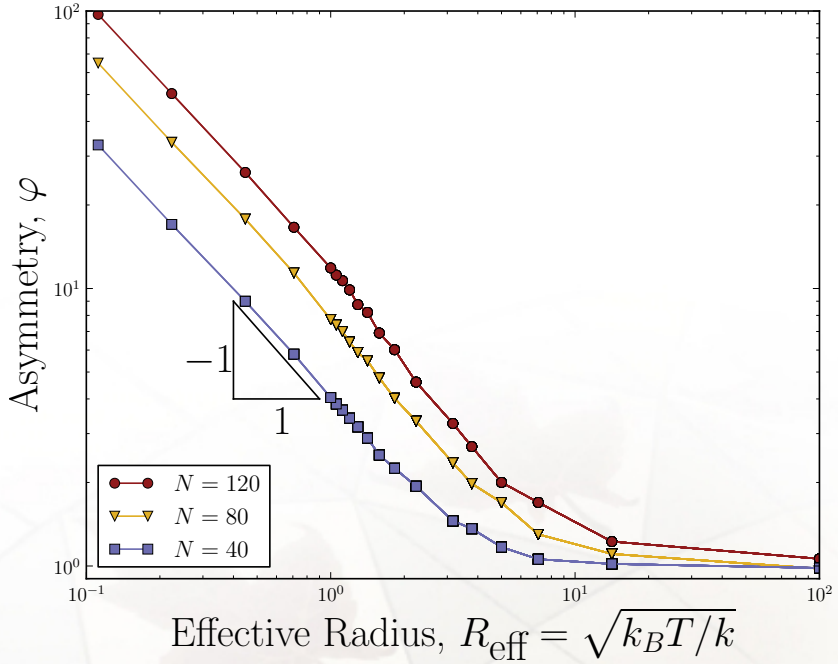
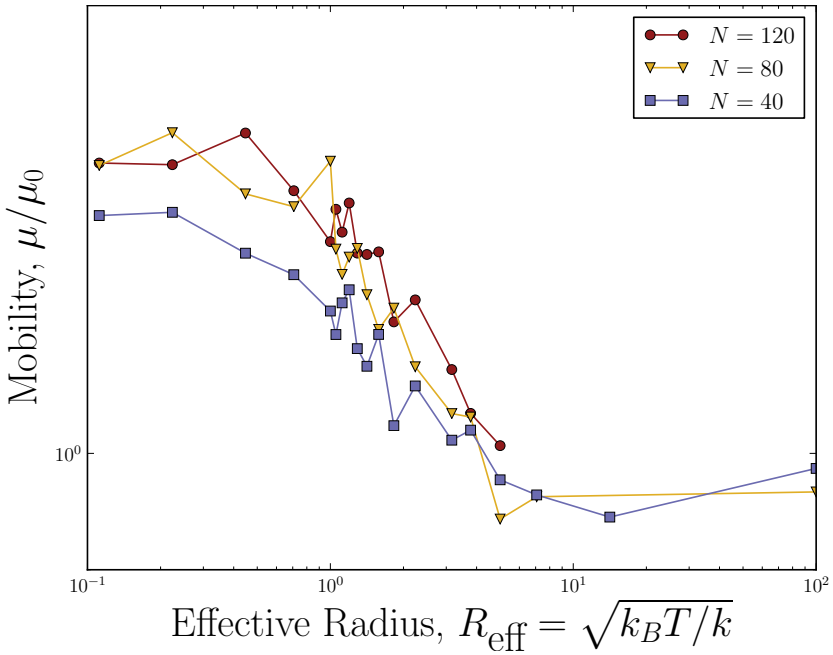


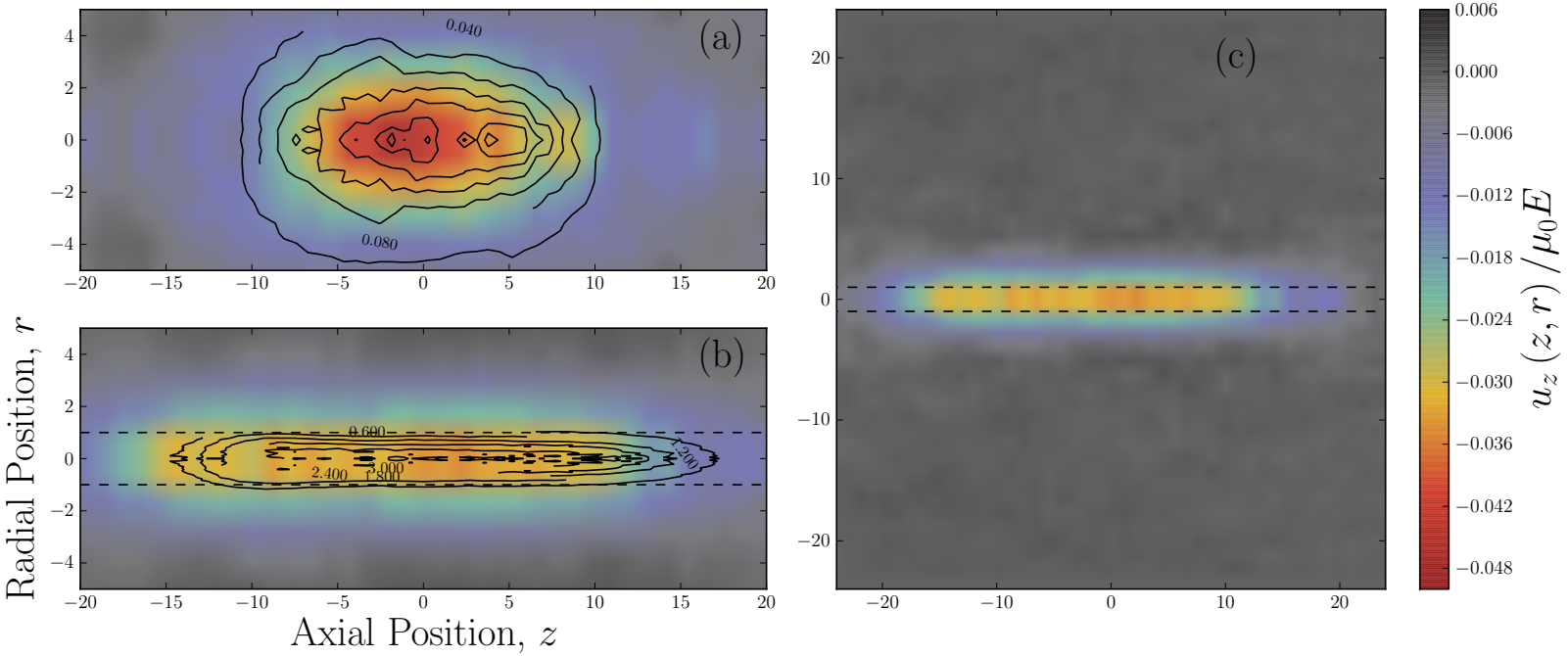
Electrophoretic Mobility



where $\varphi = R_{g,x}/R_{g,r}$

- The *conformation* has N dependence and continues to increases at strong confinement
- The *mobility* is N-independent and saturates at strong confinement

Free-draining:
far-field fluid speed remains zero



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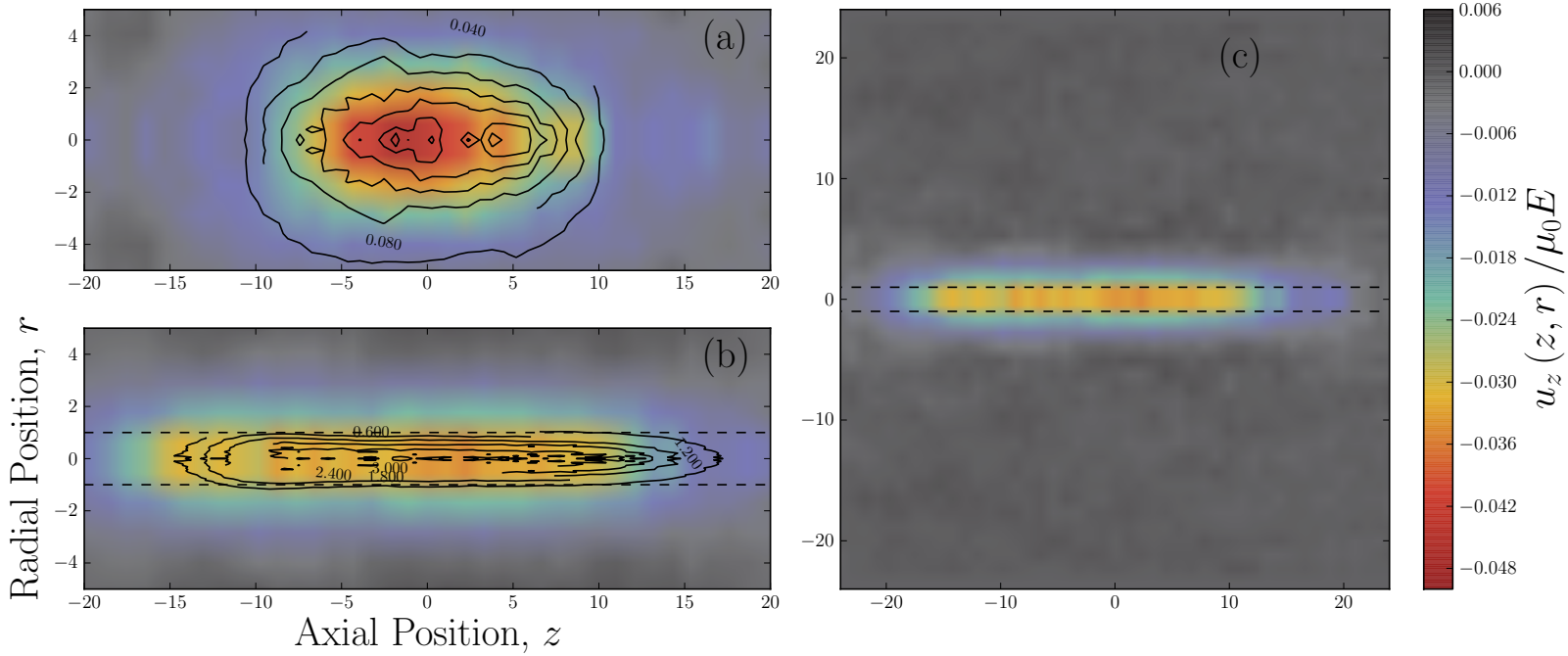
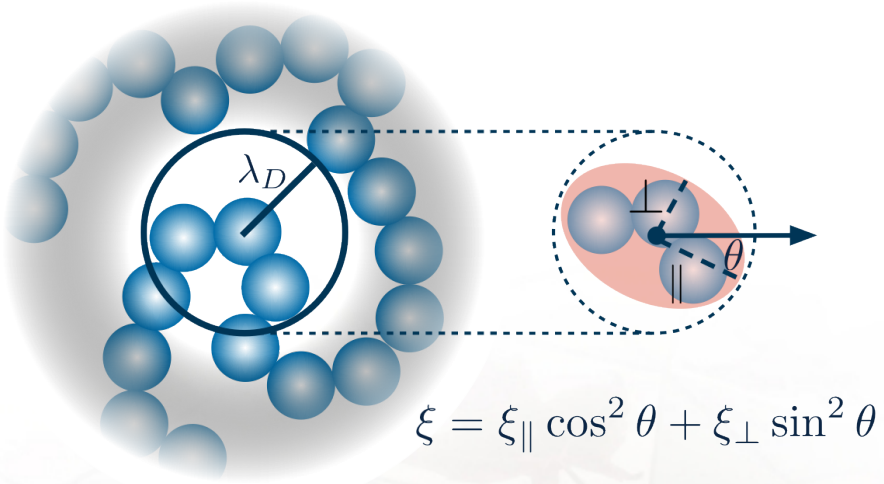


Together with the asymmetry ratio, the flow profiles suggest that *hydrodynamic interactions remain screened*.

Why Does Mobility Increase?
local hydrodynamic coupling



$$\xi = \xi_{\parallel} \cos^2\theta + \xi_{\perp} \sin^2\theta$$

- Monomers within a given λ_D are hydrodynamically coupled.
- Segments are locally rod-like

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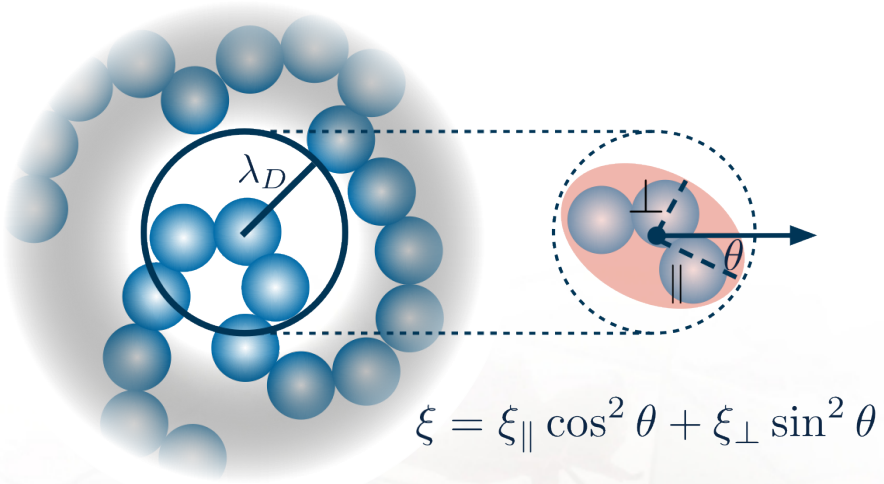

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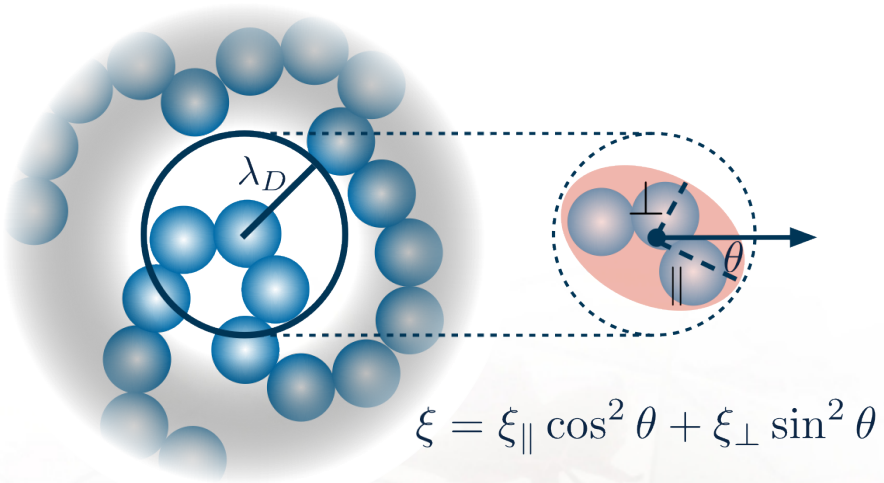

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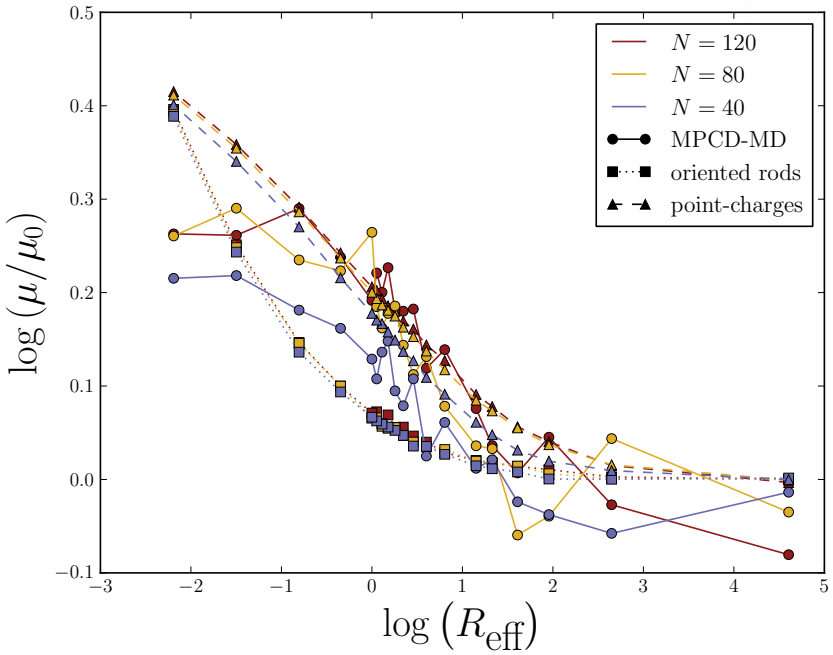

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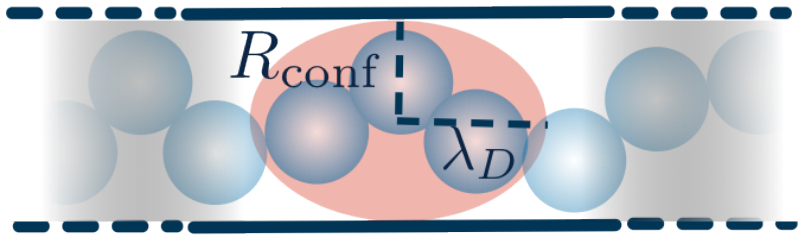

$$\xi \approx \xi_{\parallel}(\lambda_D, R_{\text{conf}})$$

Conclusion

- Conformation changes via antiparallel force are not equivalent to perpendicular force
  - mobility independent of conformation (while $R_{eff} > \lambda_D$)
- Mobility varies in strong confinement
  - even in the absence of walls
  - requires finite λ_D
  - strong confinement decreases each segment's effective friction coefficient
- Future work:
  - improved simple models of effective friction coefficient
  - vary Debye length
  - steeper confining potential
  - fluid impenetrable walls

Thank you,

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