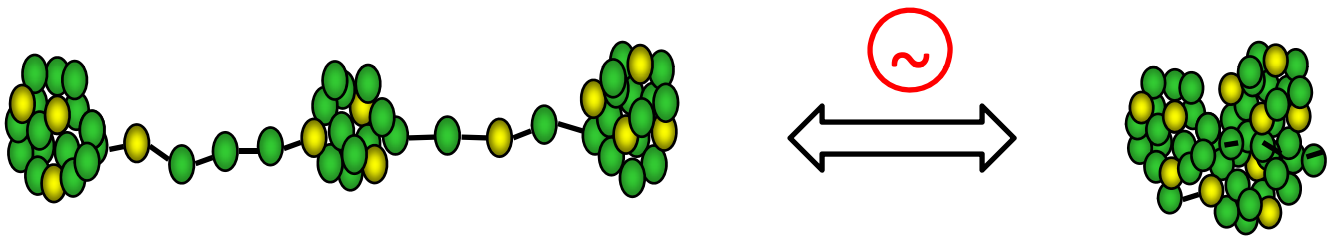
AC-Electric Manipulation of Flexible Polyelectrolyte Conformational Dynamics



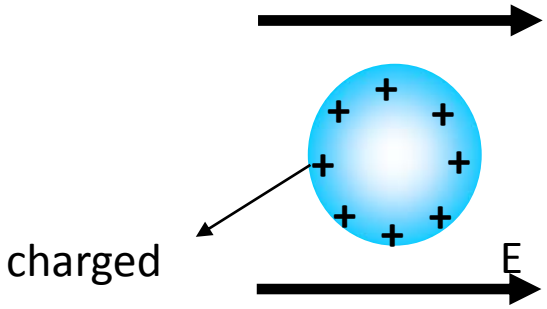
Y. Elaine Zhu

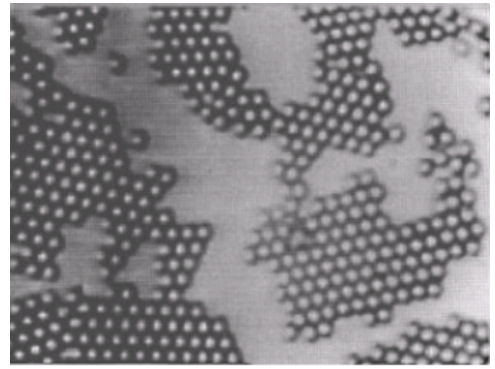
Dept. Of Chemical and Biomolecular Engineering
University of Notre Dame

Effect of Electrical Fields on Colloids

Electrophoresis

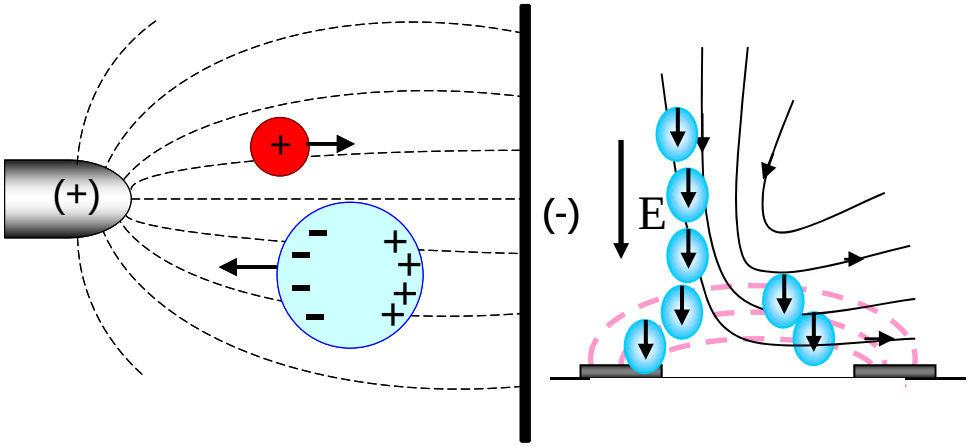
Charged particles move toward the opposite field





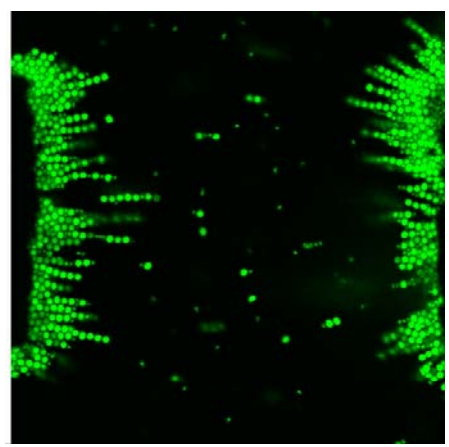
Trau & Saville, Langmuir(1997)

Dielectrophoresis

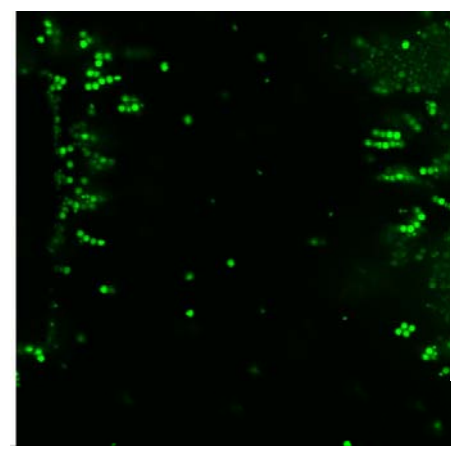


AC-Induced Binary Colloidal Assembly

100 kHz

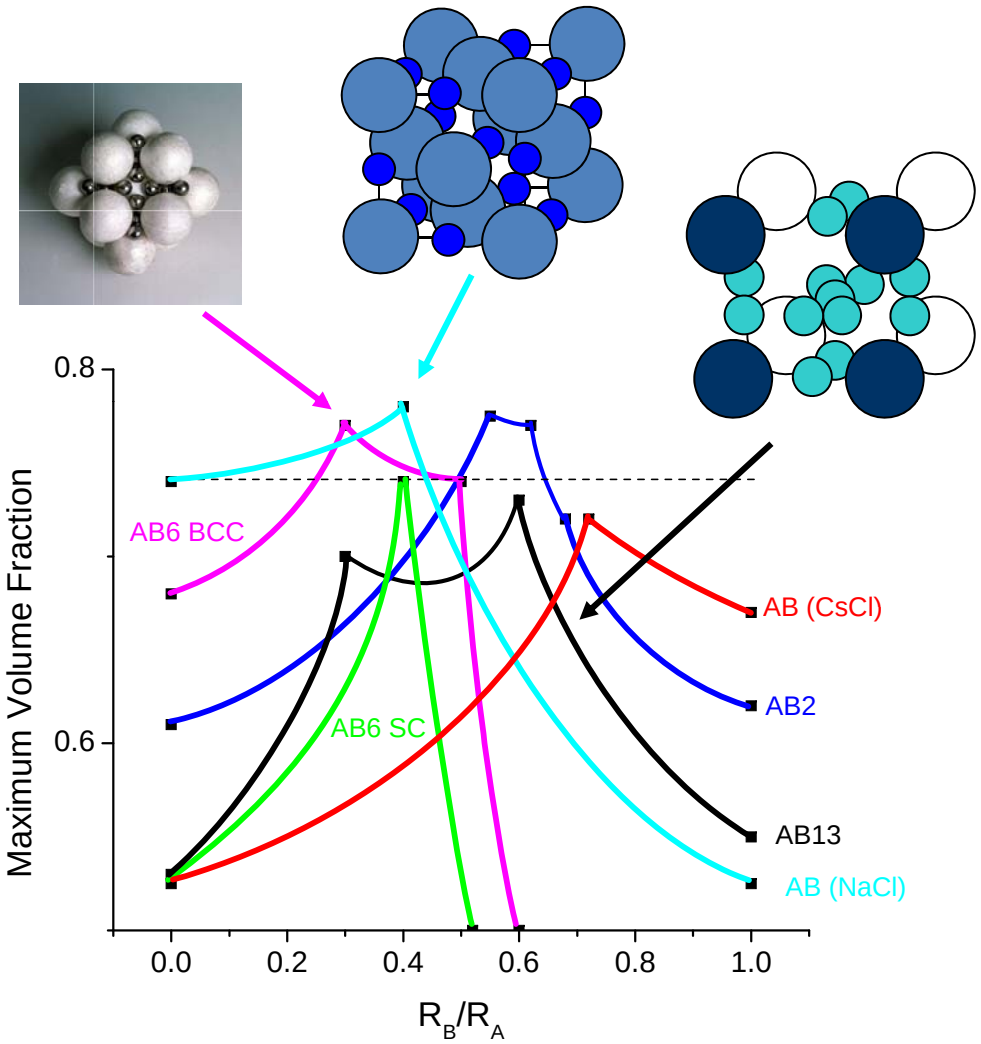


700 kHz

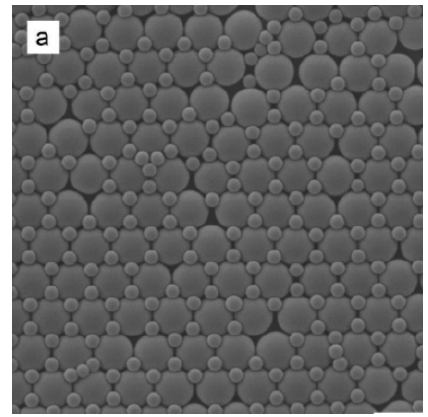


✓ Versatile for various materials ✓ Highly controllable with precision ✓ Rapid assembly

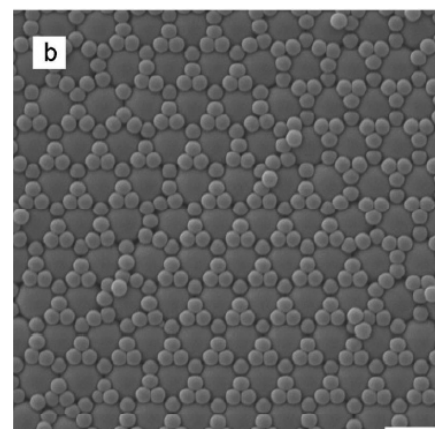
Can DEP Induce Binary Crystal Formation?



Size ratio: 0.34 (0.24/0.70)



0.56% (240 nm)



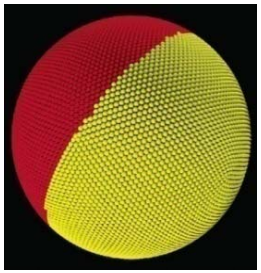
1.2 % (240 nm)

Ongoing: 2D binary crystal by DEP+confinement

(Schofield, et al)

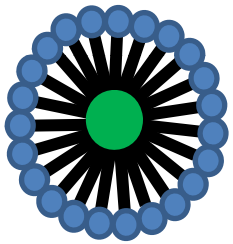
AC polarization and assembly of amphiphilic colloids and macromolecules

Janus Particles

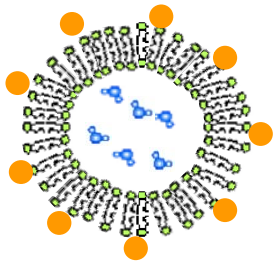


Asymmetric surface chemistry

Micelles and Liposomes



Micelles
(d~ 3-10 nm)



NPs
(d~ 5-50 nm)

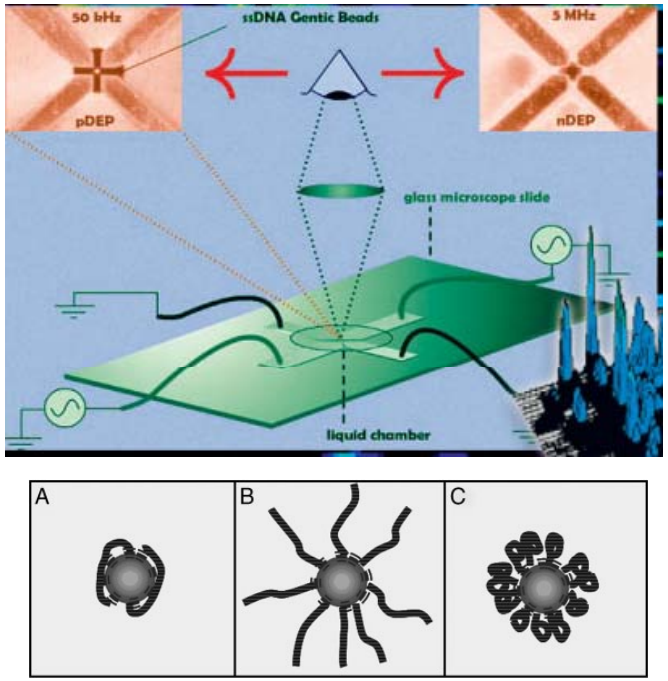
Polyelectrolytes

Macromoleculess
(d~ 5-1000 nm,
MW dependent)

Conformations of Polyelectrolytes Under AC Electric Fields

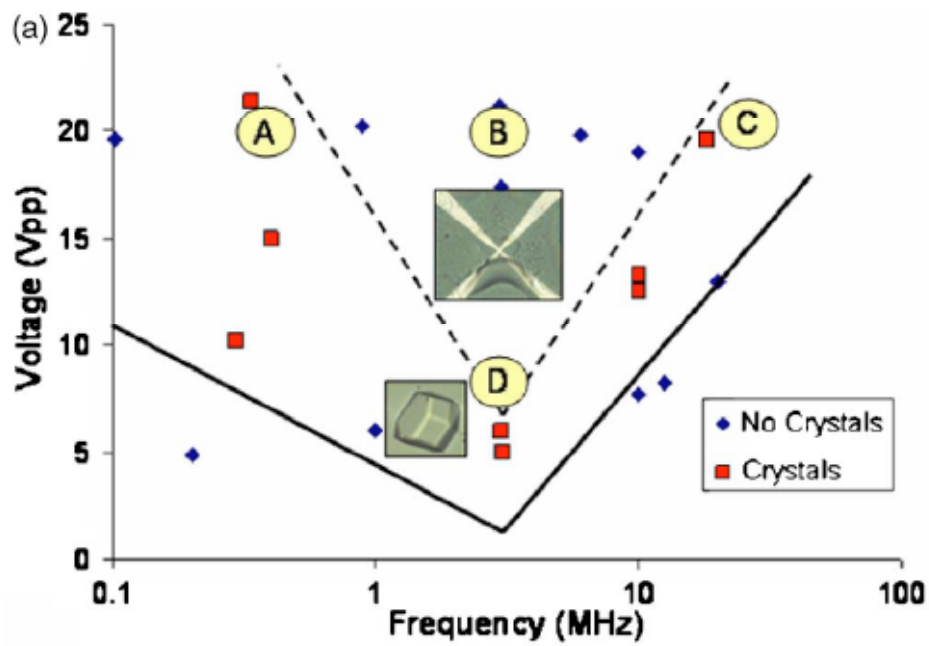
Application of AC-electrokinetics on biomacromolecules and medical diagnostics

DNA-nanocolloid complex



Gagnon et al. Electrophoresis 29, 4808 (2008)

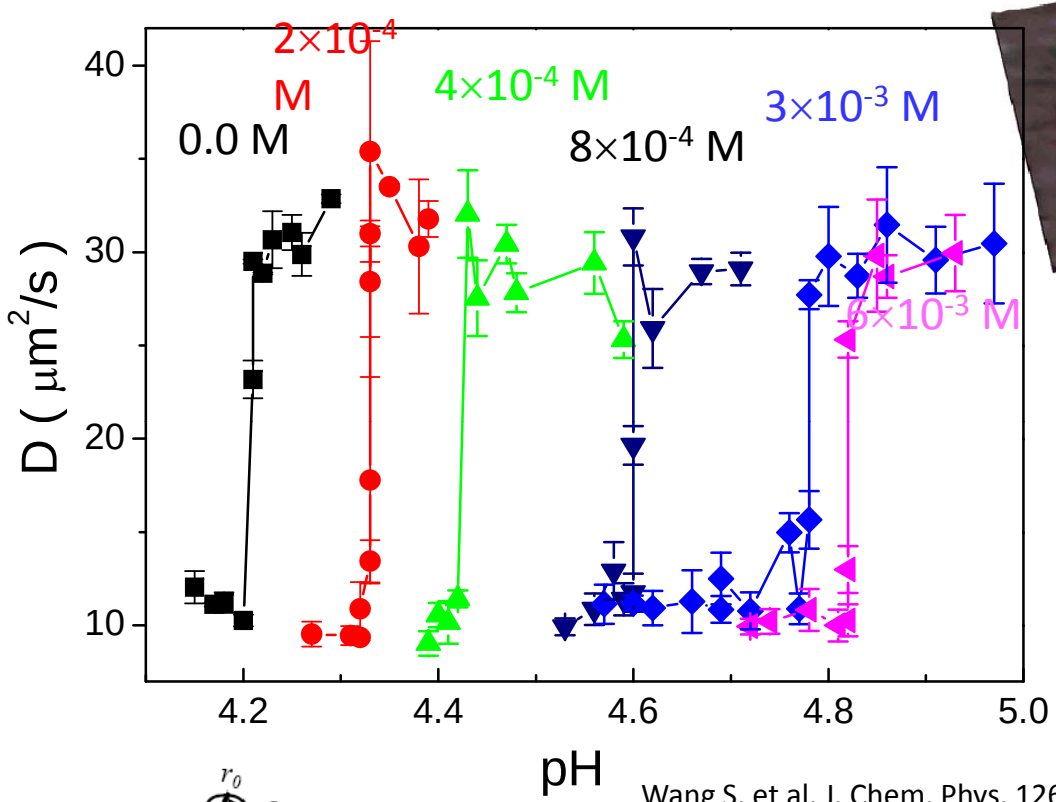
Protein crystallization in AC-fields

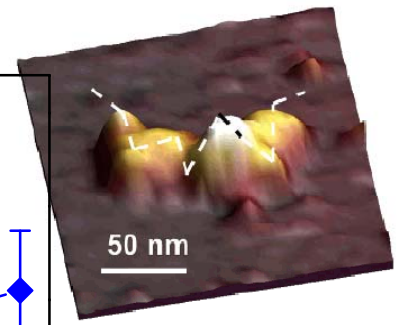


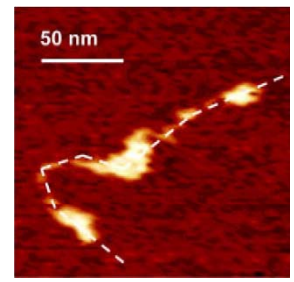
Hou et al. Appl. Phys. Lett. 92, 223902 (2008)

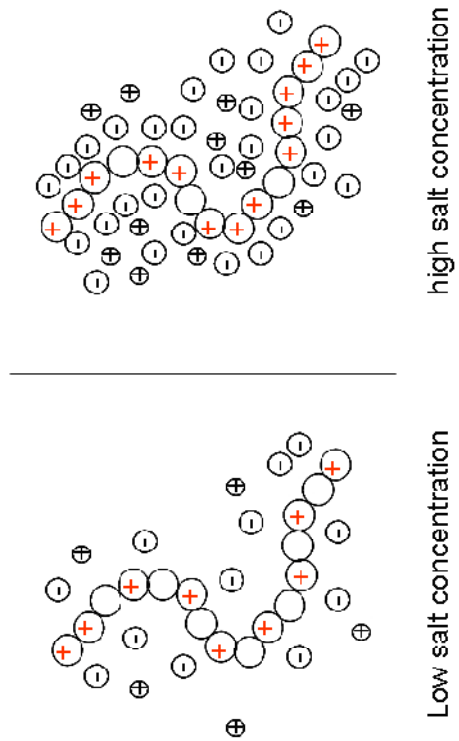
Inadequate understanding of structural dynamics of biomacromolecules in response to AC-electric fields of varied voltage and frequency

1st Order Conformational Transition of Weak Polyelectrolytes

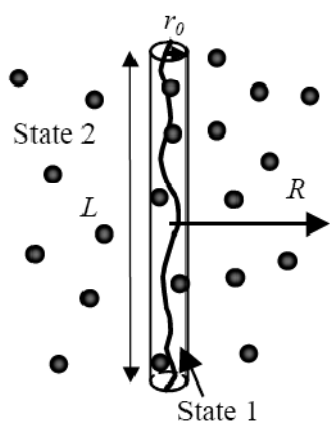








Wang S. et al. J. Chem. Phys. 126, 091104 (2007); Roiter Y. et al. JACS. 127, 15688 (2005)



Counterion Condensation of Polyelectrolyte

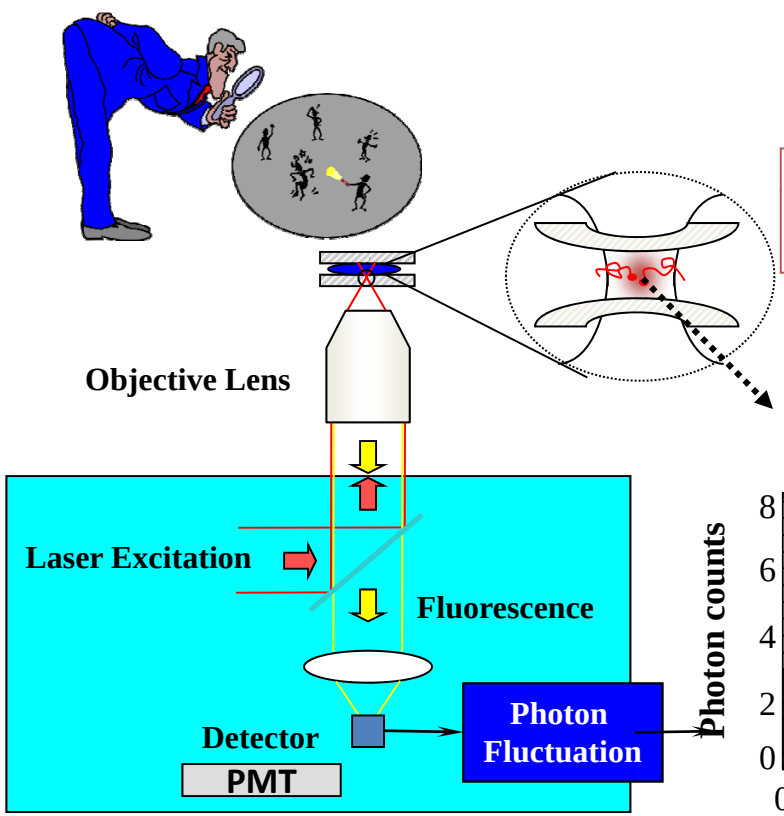
Question:

- o Modulate counterion condensation degree by AC-fields?
- o AC-electric induced conformational transition?

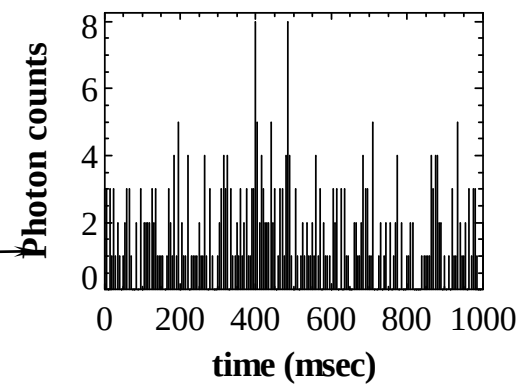
Single Molecule Spectroscopy Employed to the AC-electrokinetic Study of Nanocolloids

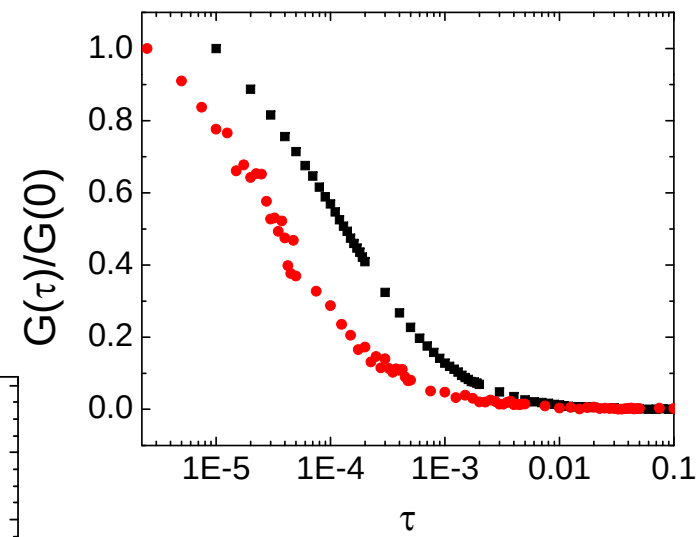
Fluorescence correlation spectroscopy (FCS)

$$G_D(\tau) = \frac{1}{c\pi^{3/2} z^2 w}\left(\frac{1}{1+4D\tau/\omega^2}\right)\left(\frac{1}{1+4D\tau/z^2}\right)^{1/2}$$



$$G(\tau) = \frac{\langle \delta I(t)\delta I(t+\tau)\rangle}{\langle \delta I(t)\rangle^2}$$





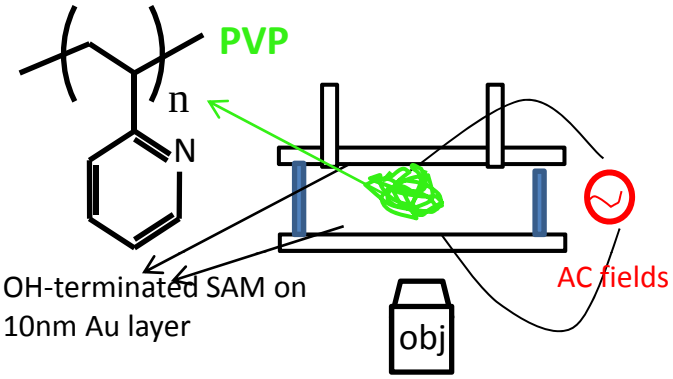
$$D = \frac{kT}{6\pi\eta R_h}$$

G(0)~ <N>

Experimental Setup

Construction of Uniform AC-Electric Fields

Uniform AC-Electric Field

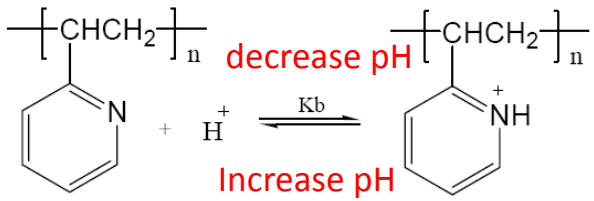


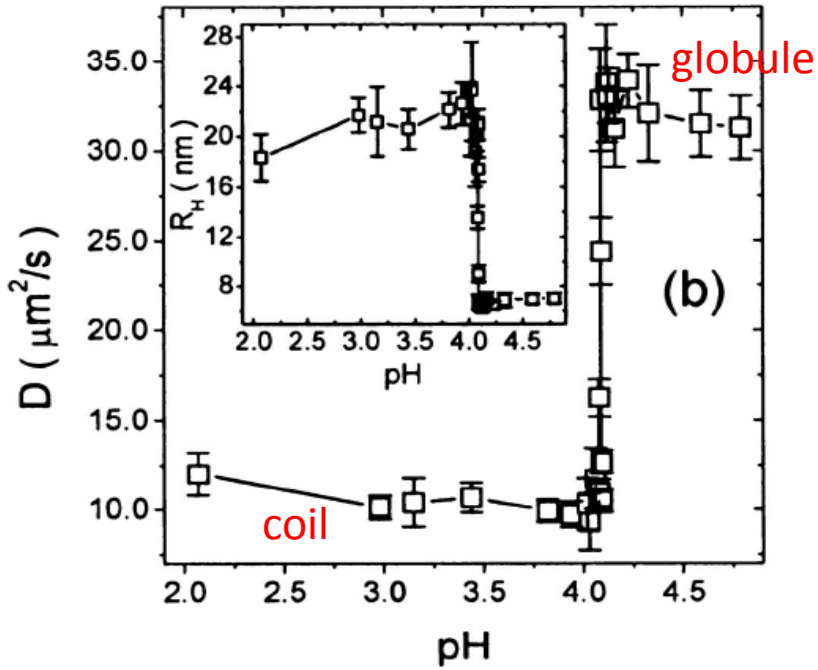
Electrode: OH monolayer coated 10nm Au layer

Weak hydrophobic polyelectrolyte

Polyelectrolyte: Poly (2-vinyl pyridine)
(Mn=135K, Mw/Mn = 1.03)

Labeled by Alexa 488

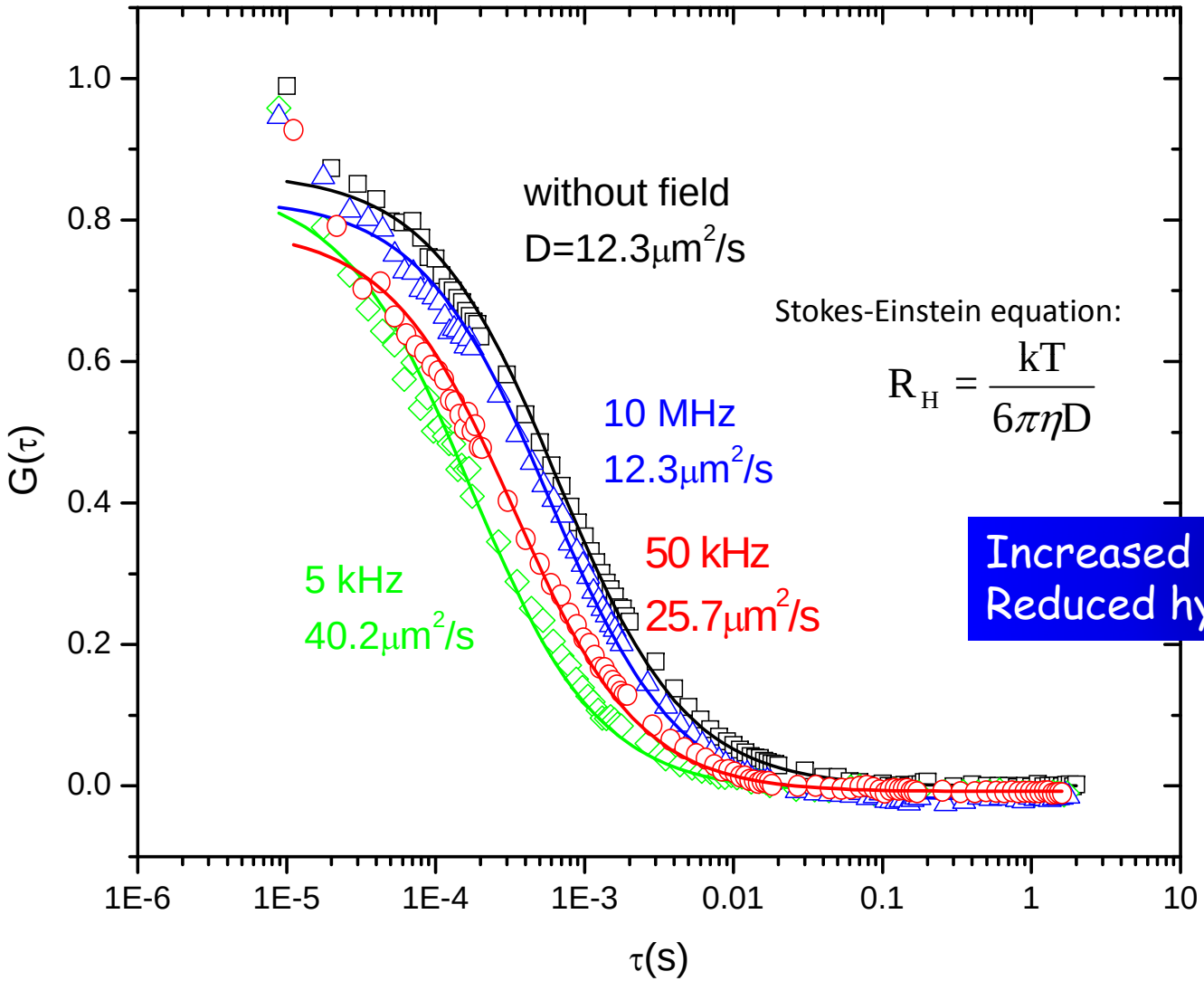




Coil-to-globule transition

Wang S. et al. J. Chem. Phys. 126, 091104 (2007)

AC-Frequency Dependence of PVP Diffusivity



pH= 4.16

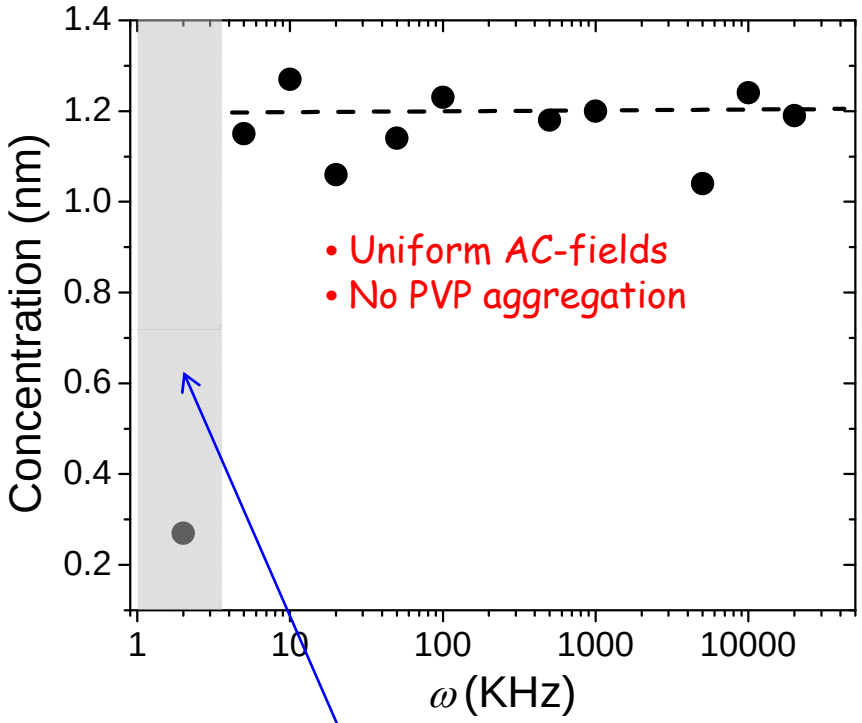
V_{PP} =10 V

Stokes-Einstein equation:

$$R_H = \frac{kT}{6\pi\eta D}$$

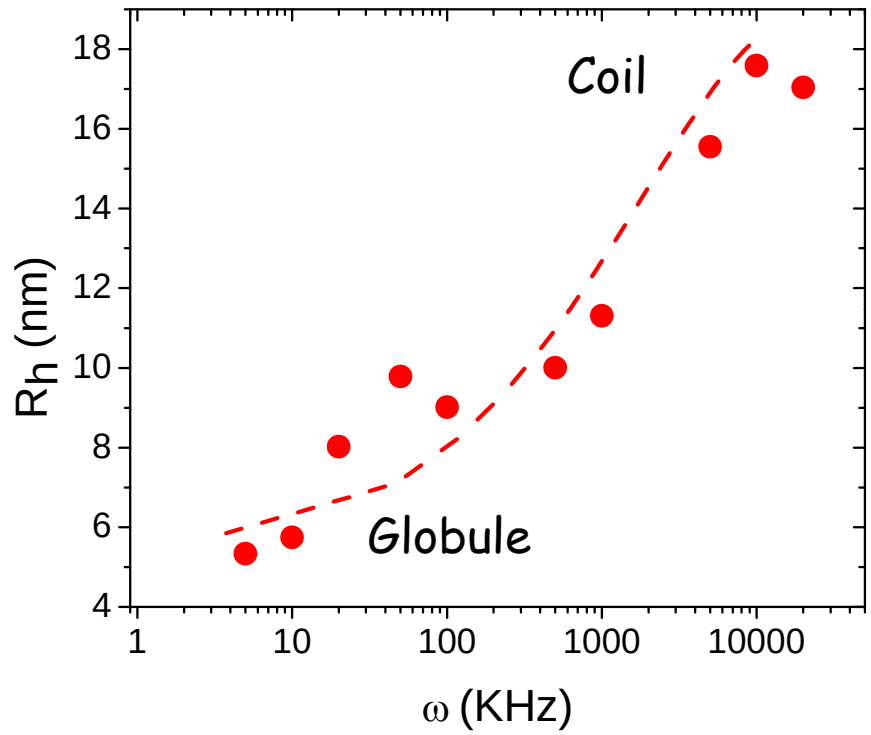
Increased diffusivity → Reduced hydrodynamic radius

Conformation Transition of PVP under AC-fields



Threshold frequency for molecular adsorption onto electrodes (DC Screening)

$$\omega_0 = \frac{D}{\lambda L} \approx 5kHz$$

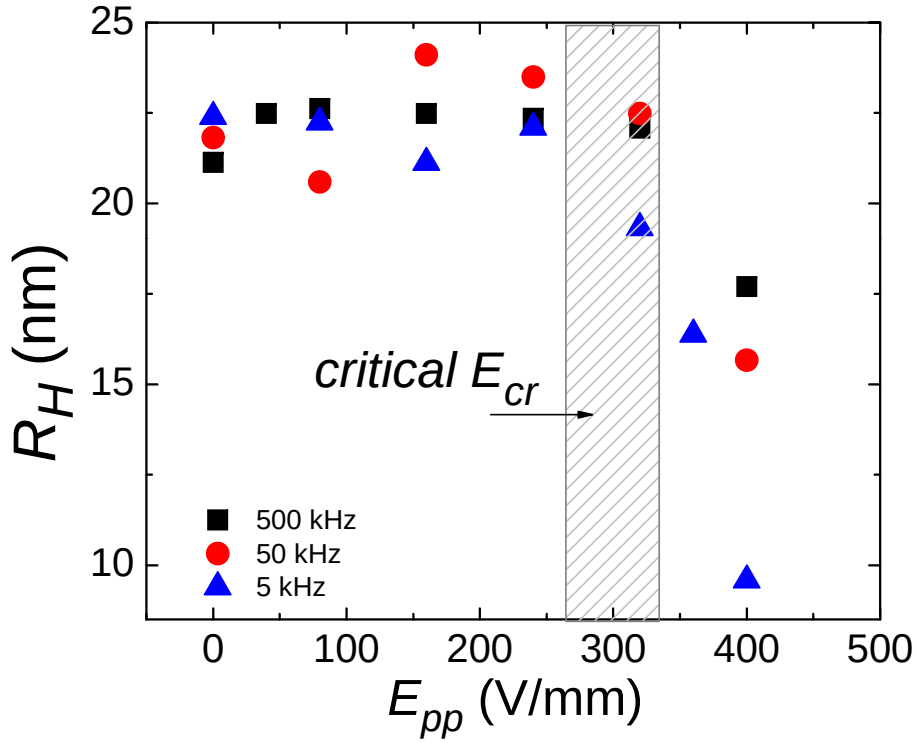


Coil to globule transition (CGT) as decreasing AC frequency

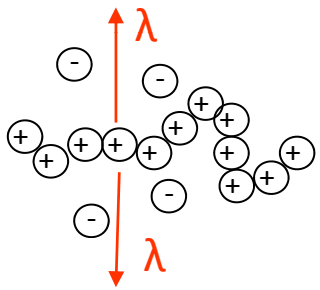
pH= 4.16; V_{PP}=10 V

AC-Voltage Dependence of PVP Conformation Transition

pH=4.16



Induced counterion migration near polyelectrolyte:

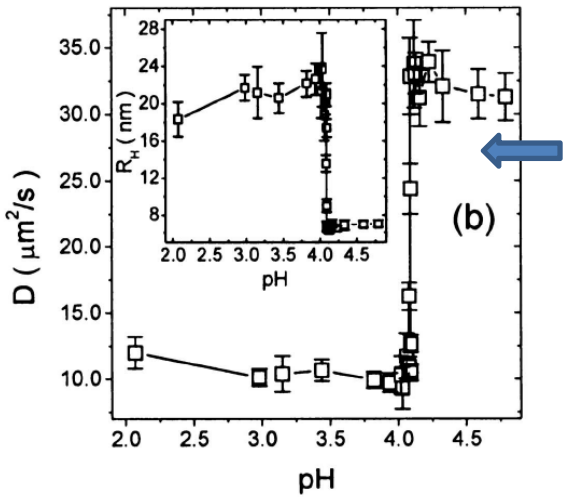


$$v_0 \sim \frac{k_b T}{e}\frac{L}{2\lambda} \sim 15V$$

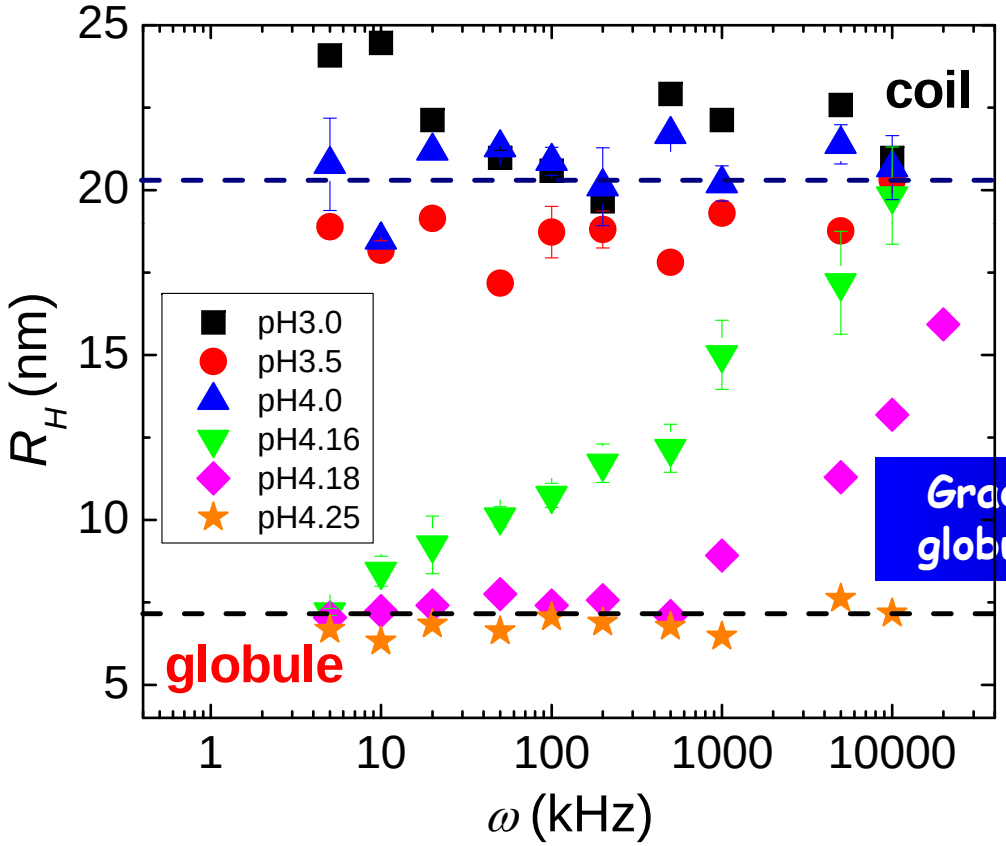
A very rough estimation

- A critical AC-voltage to induce the coil-to-globule transition
- The critical AC-voltage weakly depends on AC-frequency

Induced Conformation Transition near PVP Critical pH



1st order transition

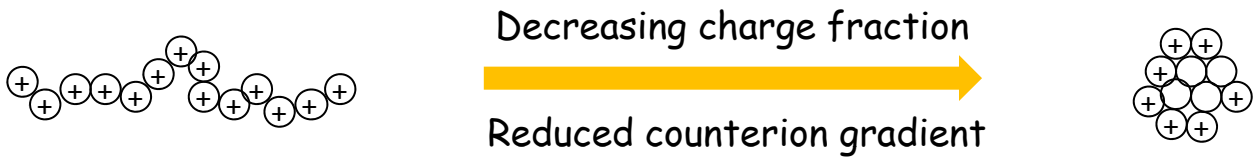


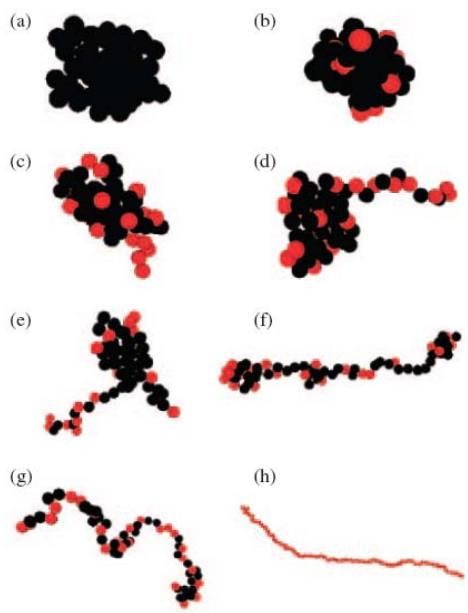
Gradual coil-to-globule transition

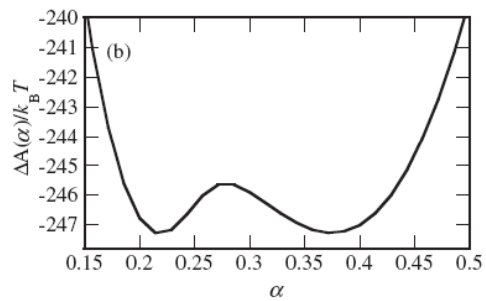
Conformation Transition of Hydrophobic Polyelectrolytes
(Theoretical and Simulation Prediction)

Conformational transition in **weak hydrophobic polyelectrolyte** (similar to protein folding)

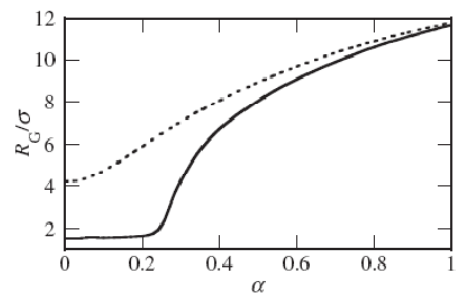
Multiscale interactions: Electrostatic, Hydrophobic interactions,
Hydrogen bonding; Van der Waals







Energy profile



Radius profile

- Uyaver, S.; Seidel, C. *Europhys. Lett.* **2003,** 64, 536 and *J. Phys. Chem. B* **2004,** 108, 18804.
- Yamaguchi, T et al. *Bull. Chem. Soc. Jpn.***2005,** 78, 2098.

Possible Mechanism:
Local counterion gradient modulated by AC-fields

System energy fluctuation with frequency

Blob size, R increases as lowering the local counterion concentration

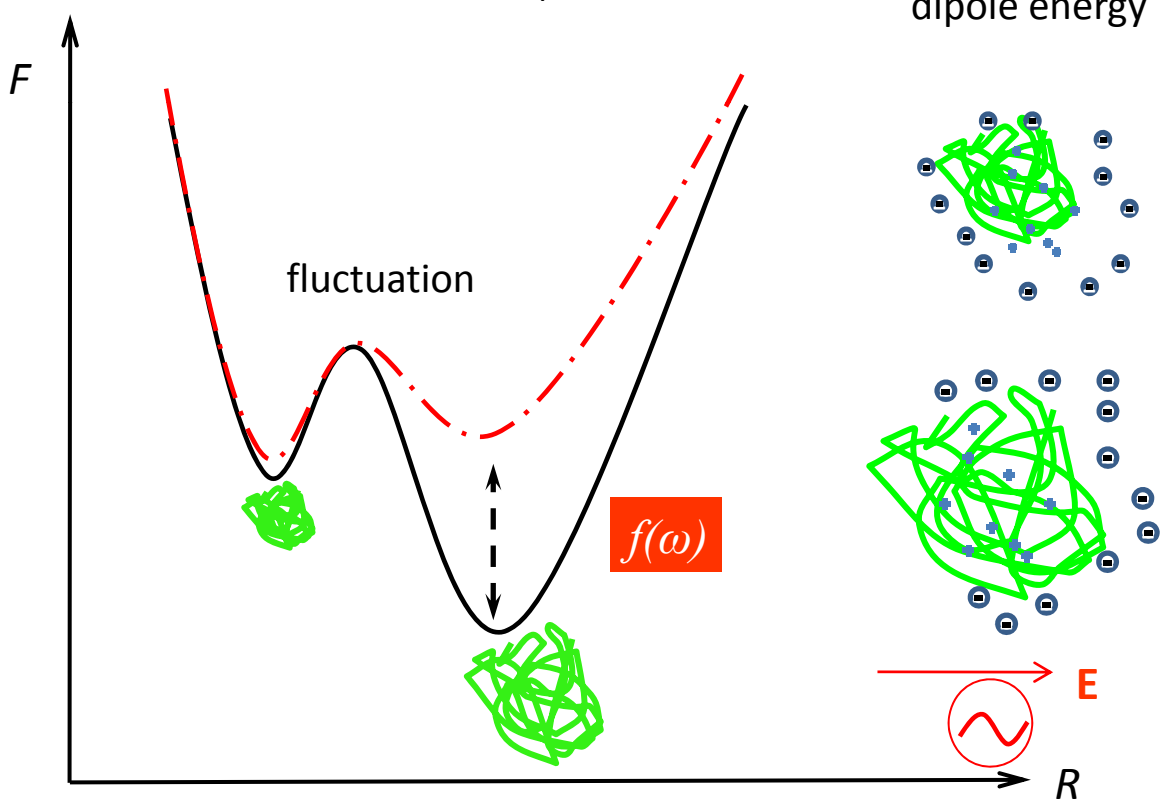
$$W(R) = \frac{3}{2}k_B T\left(\frac{R^2}{a^2 N} + \frac{a^2 N}{R^2}\right) + 4\pi\varepsilon R^3 K(\omega)E^2 + k_B T\left(\nu_2 \frac{N^2}{R^3} + \nu_3 \frac{N^3}{R^6}\right)$$

entropic

time-averaged induced-dipole energy

2-body and 3-body interactions

(ν_2 : negative)



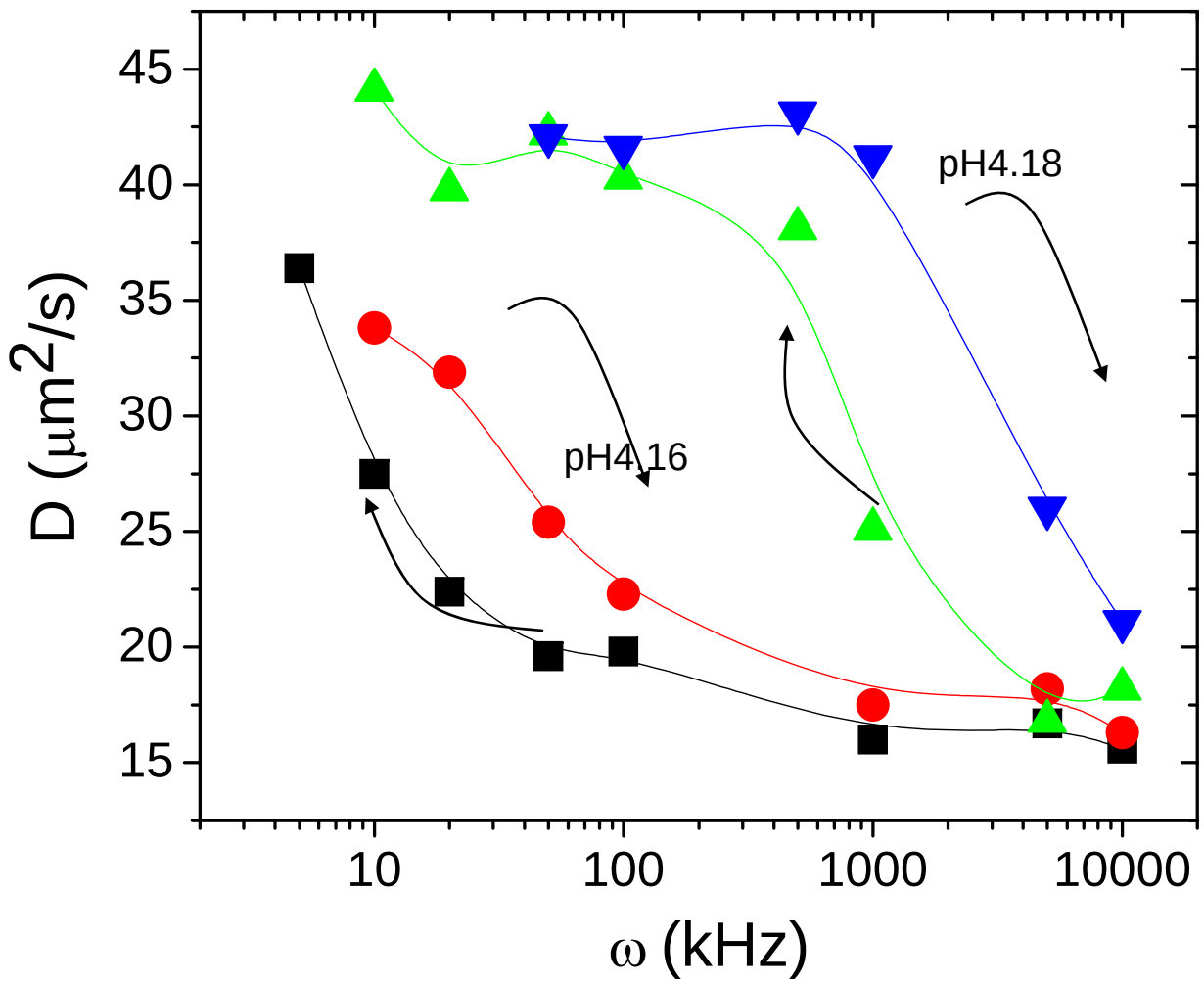
$$\frac{1}{t} \approx A\exp\left(-\frac{\Delta F}{k_b T}\right)$$

- Hopping between coil and globule
- Hopping rate depends on two time scales:

$t >> t_1$ (back to coil)> t_0 (to globule)

- Measured averaged radius

Hysteresis in AC-Induced Conformation Transition

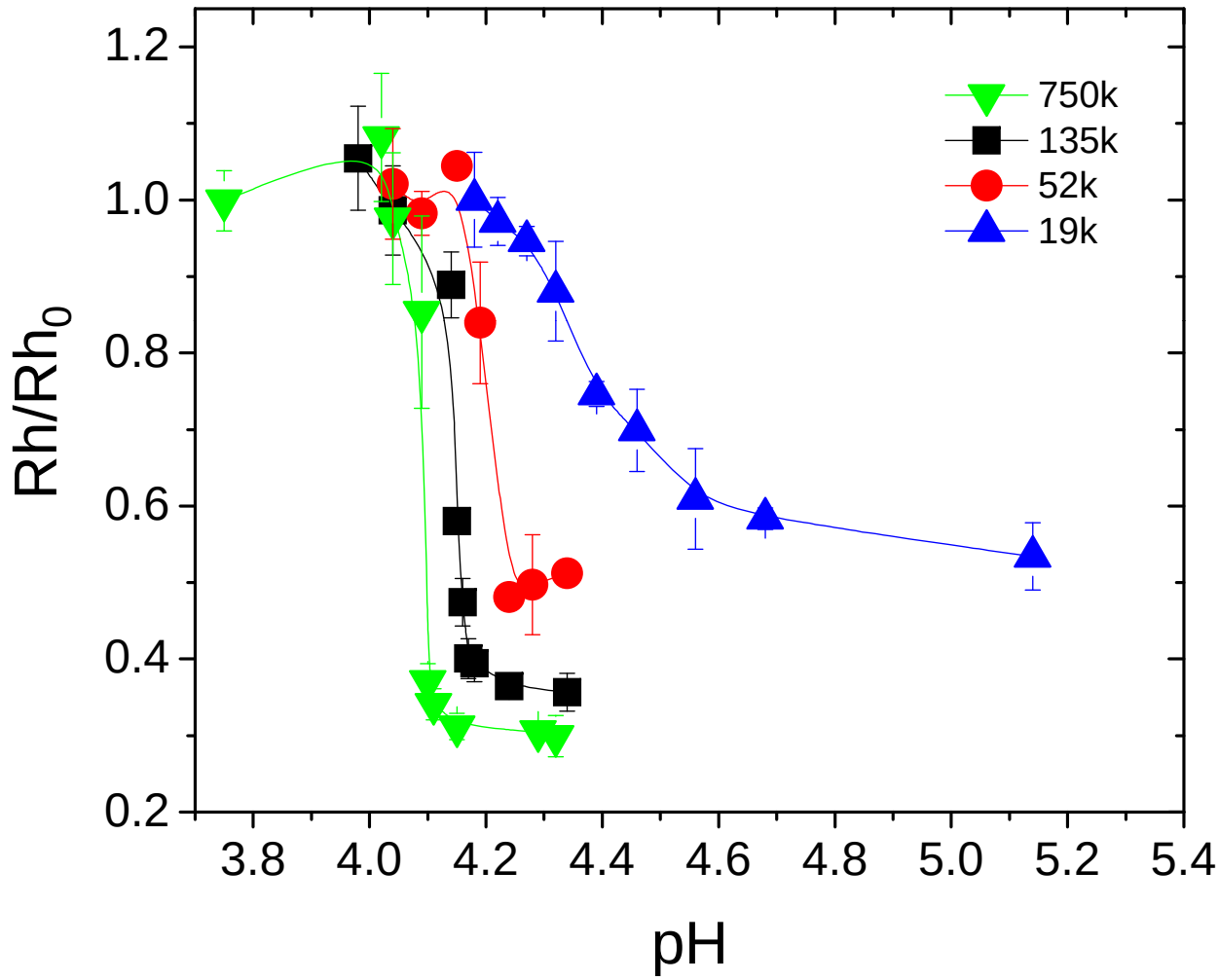


Note:

PVP globule ⟶ coil
without AC-fields in 2 hrs

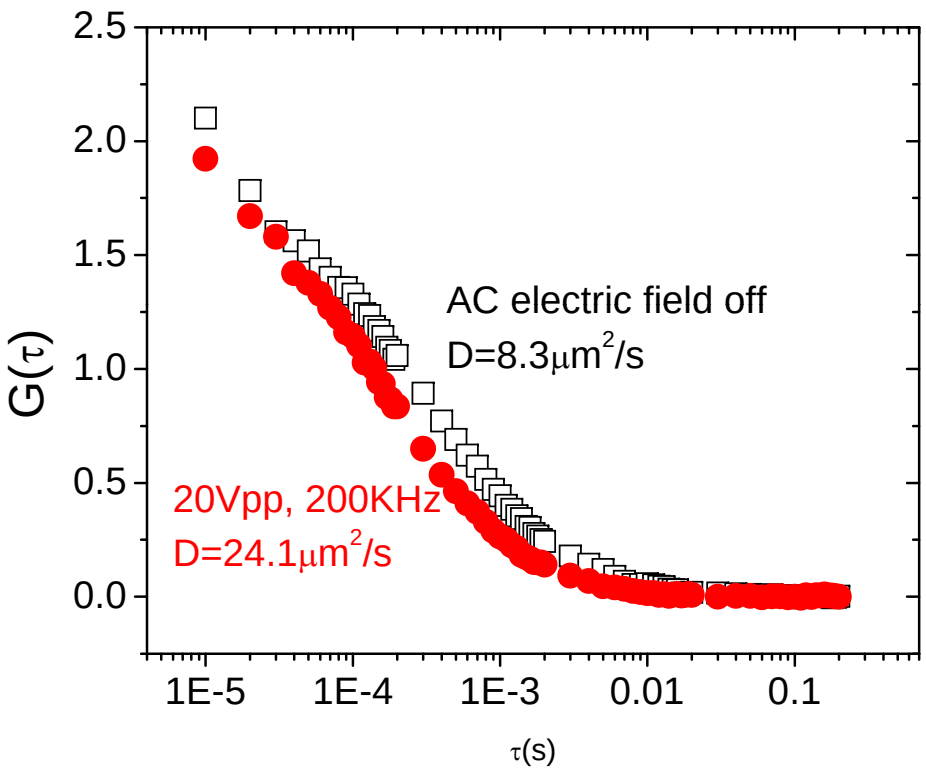
- The onset frequency is dependent on the solution pH
- Hysteresis exists in the conformation transition

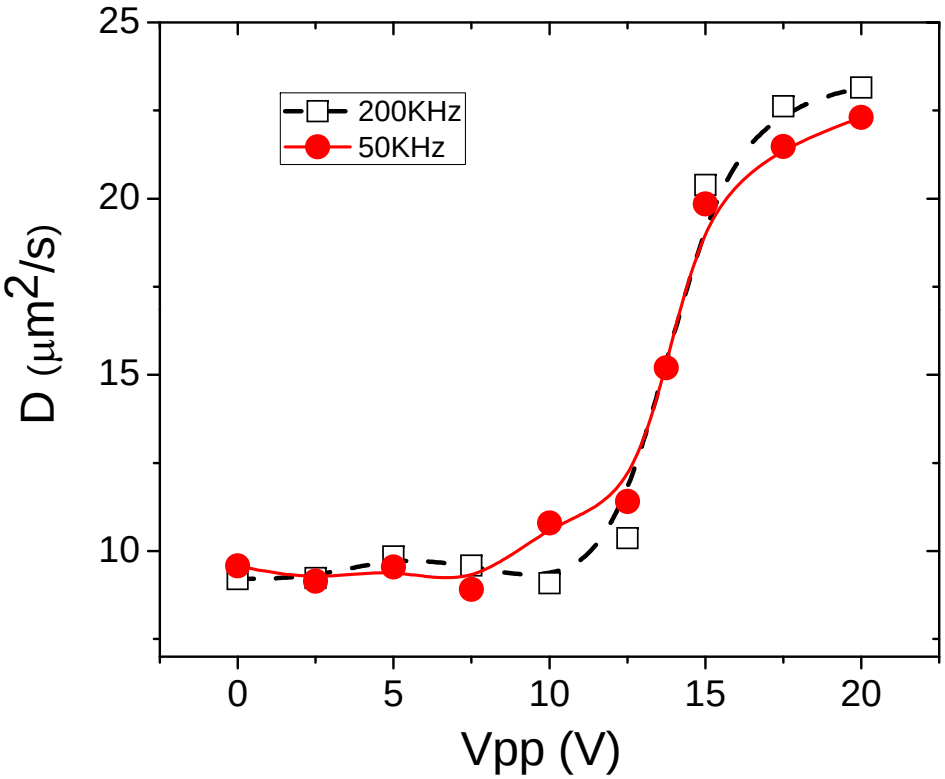
MW Dependent Critical CGT pH



PVP Molecular Weight Dependence

PVP Mn: 750 K

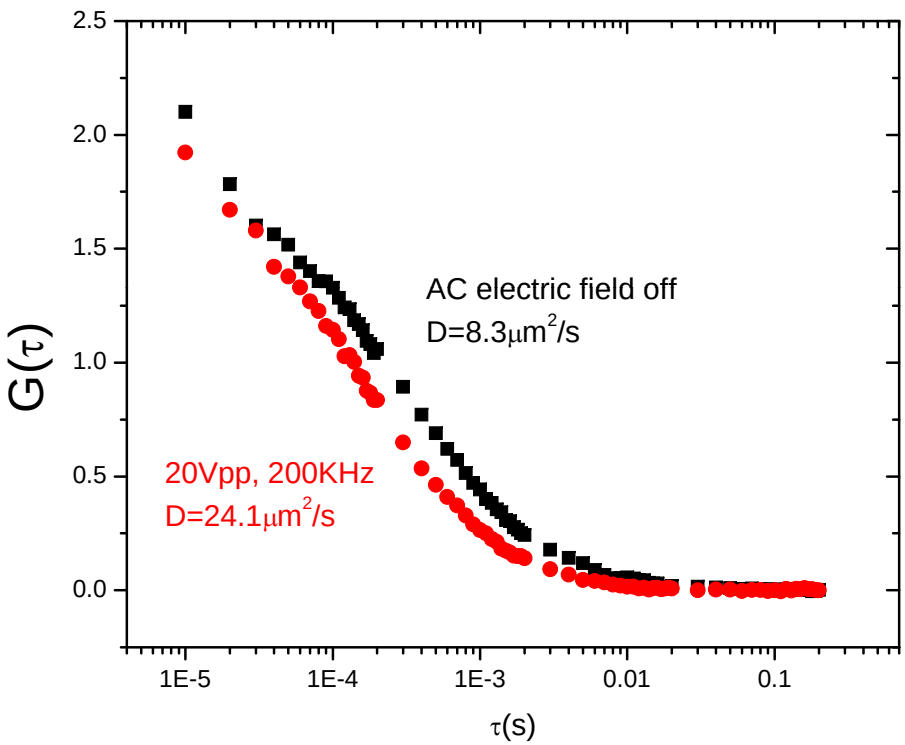


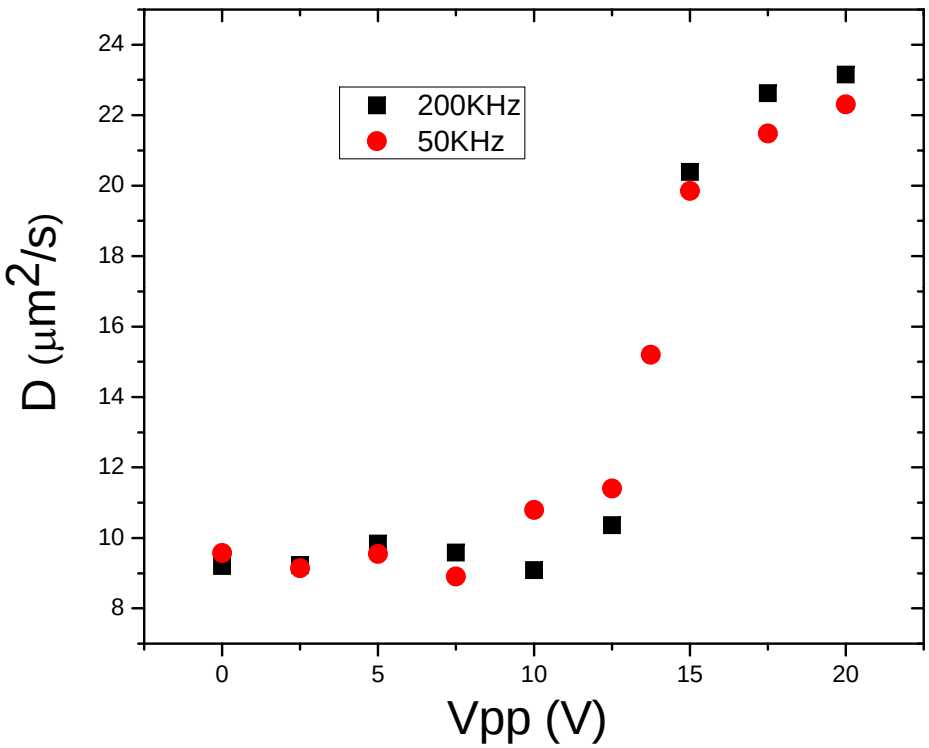


- Conformation transition of higher molecular weight PVP under AC electric field.
- The onset voltage to induce conformation transition: 12.5 Vpp (cf. ~9.0 Vpp for PVP of Mn~ 135 K).

Molecular Weight Dependence

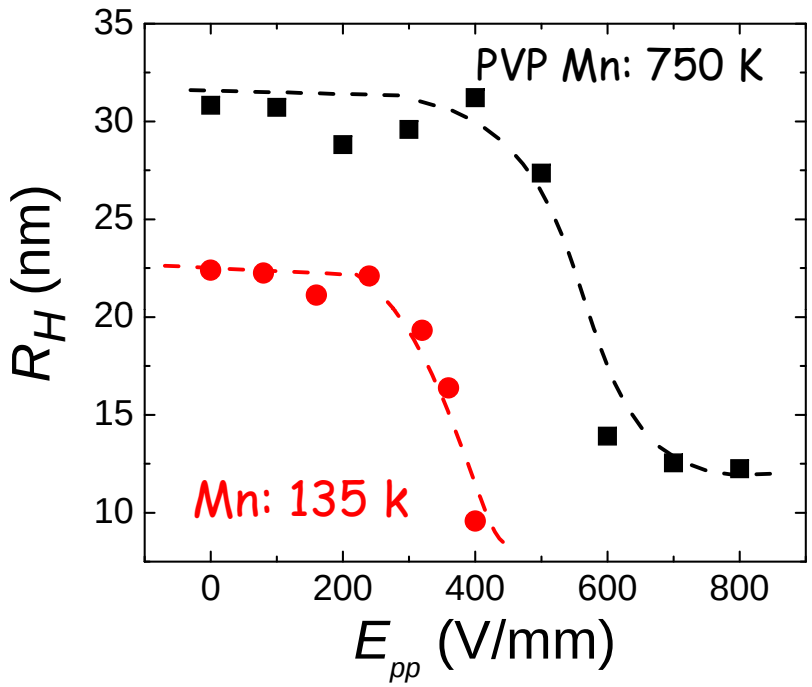
PVP Mw: 750K

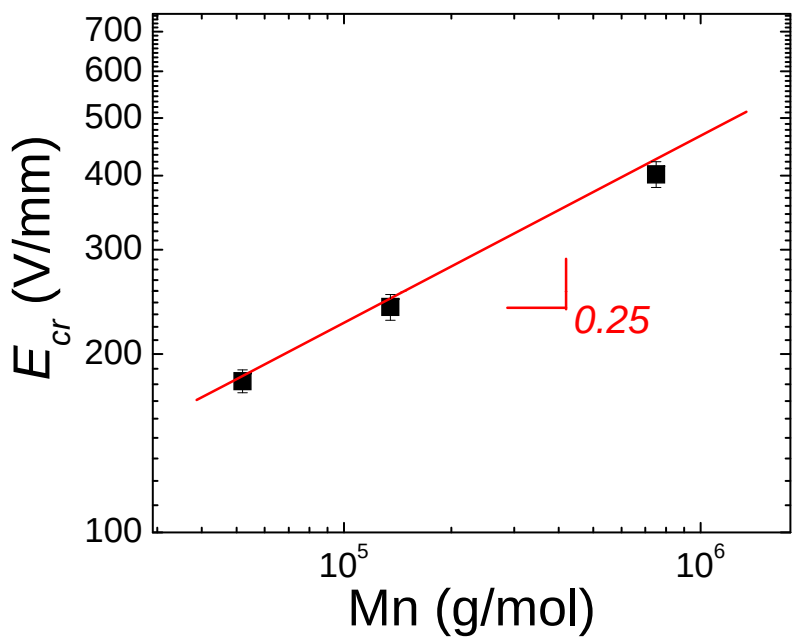




- MW-dependence of AC-induced PVP conformation transition
- Weak dependence of the onset AC-voltage with MW: olecular weight is increased about 5 times from 135K to 750K, which is attributed to the stronger electrostatic potential of higher molecular polyelectrolyte.

PVP Molecular Weight Dependence



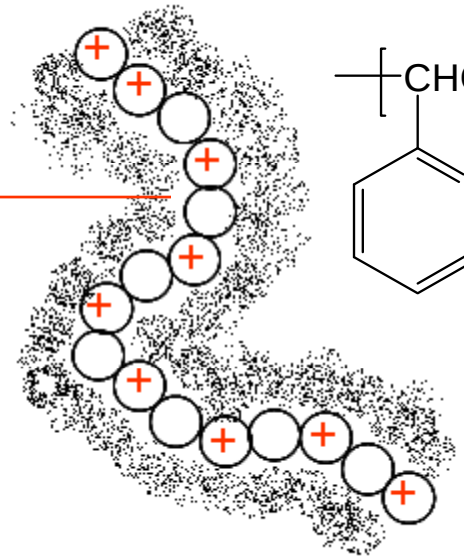


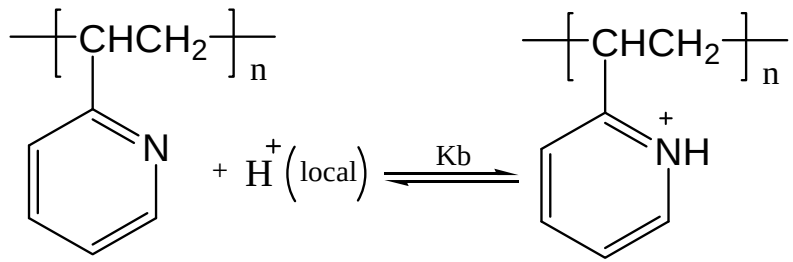
- Conformation transition of higher molecular weight PVP under AC electric field.
- The onset voltage to induce conformation transition: 425 V/mm (cf. ~250 V/mm for PVP of Mn~ 135 K).

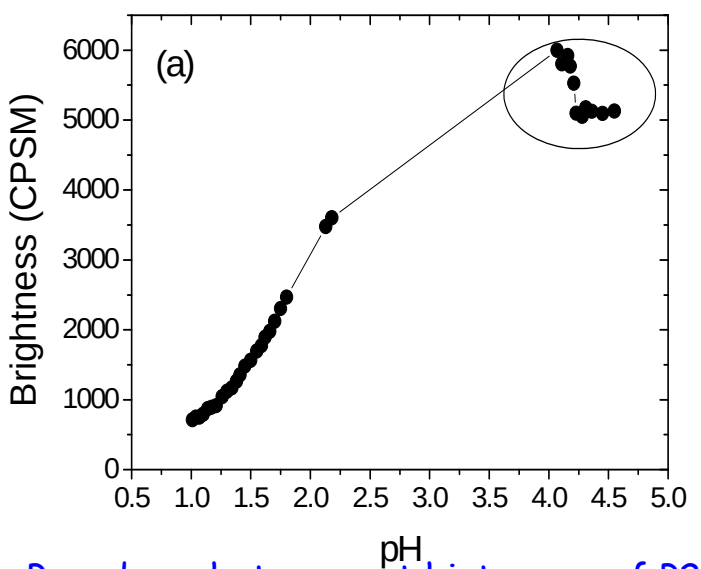
Determine Local Counterion Distribution under Varied AC-Fields

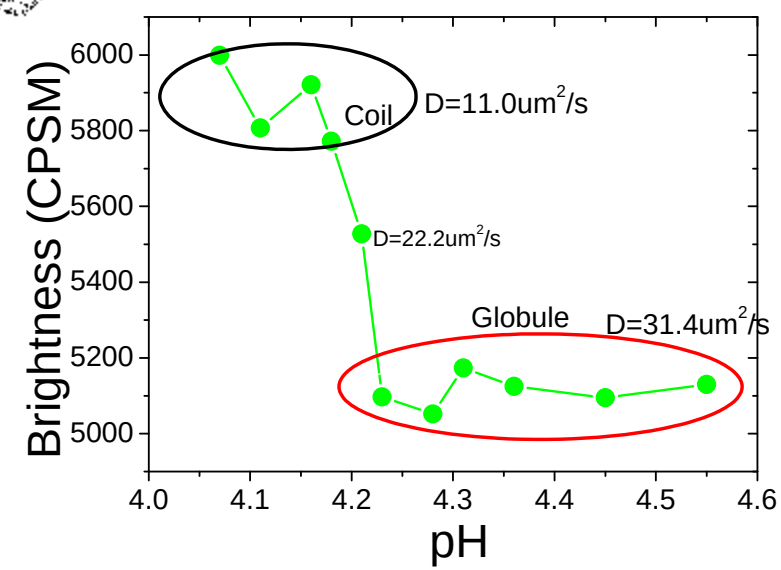
Local pH ?

Bulk pH







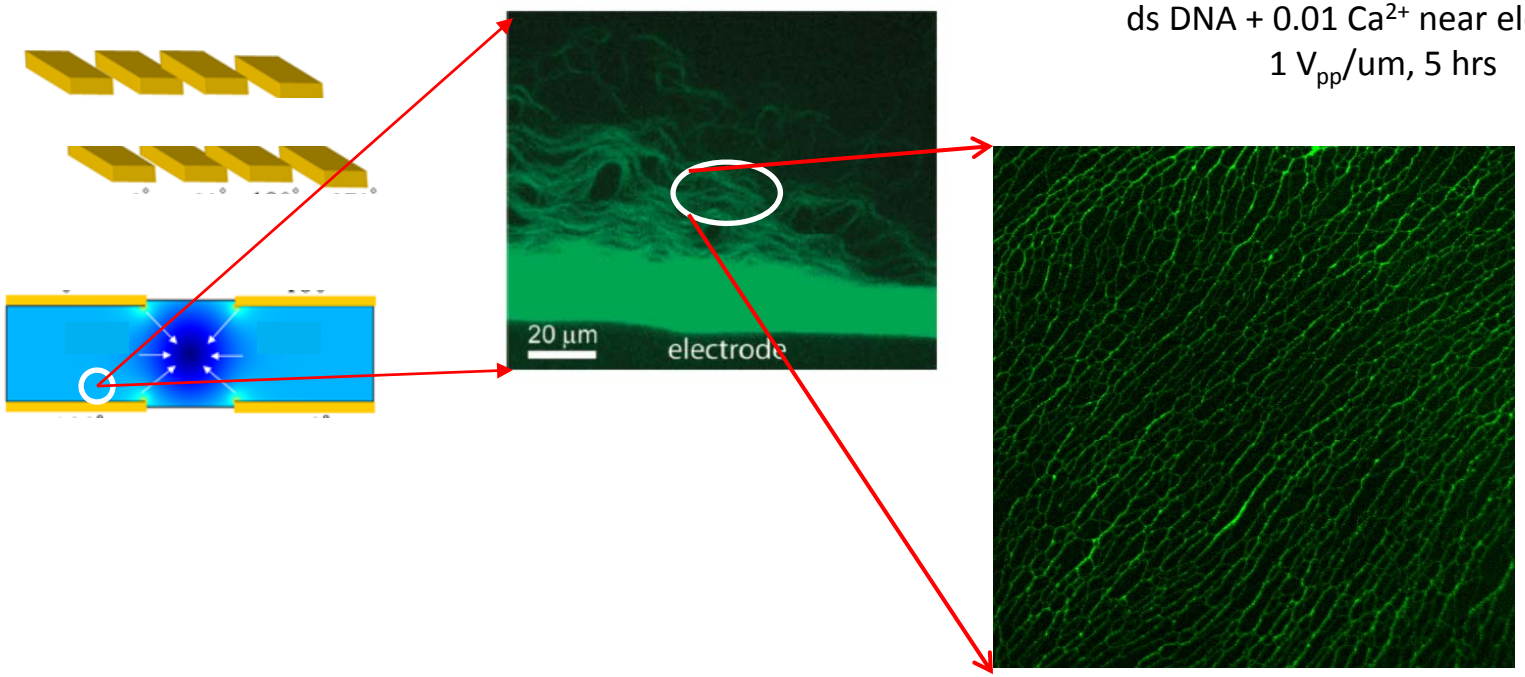


Based on photon count histogram of P2VP-Oregon Green

Polyelectrolyte Assembly by AC-Electric Fields

Preliminary work:

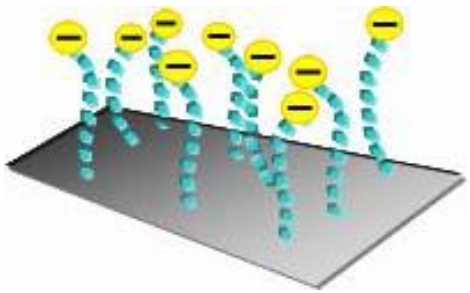
Actin filament and DNA bundle formation under AC fields



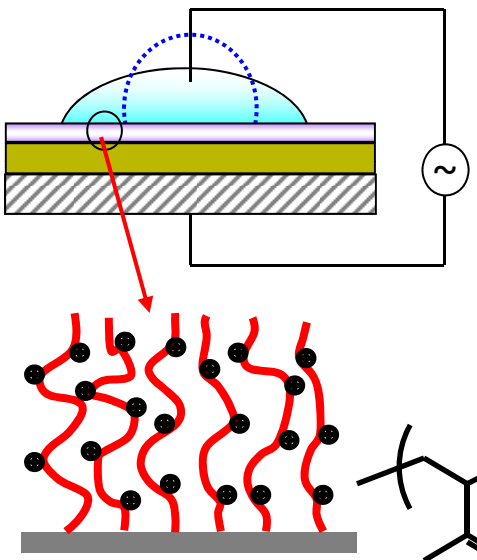
ds DNA + 0.01 Ca^{2+} near electrode
1 V_{pp}/um, 5 hrs

Application of AC-electrokinetics on biomacromolecular manipulation and assembly:

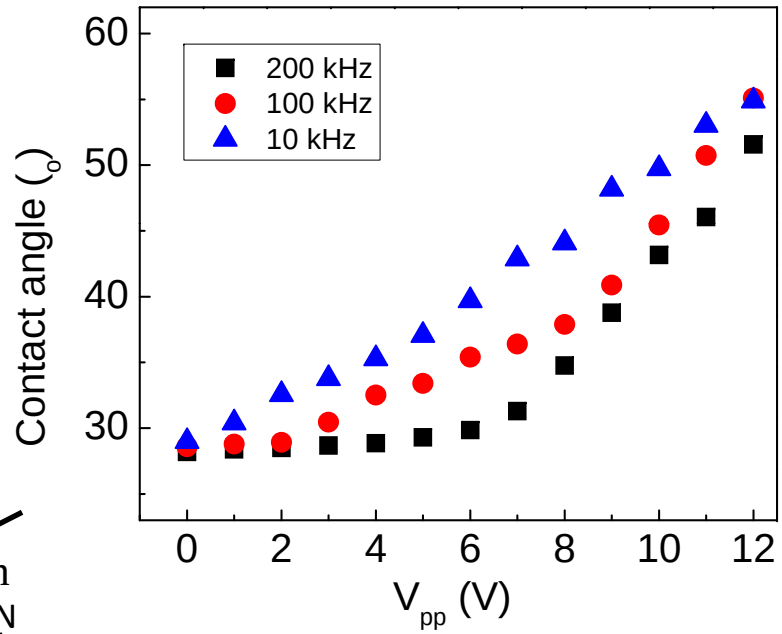
- A variety of synthetic and biological polyelectrolytes, i.e. DNA, actin and peptide
- Effectively modify local ionic environment and electrostatic interactions
- Wide AC-field parameter ranges

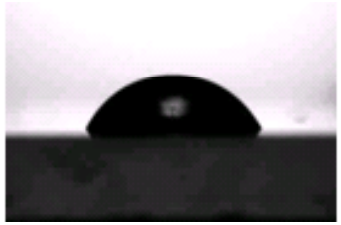


AC-Electric Responsive Polymer BrushSurfaces



Poly (2-vinyl pyridine) (PVP) brushes





After

Frequency: 100 kHz

Before

Drop size ~ 2mm; pH=4.05

Critical Voltage

Opposite to AC-electrowetting

⇨ AC-induced conformational change ?

AC-Field Induced Conformation Transition of Polyelectrolytes

- AC-electric field can effectively induce conformation transition of weak polyelectrolyte, i.e. PVP at constant pH.
- Strong AC-frequency dependence of PVP coil-to-globule transition: A gradual process by AC-fields vs. 1st-order transition in solution by pH.
- Curious hysteresis upon AC-frequency sweep, but no voltage sweep
- A possible mechanism based on stochastic resonance frequency
- Ongoing/future work:
  - Molecular weight dependence
  - Local counterion profile/pH detection under AC-fields
  - Biological polyelectrolytes: ssDNA, peptide
  - AC-Responsive Polymer Brush Surfaces

Acknowledgement: DoE-BES