THE DEPARTMENT of
MATERIALS SCIENCE
AND ENGINEERING

MSE TEAM NUMBER 3
Method for Electrostatic Dispersion of Nanoparticles in Polymer Coating
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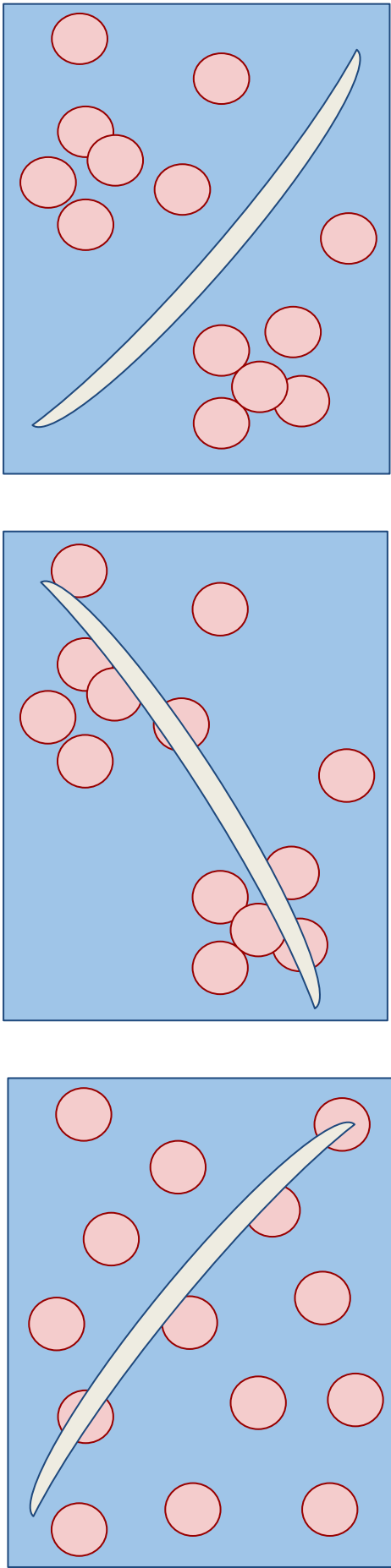
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Problem Definition

Nanoparticle agglomeration in polymer matrices leads to inconsistent material performance and reduced functionality. In destructive testing, induced defects may hit an inconsistent concentration of functional particles. Without controlled dispersion, determining critical properties such as coating recovery, recovered toughness, and cycle lifetime becomes difficult and unreliable. Such challenges limit the progress of functional nanoparticle research.

Objective: Design a procedure, using a combined approach, which leverages DLVO interactions and Electrostatic Repulsion to improve uniformity of nanoparticle dispersion in polymer matrix.
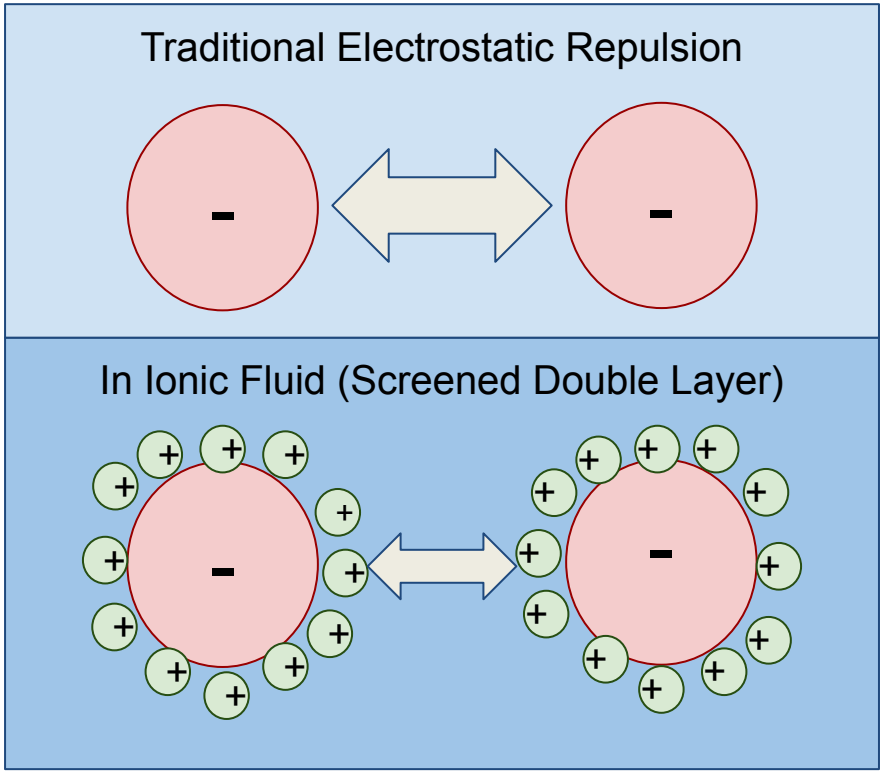
Design Calculations & Analysis

Required Surface Charge:
- **Gouy-Chapman theory:**

$$\sigma = \varepsilon_0 \varepsilon_r \kappa \zeta \qquad \lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2 N_A e^2 I}} \qquad \kappa = 1/\lambda_D$$

  - For small potentials and low ionic strength, we can use the Debye-Hückel approximation
  - The inverse Debye length(κ) incorporates ionic strength, temperature, and electron charge
  - Approximating the particles as a perfect sphere, the surface charge density(σ) and subsequent surface charge(Q) can be determined to give a charge that would provide repulsion of particles

Achievable Charge via Electron Bombardment:
- **Molecules per surface for PSS**
  - Determined by dividing the surface area of the particle by the cross sectional area of the molecule
- **Assumptions made for electron addition**
  - 15 elementary charge sites on each molecule, including the 3 exposed Oxygens which act as available and strong attractors for incoming electrons
  - Surface Molecules only, not using an electron source with great enough energy to enter bulk due to risk of damage
  - Using the electrospray method, maybe 1/1000 electrons actually meet an exposed, available oxygen

Constants	Value	Units	Debye Length(m)
Zeta potential	-0.03	V	1.71E-06
Vacuum Permittivity	8.85E-12	F/m	
Boltzmann Consta	1.38E-23	J/K	Charge Density(C/m^2)
Temperature	298	K	-1.22E-05
Avogadro's numl	6.02E+23	C/mol	
Electron charge	-1.60E-19	C	Surface Charge(C)
Particle diamete	3.00E-07	m	-3.45E-18
Intrinsic values value		**Units**	
Permitivity	78.5	of Water	
Ionic Potential	3.16E-05	mol/m^3	

**Derjaguin–Landau–Verwey–Overbeek (DLVO)**
Theory: Explains the aggregation and kinetic stability of aqueous dispersions and describes the force between charged surfaces interactions in a liquid medium

$$U_{\text{total}}(h) = U_{\text{elec}}(h) + U_{\text{vdW}}(h)$$

$$U_{\text{elec}}(h) = 64\pi\varepsilon_0\varepsilon_r \left(\frac{k_B T}{e}\right)^2 \tanh^2\left(\frac{e\zeta}{4k_B T}\right) \cdot r \cdot e^{-\kappa h}$$

Thermal voltage reflects how thermal motion influences ion distribution, depends on the square of the potential.

Reduced surface potential approximates how ion concentrations decay within the electric double layer

Exponential decay of potential as particles separate

Traditional Electrostatic Repulsion

In Ionic Fluid (Screened Double Layer)
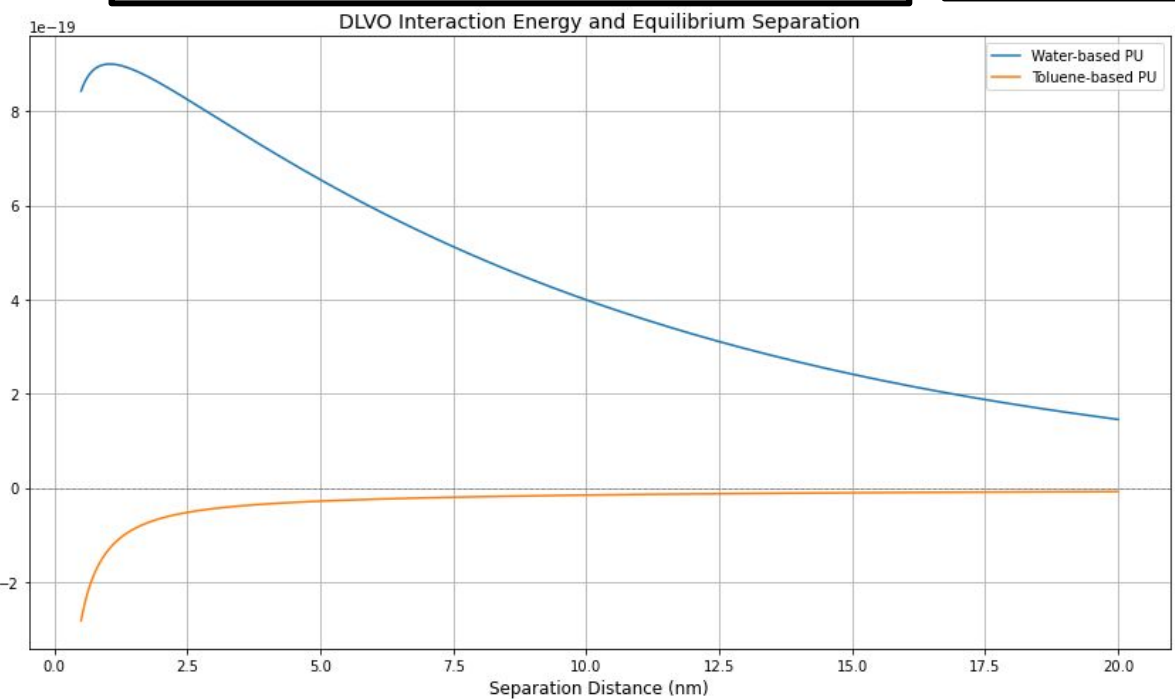
From the DLVO graph and calculations we know that there is a stability range for this colloidal system when the particles are only spaced between .5 and 1.5 nm apart. This proves that particles will flocculate insead of evenly disperse, before intervention is applied

Final Design

Goal of this design:
- To increase the repulsive force interactions between nanoparticles in a polymer matrix solution. This will cause the nanoparticles to become more uniformly dispersed within the matrix upon deposition, and decrease clumping once the coating is cured.

Approach:
- Using the DLVO theory, the electric double layer strength that is created by the electrons on the surface was able to be calculated to show how repulsive the particles can be. We found that the charge that would achieve this repulsion was -3.45E-18 C.
- The Zeta potential combines the ionic strength of the matrix to determine what pH levels will also help in causing repulsion between the nanoparticles we can manipulate the [H⁺] potential and move the zeta potential into a more dispersive region (pH below 4 or above 7.5).
- Using an electron bombardment method, the electric double layer will be increased by adding up to 15 electrons to the shell of each particle.
- Additionally, utilizing pH of the solution,

Additional Considerations used in the design:
- The type of nanoparticle was considered as each will have different size, charge capacity, and chemistry for electron interaction.
- The concentration of the particles in the matrix would cause greater interactions as there are more forces acting on each individual particle.
- The viscosity of the matrix was also considered as this would affect the speed at which the particles disperse and use of a UV curable matrix could allow for particle freezing at a desired dispersion.

Procedure:
- **Substrate Preparation**
  - Cut steel sheet down to 1cm x 1cm samples using an angle grinder, Sand any sharp edges for safety
  - Immerse in a 10% solution of sodium metal silicate for 10 minutes
  - Sonicate to increase wettability of the substrate
- **Electron Bombardment**
  - Accelerating Voltage: 50V
  - Total Absorbed Dose: -2.33 × 10^-4 C per gram
  - Total Applied Dose: (Absorbed Dose)(1/Efficiency)
- **Addition to Matrix Solution**
  - The particles will be added to the polymer matrix solution via mechanical mixing of the polymer to create a colloidal system
- **Coating Deposition**
  - Complete dip coating method by dipping the prepared substrate into the solution at a controlled rate.
  - UV Cure coating as quickly as possible following dipping to "lock in" nanoparticle positions and maintain dispersion.
- **Characterization**
  - Dynamic light scattering (DLS)
    - Measures the hydrodynamic diameter of particles in suspension.
    - Confirms reduction in aggregation by comparing size distributions before and after dispersion treatment.
    - Used to estimate z-average and polydispersity index (PDI)
  - Scanning Electron Microscopy (SEM):
    - Provides high-resolution images of nanoparticle distribution.
    - Used to detect particle clustering or sedimentation in the film.

Prototype & Test Results

DLVO Dispersion Over Time from Initial Agglomeration
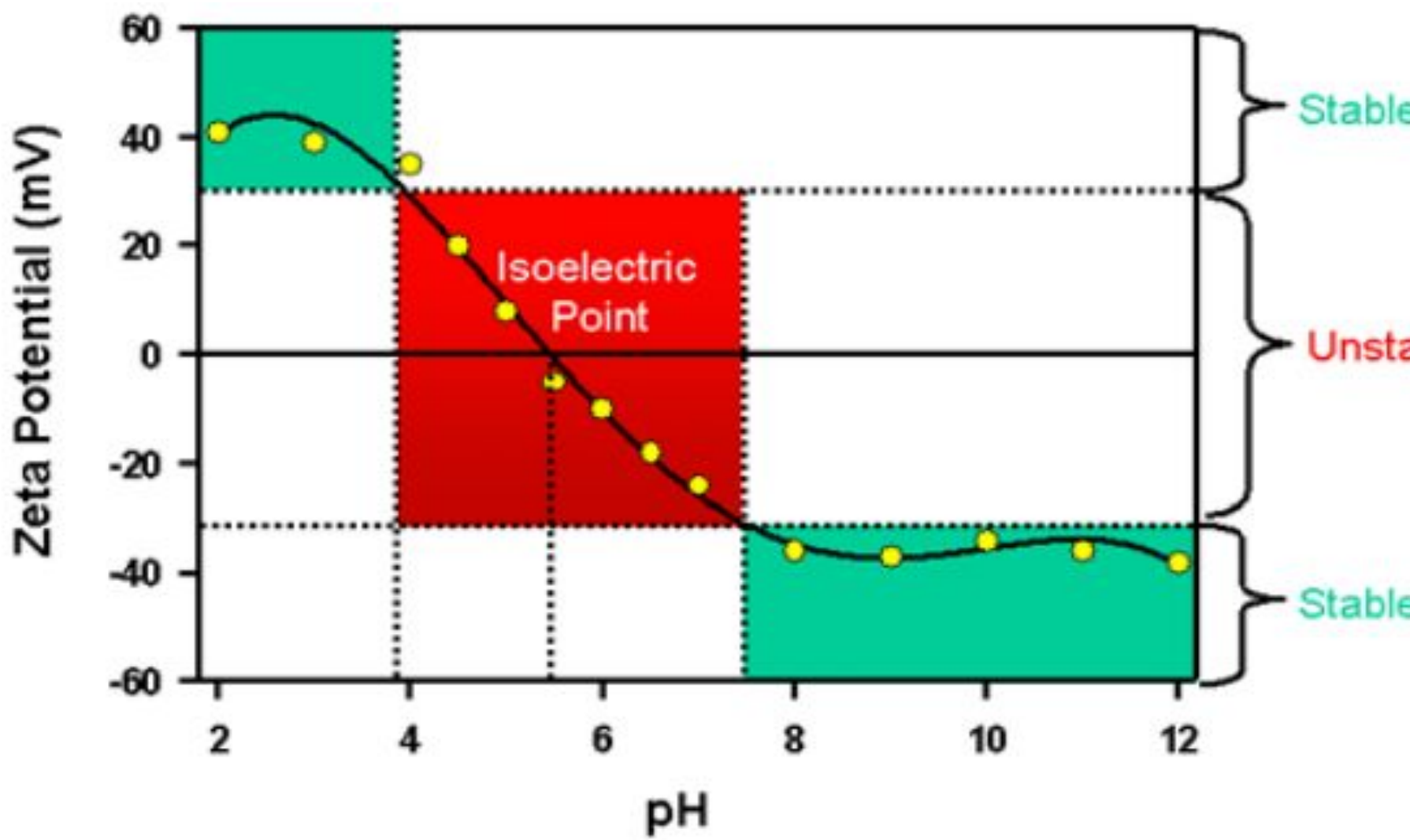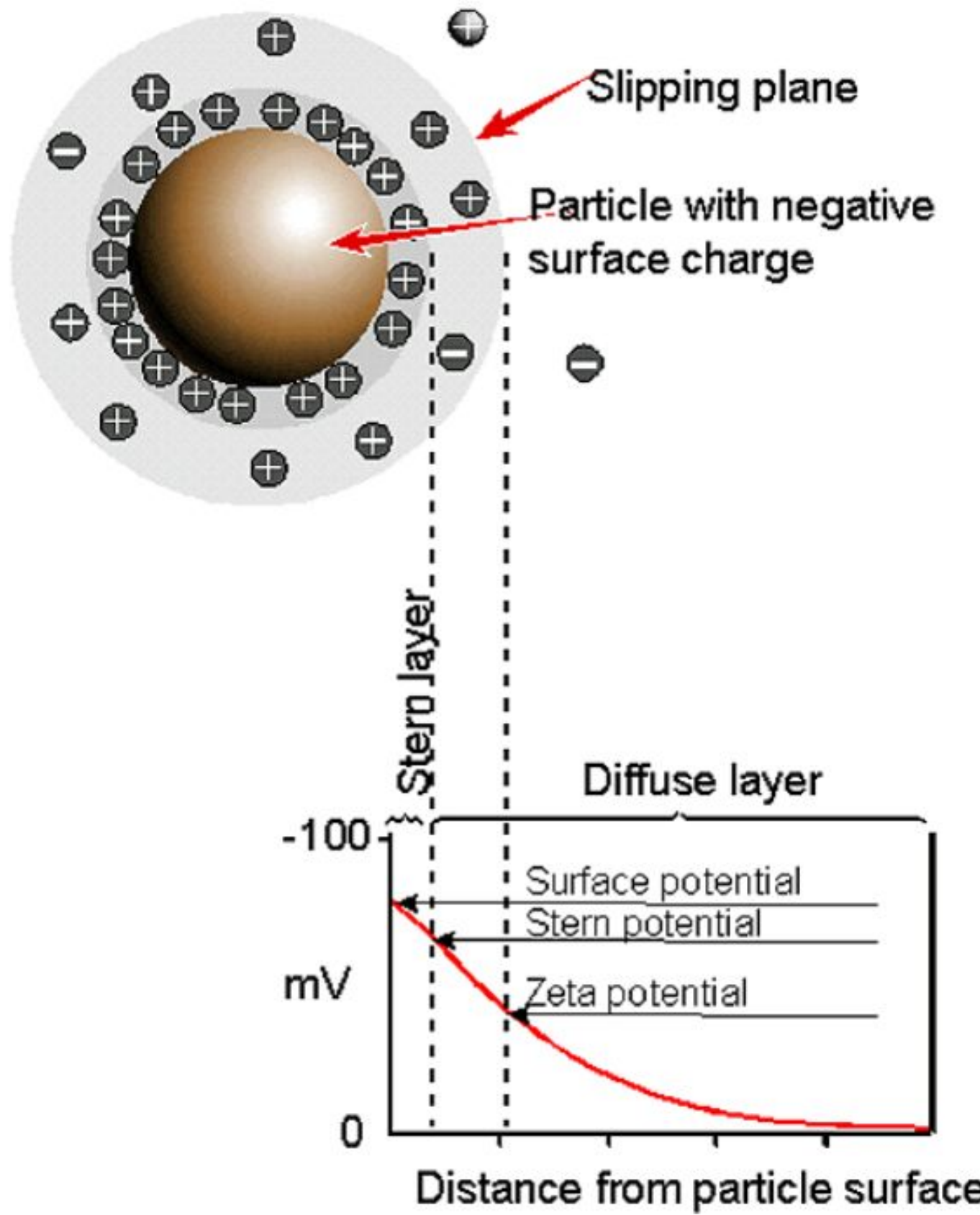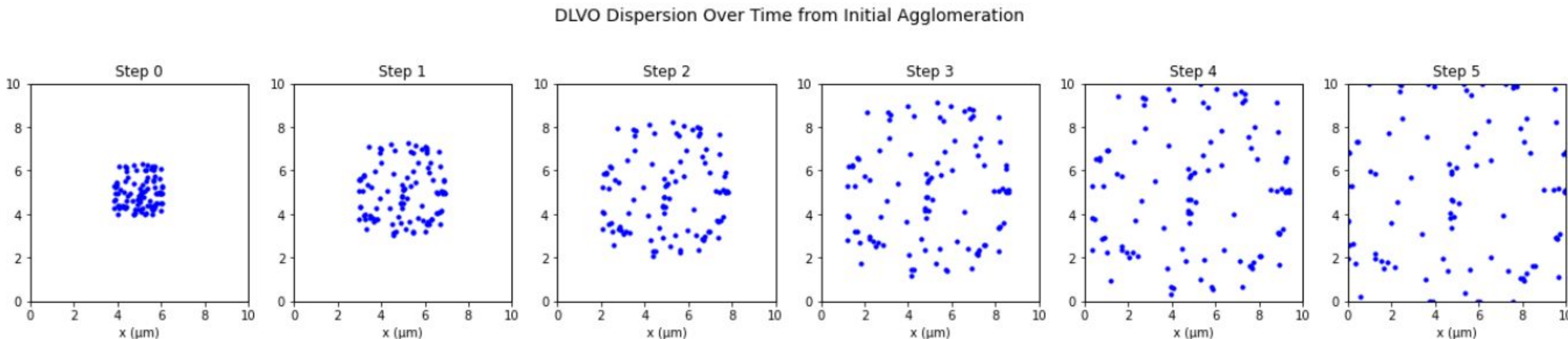
The above simulation shows the dispersion of 100 particles based on the DLVO repulsion forces in a 10µm x 10µm sample when initially starting as an agglomeration of particles. As time increases, the particles will become more evenly spaced throughout the sample. This simulation accounts for particle charge, ionic potential, particle size, temperature, and time. This simulation suggests that the particles will even disperse when a surface charge is induced by the electron bombardment and in a pH of 7.5(slightly basic water).

Conclusion: We successfully developed and outlined a procedure for preparing and dispersing nanoparticles in a water based, UV curable polymer solution through the utilization of pH manipulation and electron bombardment of nanoparticles to increase the strength of the electrostatic double layer repulsion.

Future Work: This work provides a strong basis for future practical applications of this method of particle dispersion. We hope that the progress we have made will enhance the reliability of research surrounding functional particles in polymer coatings, in self-healing superhydrophobics, drug delivery, and numerous other fields.