

Macroscopic charge segregation in driven polyelectrolyte solutions (Supporting Information)

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This document contains supporting figures and additional discussions to help develop a clearer understanding of the charge segregation phenomenon in driven polyelectrolyte solutions.

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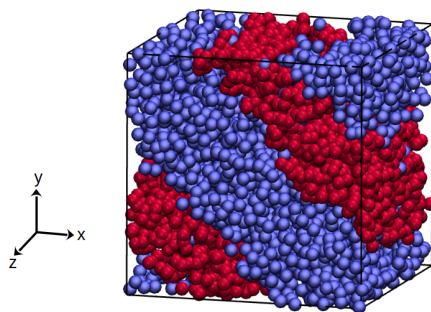


Figure S1. Simulation snapshot of the polyelectrolyte solution for $E = 0.9$ and $\rho = 0.1$. Here the red beads represent the monomers and the blue beads represent the counterions (monovalent). Electric field is along the $+\hat{z}$ direction. In some cases, charge segregation is found to be tilted with respect to both \hat{x} and \hat{y} directions. Since the density is low here, tilted configurations with multiple interfaces do not lead to a significant energy cost, thereby making such a configuration much more stable. It is possible that such a configuration is a long-lived metastable state, since inter-particle interactions are weak for low density. Nevertheless, the emergence of such long-lived tilted charge segregation is still quite remarkable. Such a charge configuration will be energetically costlier for higher ρ (stronger interactions), and therefore, unlikely to be observed at late times. Also note that all these charge configurations form spontaneously, and consequently, it is entirely possible that, for all parameters kept the same, different initial conditions will lead to different charge configurations in the NESS, but with the same average value of the order parameter Ψ .

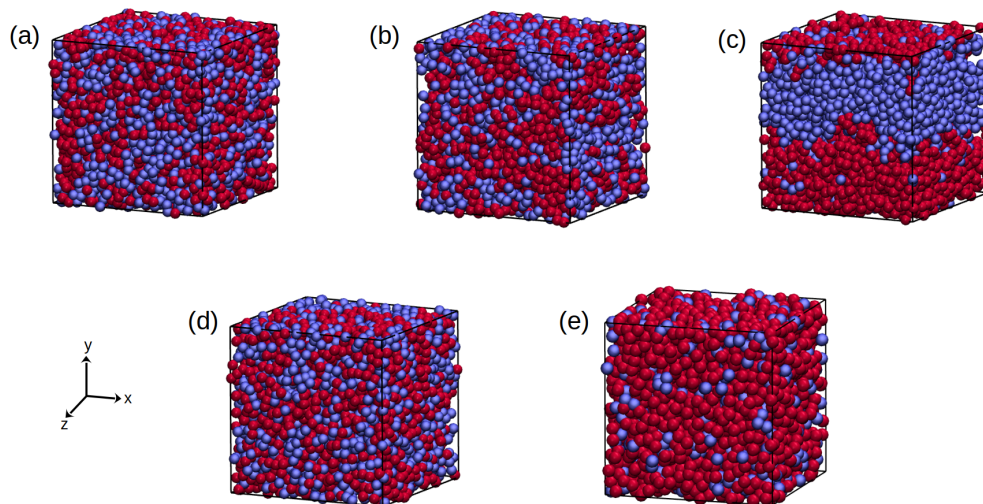


Figure S2. Simulation snapshots for different values of M_p for $E = 1.0$: (a) $M_p = 2$ (b) $M_p = 3$ (c) $M_p = 4$, (d) 1:1 electrolyte ($M_p = 1$), and (e) 1:4 electrolyte ($M_p = 1$). Electric field is along the $+\hat{z}$ direction. Only (c) shows a clear charge segregation. None of the rest show any discernible structure in their charge distribution, implying a homogeneously mixed phase, $\Psi \approx 0$ (no segregation); see Fig. 1h in main text.

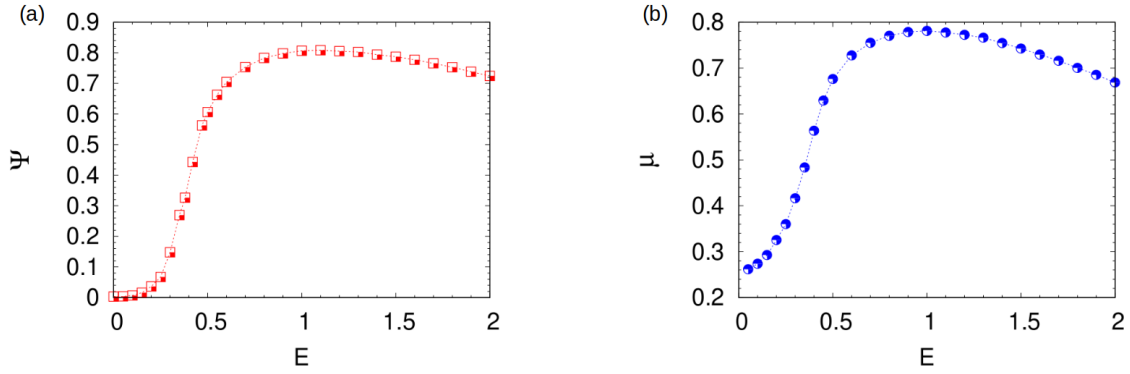


Figure S3. Variation of (a) order parameter Ψ , and (b) mobility $\mu = \mu_p = \mu_c$ with the external drive in the range $0 \leq E \leq 2$. For $E \gtrsim 1.0$, we find that Ψ and μ decrease with increasing external drive. Here $N = 6000$ and $\rho = 0.25$.

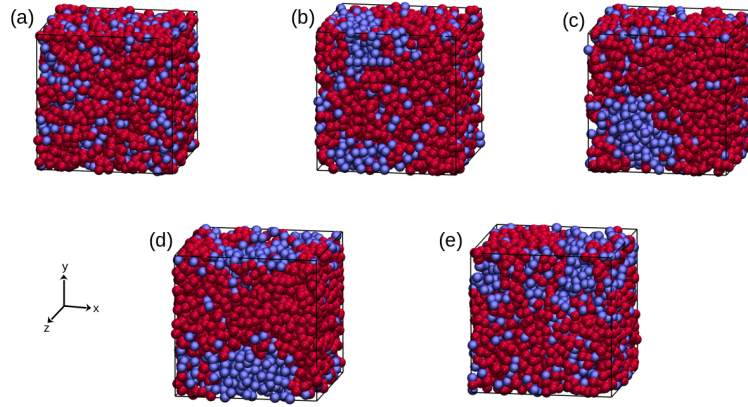


Figure S4. Simulation snapshots of the polyelectrolyte solution with trivalent counterions for different values of the external electric field: (a) $E = 0.1$, (b) $E = 0.2$, (c) $E = 0.5$, (d) $E = 0.8$, and (e) $E = 1.2$. Here the red beads represent the monomers and the blue beads represent the trivalent counterions. Note that here the number of counterions $N_c = \frac{1}{3}N_p \times M_p$. Electric field is along the $+\hat{z}$ direction. Charge segregation is weaker here compared to a polyelectrolyte solution with monovalent counterions.

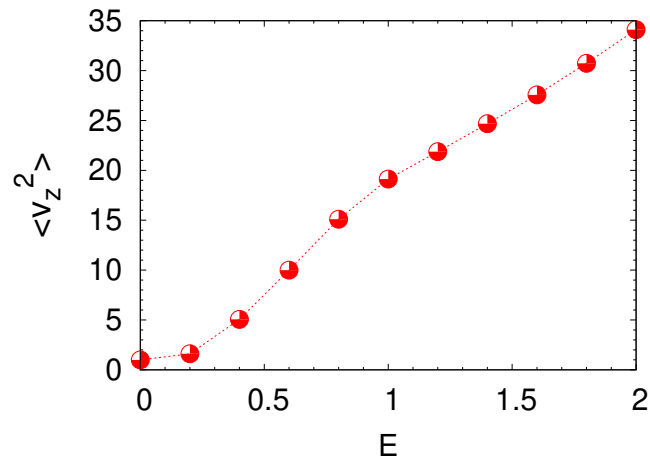


Figure S5. Variation of $\langle v_z^2 \rangle$ for the polyelectrolyte chains with the applied electric field E , for the case with trivalent counterions. In equilibrium ($E = 0$), we have $\langle v_z^2 \rangle = T$ following *energy equipartition theorem*, where $T = 1$ is the temperature of the solution set by the Langevin thermostat. Notice that it is not apparent from this data that a regime with NDM exists for $0.8 \lesssim E \lesssim 1.5$ in this case.

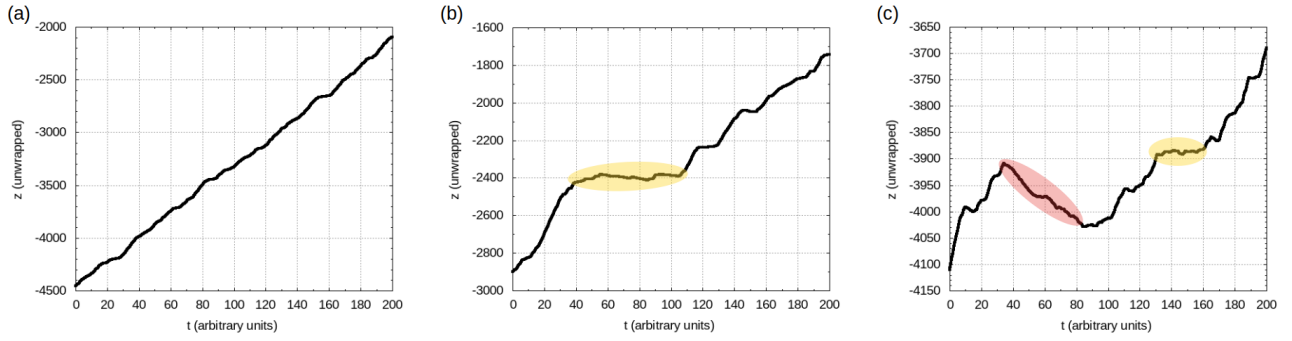


Figure S6. The z -coordinate (unwrapped) of a trivalent counterion in the polyelectrolyte solution is shown, for the electric field value $E = 1.0$ which falls inside the NDM regime (see Fig. S7 below). We choose any time instant in the NESS and label it as $t = 0$ (the origin of time is irrelevant in the NESS). Each unit spacing along the time axis (x -axis) corresponds to 1000 iterations of the Langevin dynamics simulation (with time-step $\Delta t = 0.001$). The z -position is measured in units of σ . In (a), (b), and (c), we trace the trajectories of three counterions for the same time window, $0 \leq t \leq 200$. In (a) is shown the typical trajectory of a counterion that is moving fairly unhindered in response to the applied electric field (z -coordinate increases roughly monotonically). In (b), we find that the counterion is majorly stalled for a considerable length of time, $40 \lesssim t \lesssim 100$ (no change in its z -position: yellow shaded region). This indicates the trapping by the opposite species, since there are no other mechanisms that can cause stalling, in the presence of a constant E -field drive. In (c) the counterion starts to move in the *wrong* direction (toward $-\hat{z}$ direction: red shaded region) even with the external drive switched on, for an appreciable time span, $30 \lesssim t \lesssim 80$, and for a distance $\approx 125\sigma$. This shows the effect of the *trap-and-drag* mechanism produced by the oppositely moving charges. All these features will also be present for any monomer in the solution.

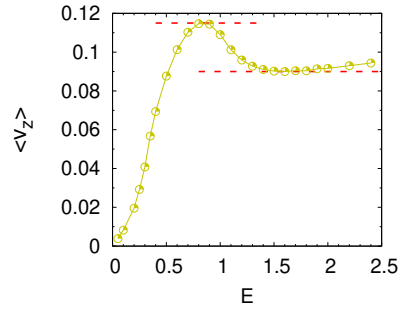


Figure S7. Variation of the $\langle v_z \rangle$ for the polyelectrolyte solution with trivalent counterions beyond $E = 2.0$ (Fig. 4c of main text). Here, $\langle v_z \rangle = -\frac{1}{q} \langle v_{zp} \rangle = \frac{1}{3q} \langle v_{zc} \rangle$ (see main text). As the external drive is increased from zero, the polyelectrolyte solution exhibits transitions from PDM \rightarrow NDM \rightarrow PDM. There is also a fairly extended regime of ZDM (zero differential mobility), for $1.5 \lesssim E \lesssim 2.0$, between the NDM and the PDM regime. The dashed lines are a guide to the eye. Note that the existence of the re-entrance regime at $E = 0.5$ (Figs. 4a and 4b in main text) is not apparent from this data.

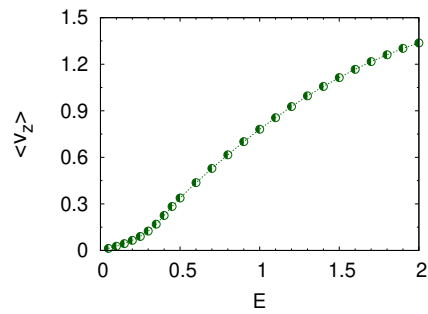


Figure S8. Variation of the $\langle v_z \rangle$ for the polyelectrolyte solution with monovalent counterions. Here, $\langle v_z \rangle = -\frac{1}{q} \langle v_{zp} \rangle = \frac{1}{q} \langle v_{zc} \rangle$ (see main text). For this case, no NDM regime is observed in the range $0 \leq E \leq 2$, unlike trivalent monomers. However, it is possible that NDM emerges for monovalent counterions at very large external drives.

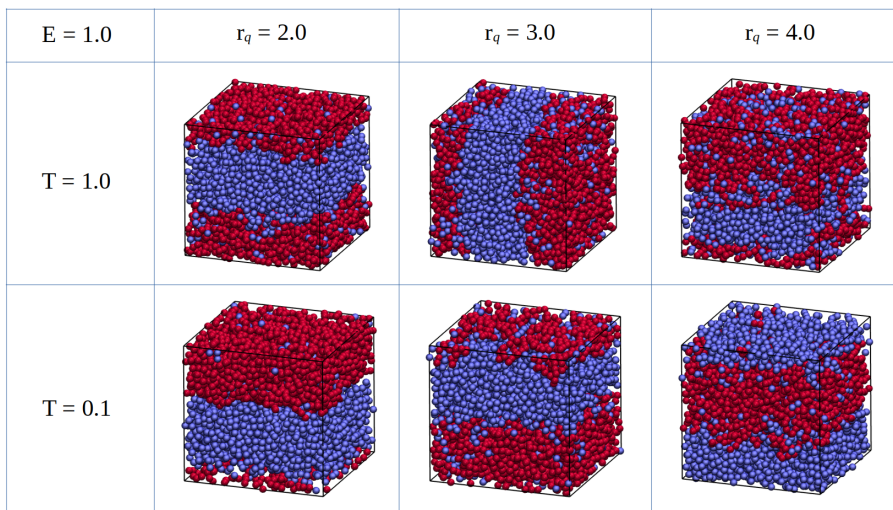


Figure S9. Simulation snapshots of charge segregation in the driven polyelectrolyte solution (with monovalent counterions) for different values of the electrostatic cutoff $r_q = 2.0, 3.0,$ and 4.0 . Here the reduced temperatures are $T = 1.0$ and 0.1 , and external electric field $E = 1$. All other parameters are the same as in Fig. 1 of the main text. Distinct monomer-rich and counterion-rich regions can be seen for all the cases, implying charge segregation (with varying degrees). For a fixed external drive E and all other parameters kept the same, the degree of charge segregation becomes lower for large r_q and higher for lower T , as explained in the main text.

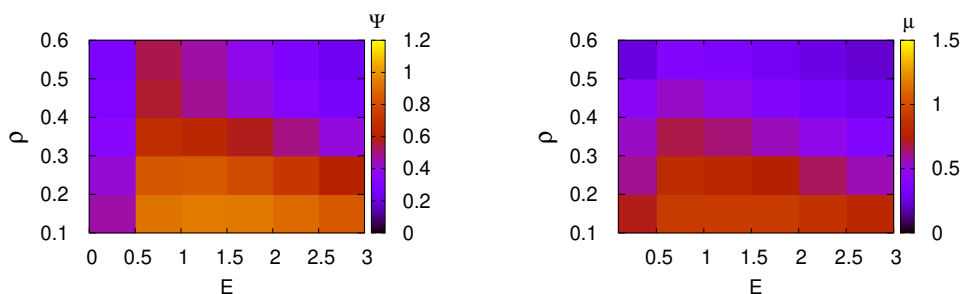


Figure S10. Phase diagrams for the polyelectrolyte solution with monovalent counterions, for temperature slightly different than the phase diagrams in the main text (we have chosen $T = 0.5$ here for computational convenience). All the other parameters remain the same. For the monovalent case one needs to go to higher external drives to get a complete picture of its phase behavior. Nonetheless, all phase diagrams have qualitatively similar features (see Fig. 7 in main text).

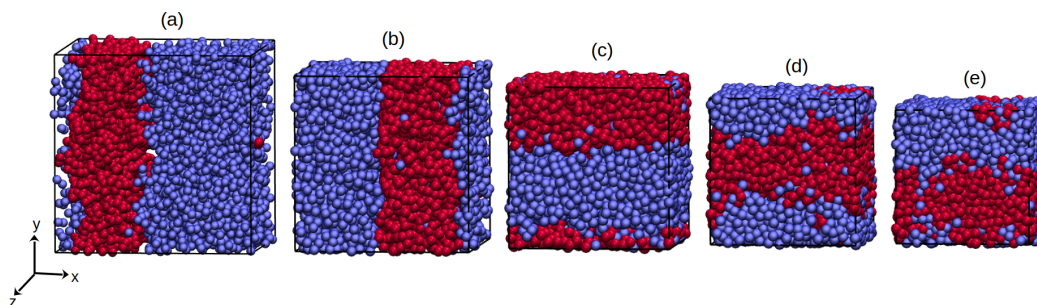


Figure S11. Simulation snapshot for a few different densities: (a) $\rho = 0.1$, (b) $\rho = 0.2$, (c) $\rho = 0.3$, (d) $\rho = 0.4$, and (e) $\rho = 0.5$ showing the charge segregation. The monomers are represented by red beads and the (monovalent) counterions are represented by blue beads. Here, $E = 1.0$ and $N = 6000$. Electric field is along the $+\hat{z}$ direction.

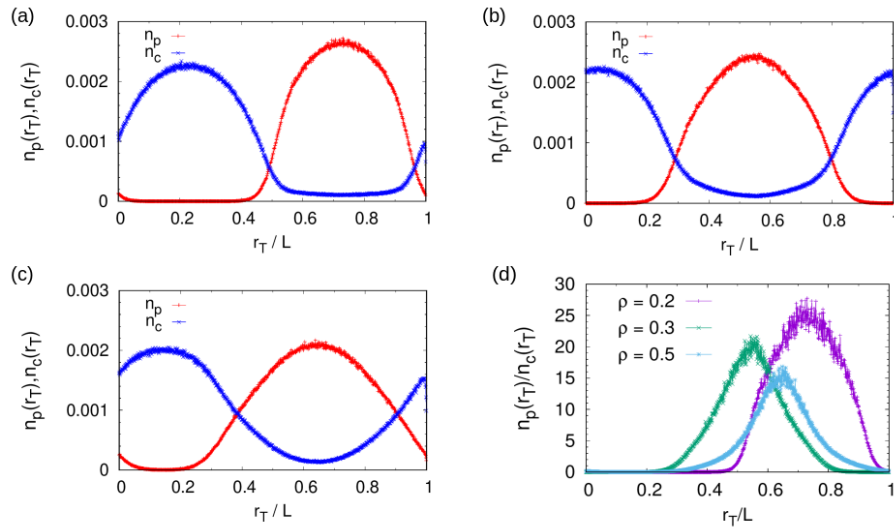


Figure S12. Number density profiles for the polyelectrolyte monomers n_p and monovalent counterions n_c , along the directions transverse to the E -field, denoted by $r_T \equiv \hat{x}, \hat{y}$, for (a) $\rho = 0.2$, (b) $\rho = 0.3$, and (c) $\rho = 0.5$. Distinct monomer-rich and counterion-rich regions can be seen clearly in all the cases (see Fig. S11 above). In (d) we show the ratio n_p/n_c , a low value of which is an indicator of the higher presence of counterions in the monomer-rich region. The ratio is more spatially diffused and has a lower peak value for higher ρ . This makes charge segregation less pronounced for higher ρ , as seen in the $\rho - E$ phase diagrams. Here the electric field is $E = 1.0$ and $N = 6000$ for all the cases.

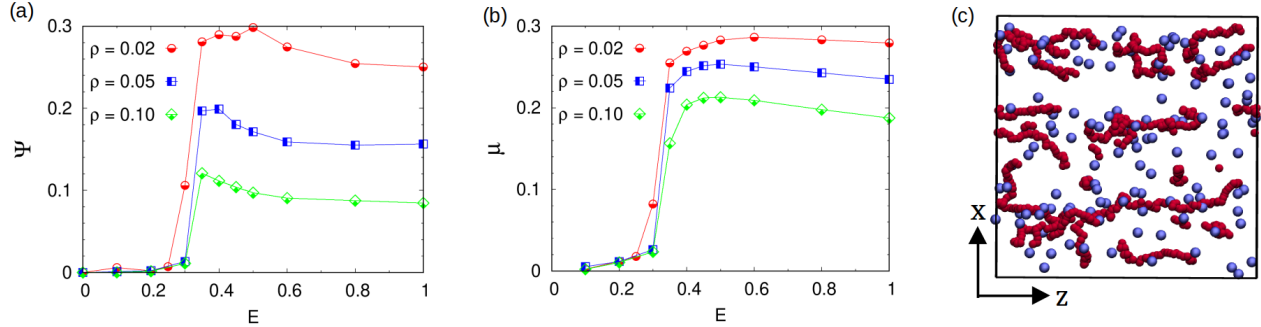


Figure S13. (a) The order parameter $\Psi(E)$ is shown for a polyelectrolyte solution with trivalent counterions in the presence of *long-range Coulomb interaction*, $V_q(r) = k_B T \ell_B / r$. The long-range Coulomb interactions have been computed with the *particle-particle particle-mesh* (PPPM) method with an accuracy of 10^{-4} . The simulation parameters used here are $N = 1000$, $M_p = 30$, $N_p = 25$, and $T = 0.5$. The equilibrium phase ($E = 0$) in this case is a clustered phase that is broken apart when the electric field drive is switched on. The order parameter has been calculated in the same way as for screened interactions. The variation of $\Psi(E)$ shows an interesting nonmonotonic behavior with the external drive, suggesting that some degree of charge segregation happens even with long-ranged Coulomb interaction when the polyelectrolyte solution is driven beyond a threshold electric field strength. As expected, charge segregation in this case is much poorer compared to screened Coulomb interactions. For the electric fields simulated, we have not found two macroscopic lanes of like charges, but multiple lanes seem to form, just as in binary colloidal mixtures with screened Coulomb interactions. The data also display a hint of a re-entrance behavior (nonmonotonic $\Psi(E)$ at higher E). (b) The corresponding mobility $\mu = \mu_p = \mu_c$ is shown as a function of the drive E for different densities. The variation of $\mu(E)$ is also nonmonotonic. A typical simulation snapshot, for $\rho = 0.02$ and $E = 0.5$, is depicted in (c), showing a slice of the x - z plane. To develop a proper understanding of the nonequilibrium properties of driven polyelectrolytes with long-range Coulomb interactions, and how they differ from polyelectrolytes with screened Coulomb interactions, extensive simulations and in-depth analyses need to be performed.