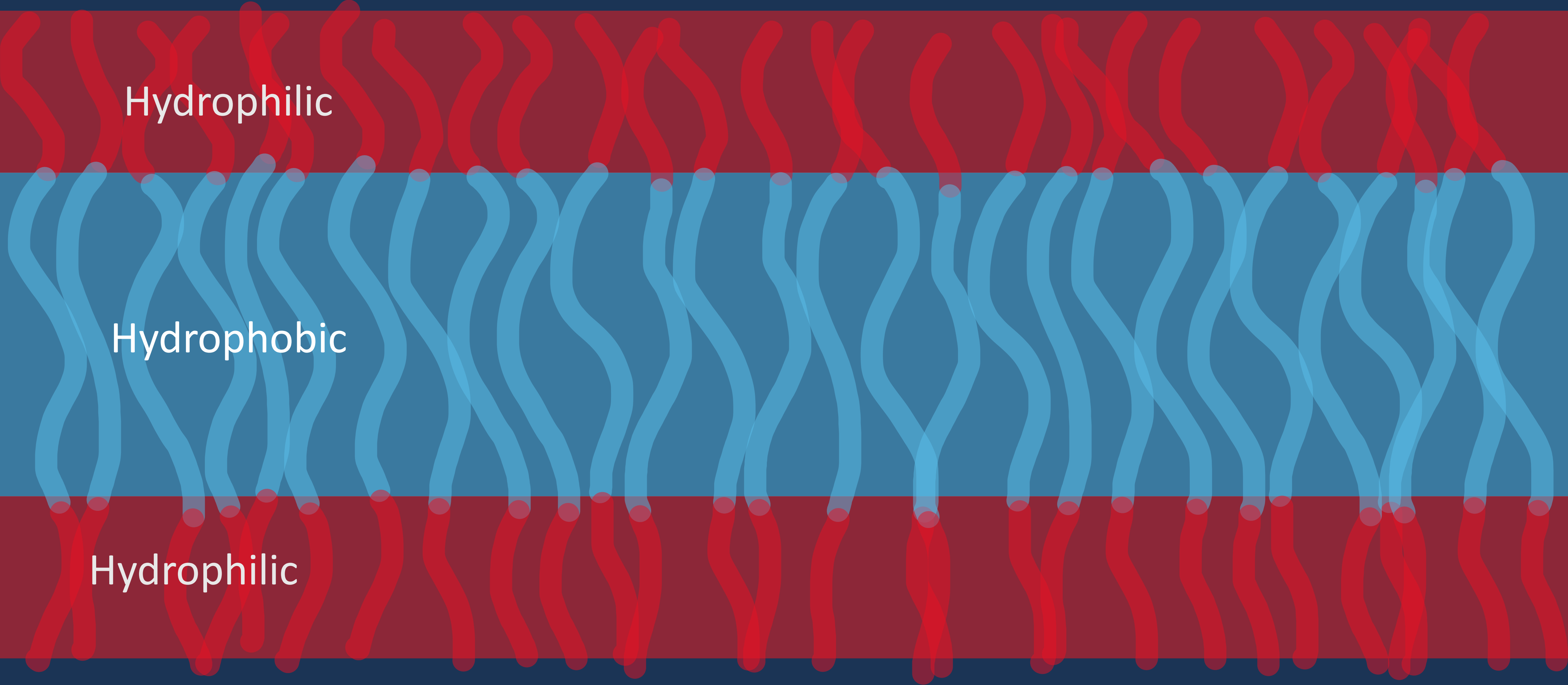
Simulation of the effects of charge on the kinetics of a triblock copolymer hopping across a membrane

Sylvia Luyben, Rob Wickham
University of Guelph

CAP Congress

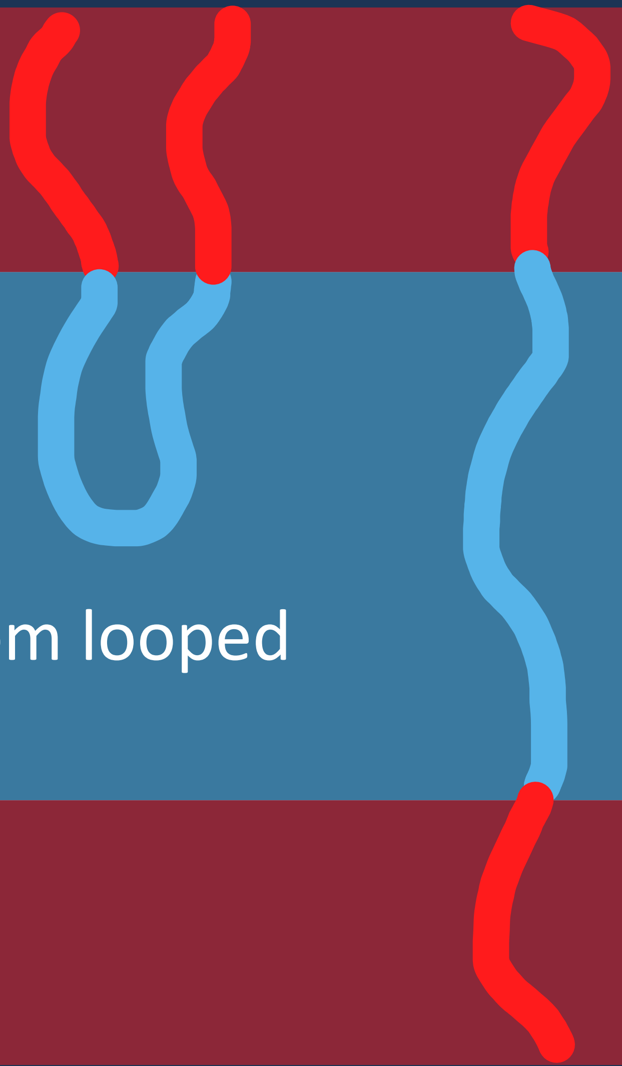
May 27, 2024

Protein Reconstitution → Polymer Hopping



Protein Reconstitution → Polymer Hopping

To enter a membrane, the polymer must insert and change conformations



The kinetics of hopping can help us understand protein reconstitution.

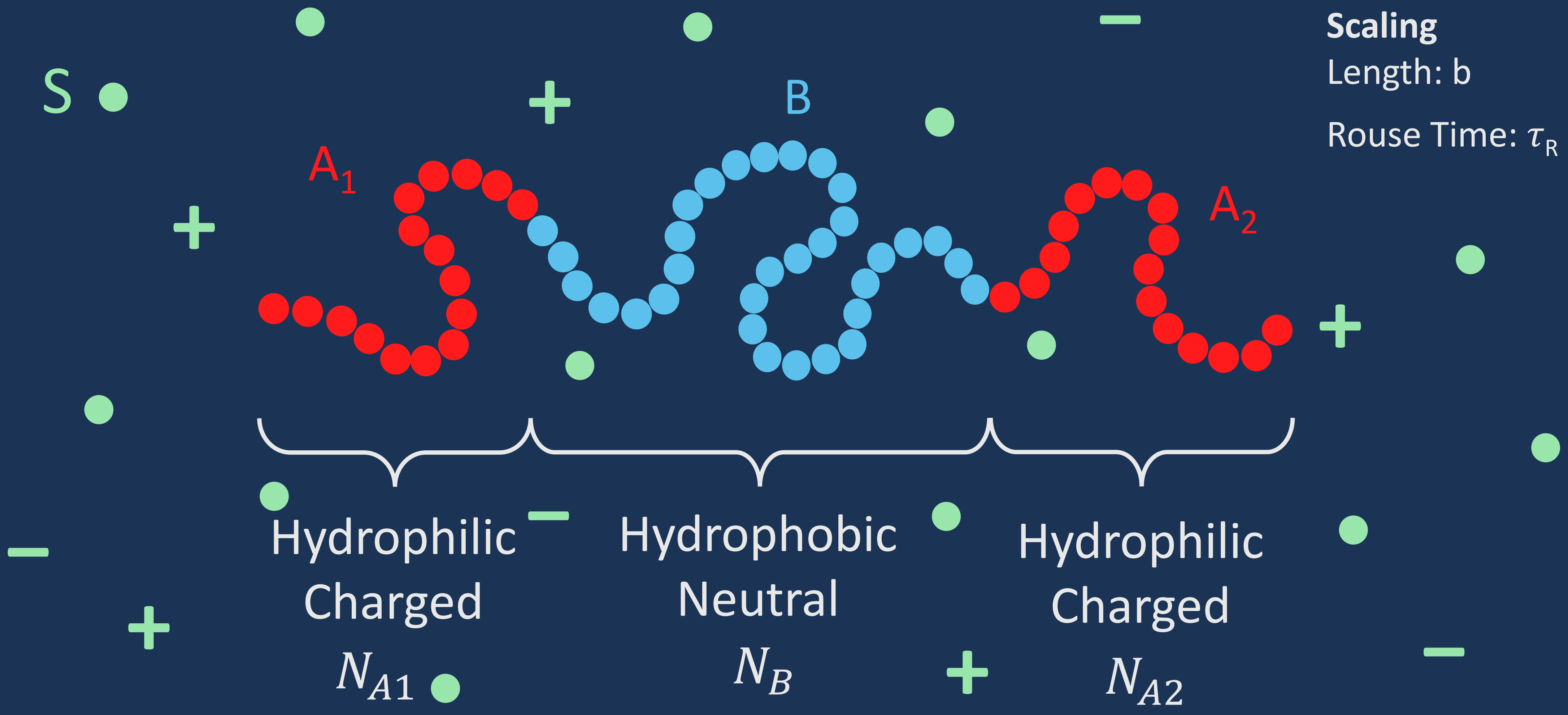
Conformation affects material strength[1].

Experimental evidence shows charge can affect both[2].

1. Hua, Kuang, and Liang. J. Am. Chem. Soc. 2011, 133, 2354–2357. dx.doi.org/10.1021/ja109796x
2. Matsen and Thompson. *J. Chem. Phys.* 111, 7139–7146 (1999) . https://doi.org/10.1063/1.480006

How does charge affect end block hopping?

The Model: Triblock Copolymer in Electrolyte Solution

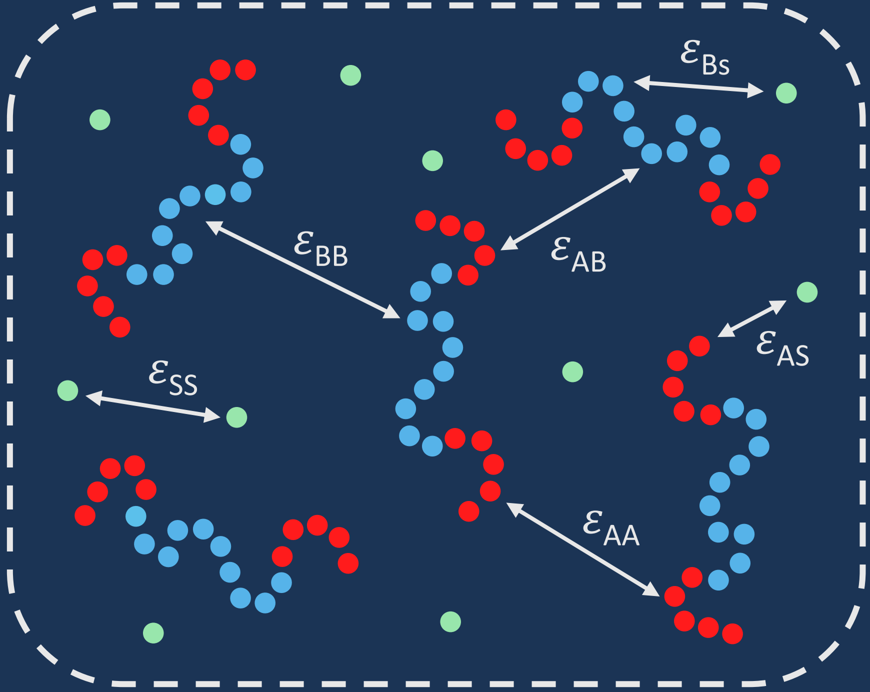


Scaling

Length: b

Rouse Time: $\tau_{\mathrm{R}} = \frac{\zeta b^2 N^2}{6\pi^2 k_B T}$

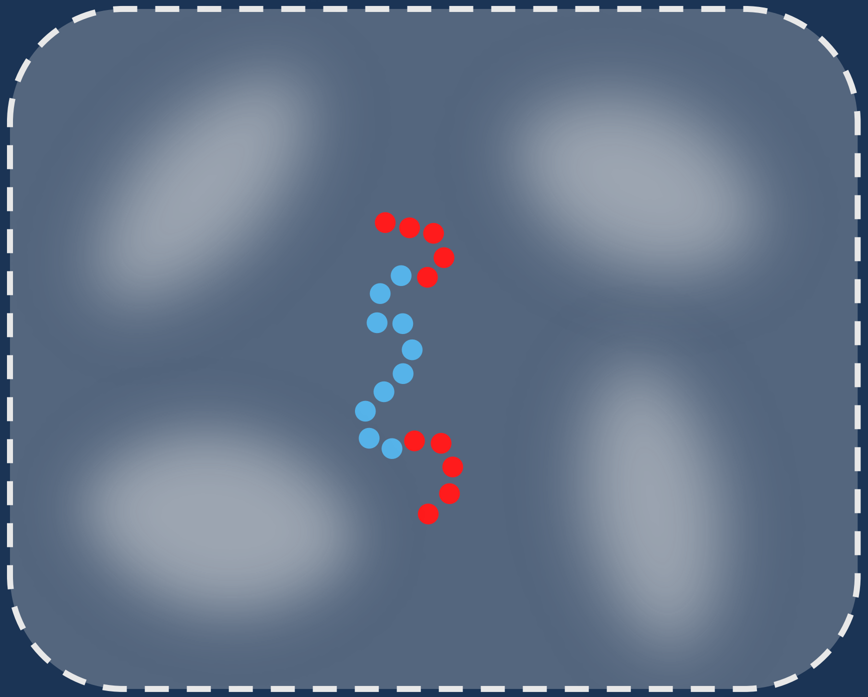
dynamical Self-Consistent Field Theory



Many interacting chains

Dynamical partition function

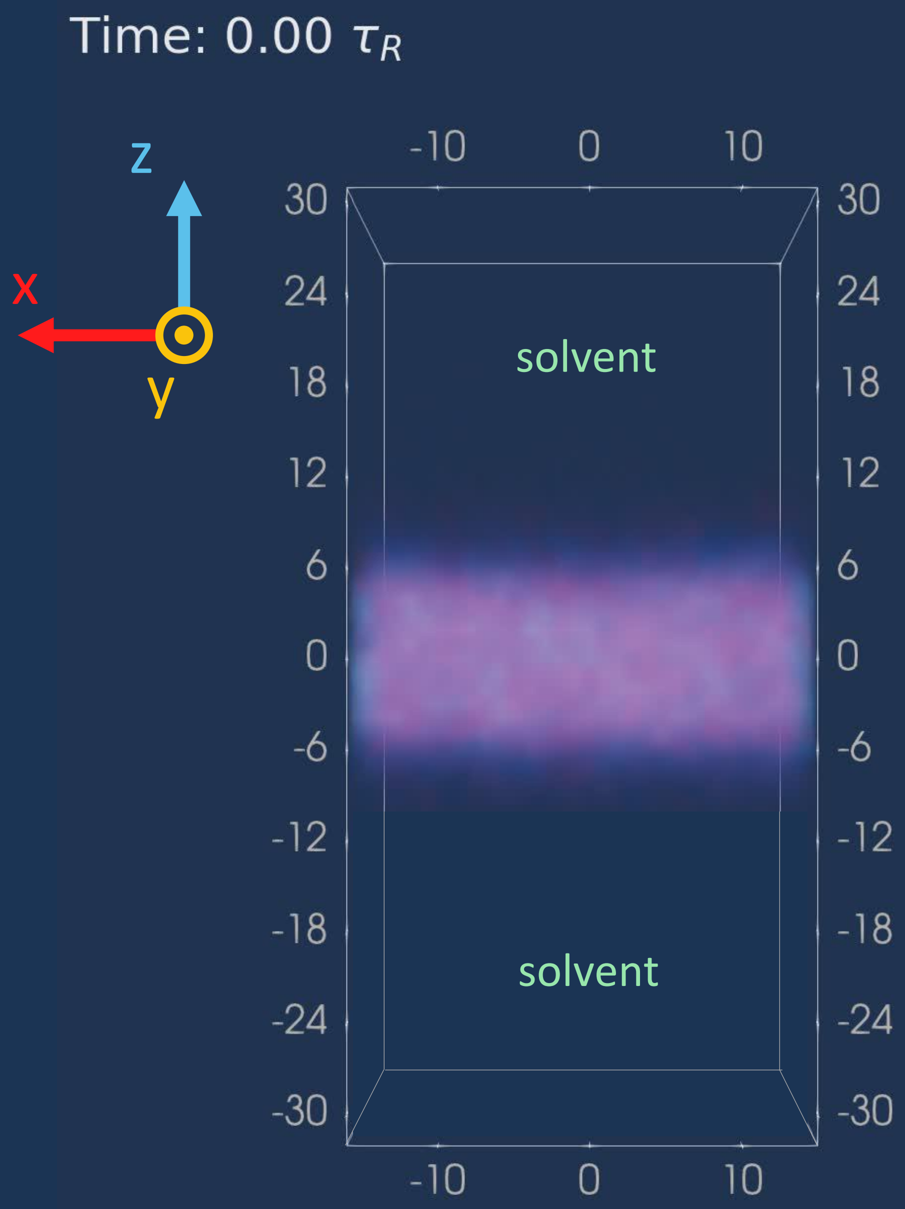
Saddle point approximation



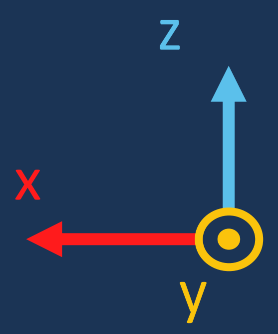
Single chain in a dynamic mean field

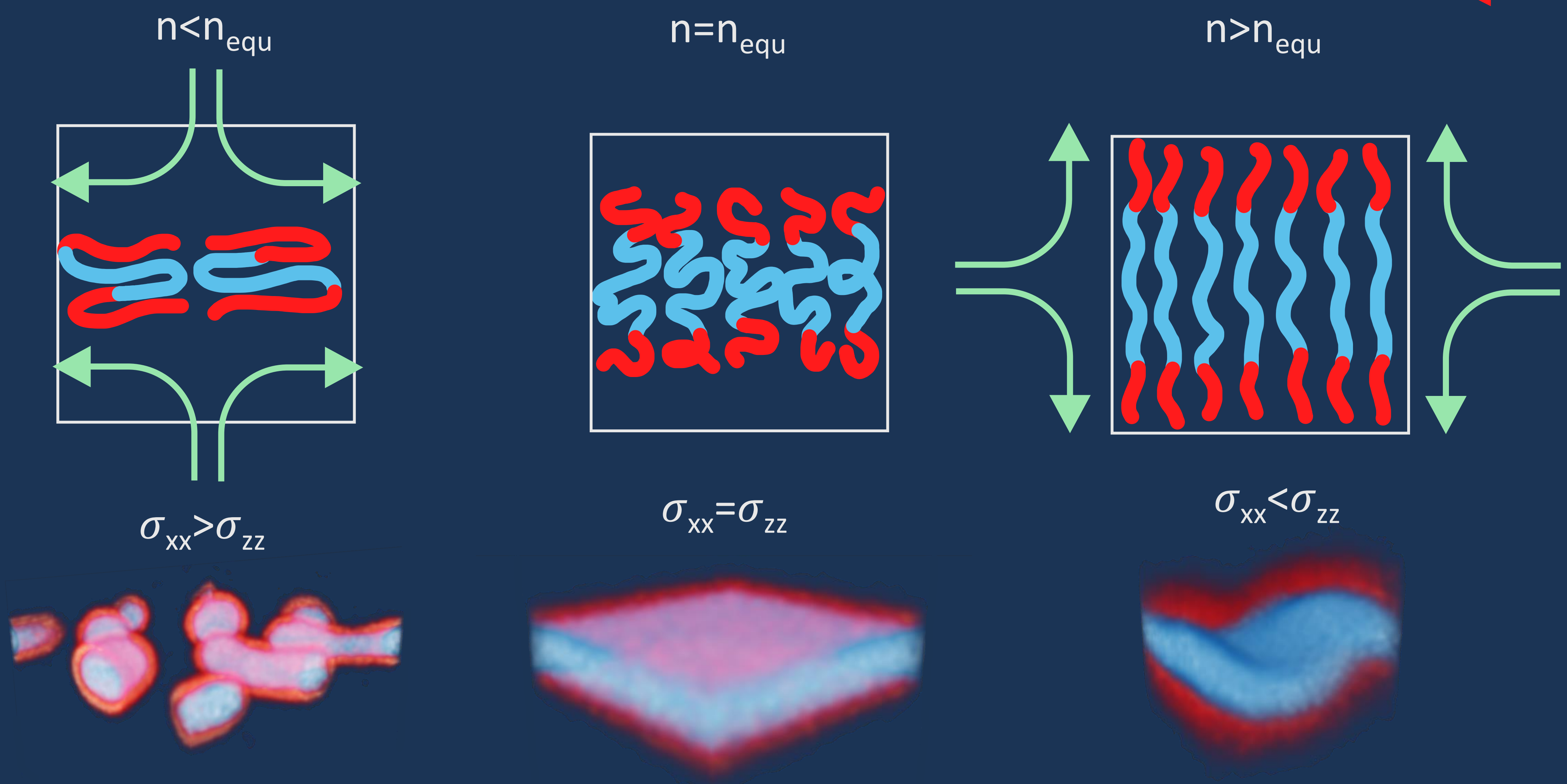
Neutral Membrane Formation

Charge	$0.0e$
ε_{AA}	0.075
ε_{AB}	0.075
ε_{AS}	0.09
ε_{BB}	0.085
ε_{BS}	0.09
ε_{SS}	0.075
N_{A1}-N_B-N_{A2}	8-32-8
n	220

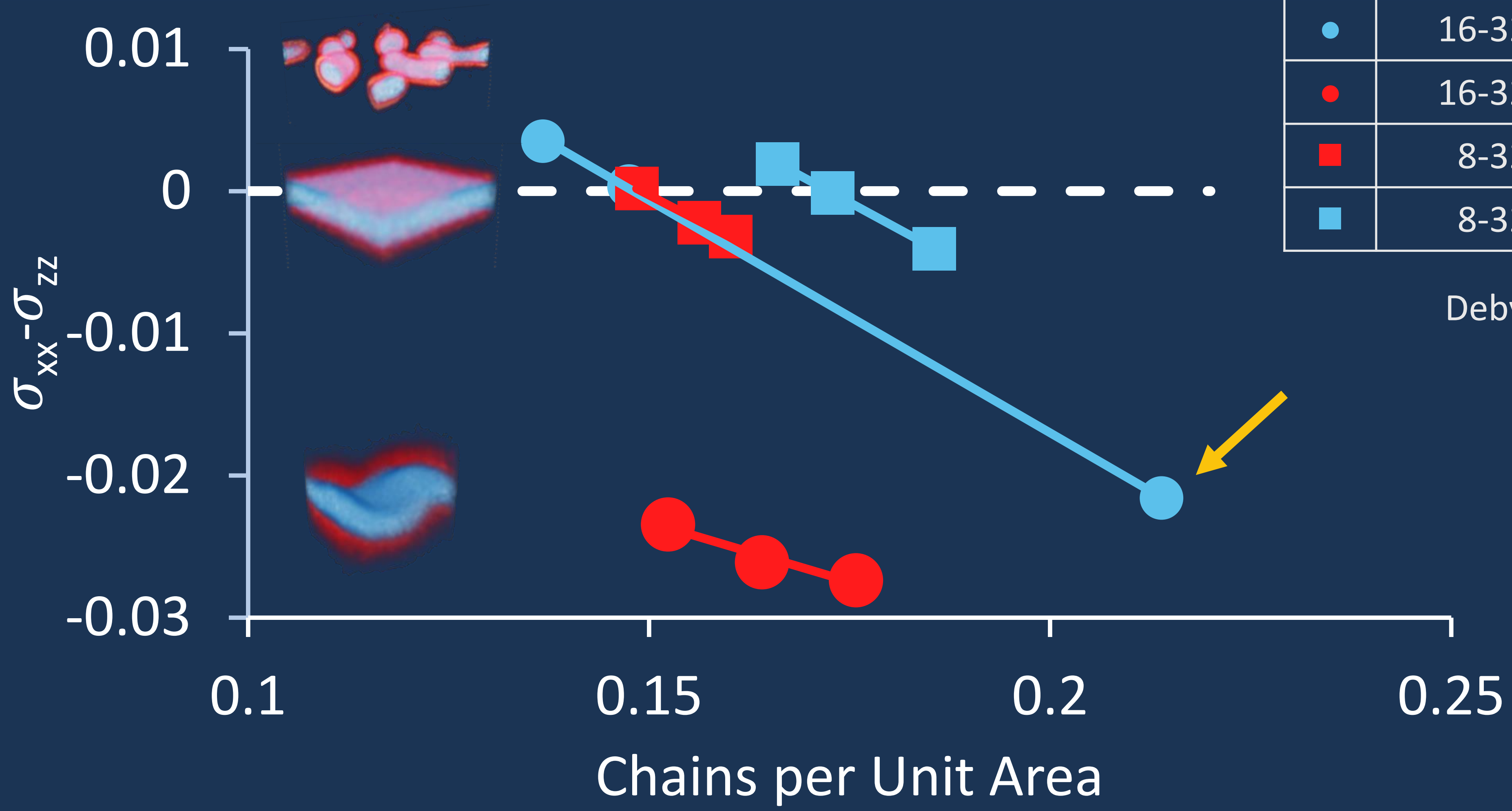


Membrane Stress, σ





Stress vs. Density

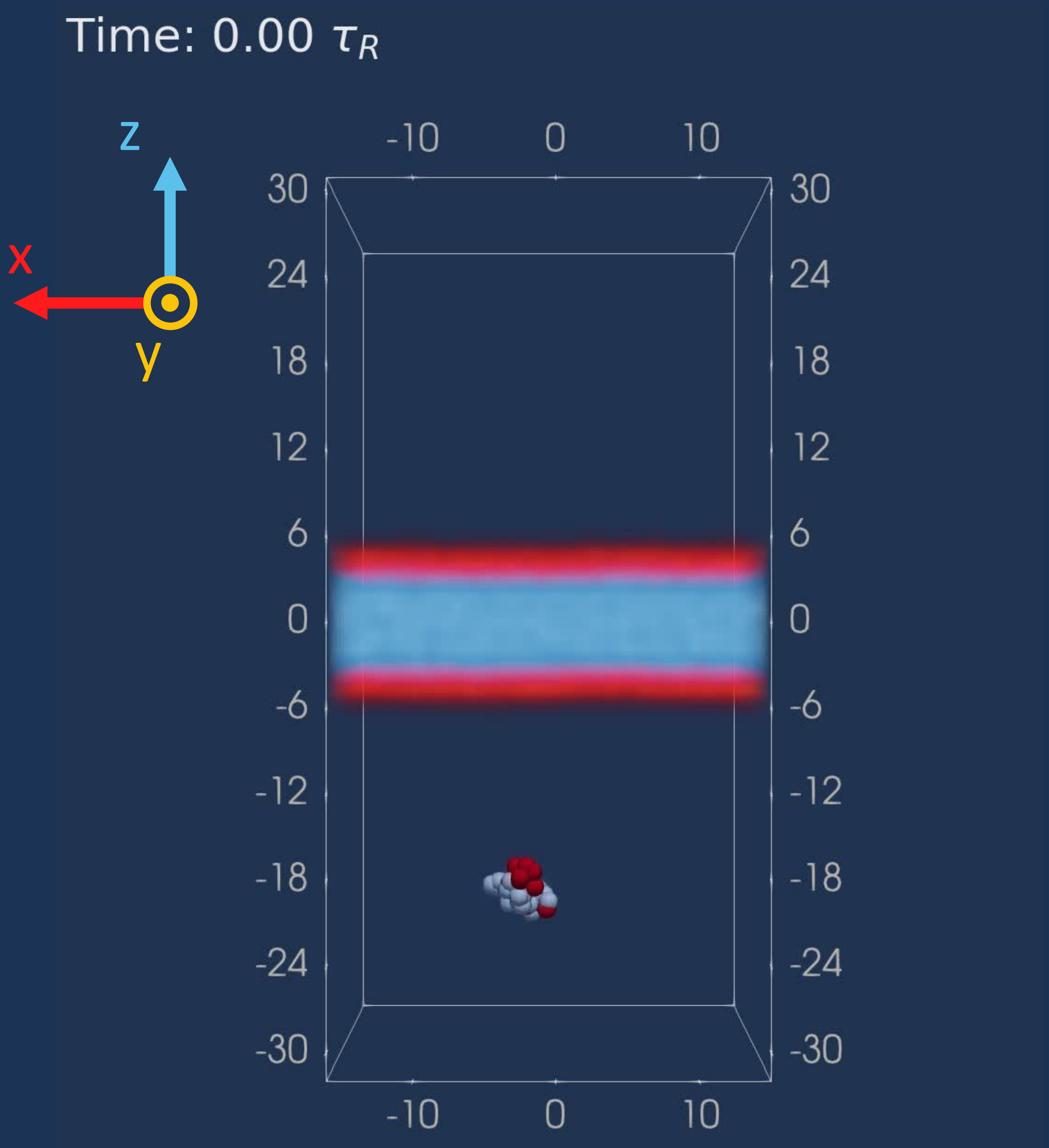


	N_A-N_B-N_A	Charge /*e*
●	16-32-16	0.0
●	16-32-16	0.5
■	8-32-8	0.5
■	8-32-8	0.0

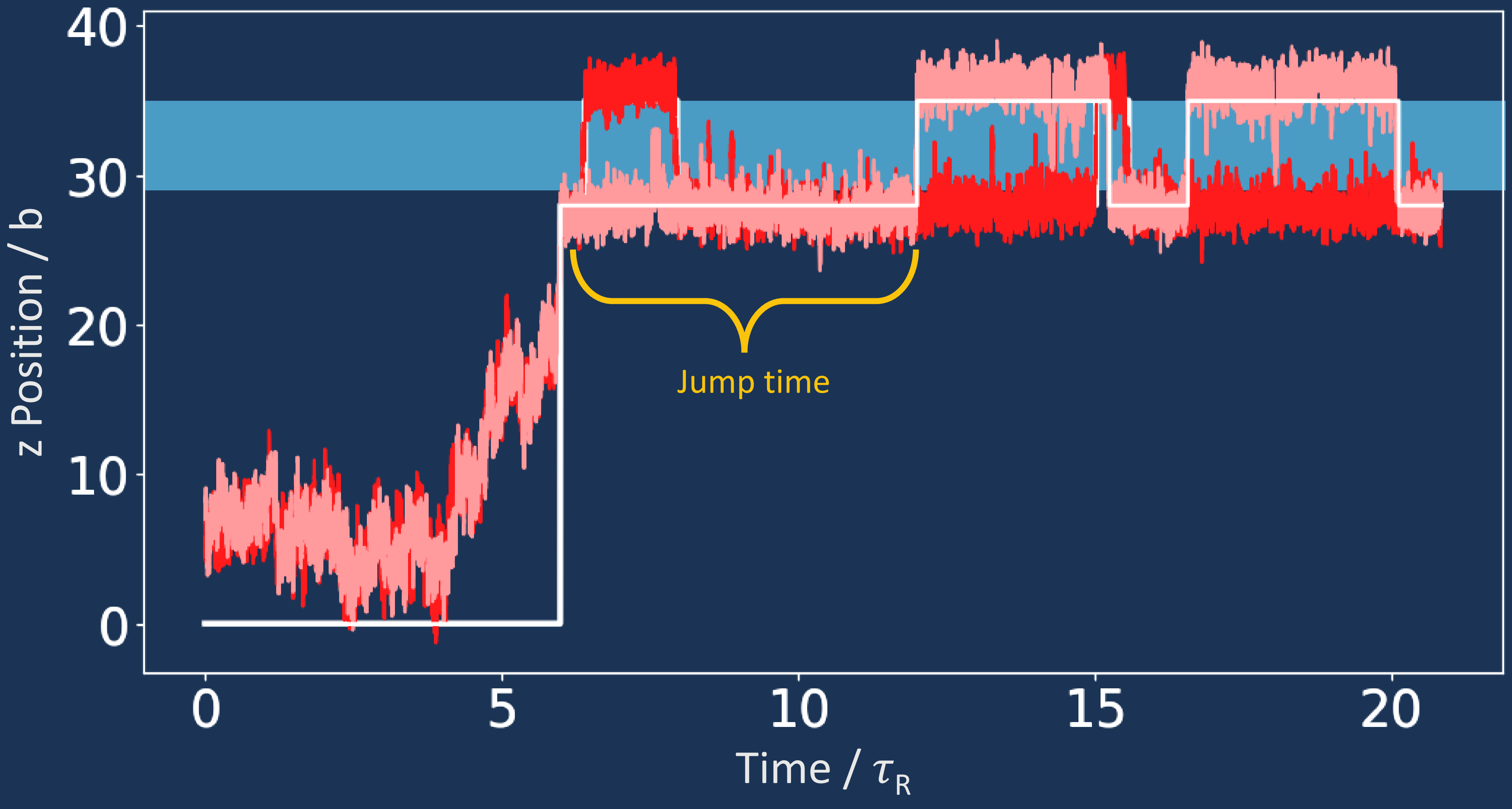
Debye length = 1b

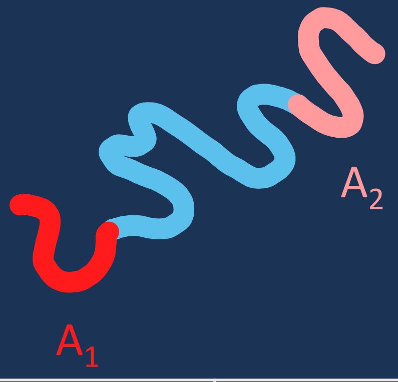
Neutral Polymer Insertion

Charge	0.0e
ε_{AA}	0.075
ε_{AB}	0.075
ε_{AS}	0.09
ε_{BB}	0.085
ε_{BS}	0.09
ε_{SS}	0.075
N_{A1}-N_B-N_{A2}	8-32-8
n	220



Neutral Polymer Block Centers of Mass



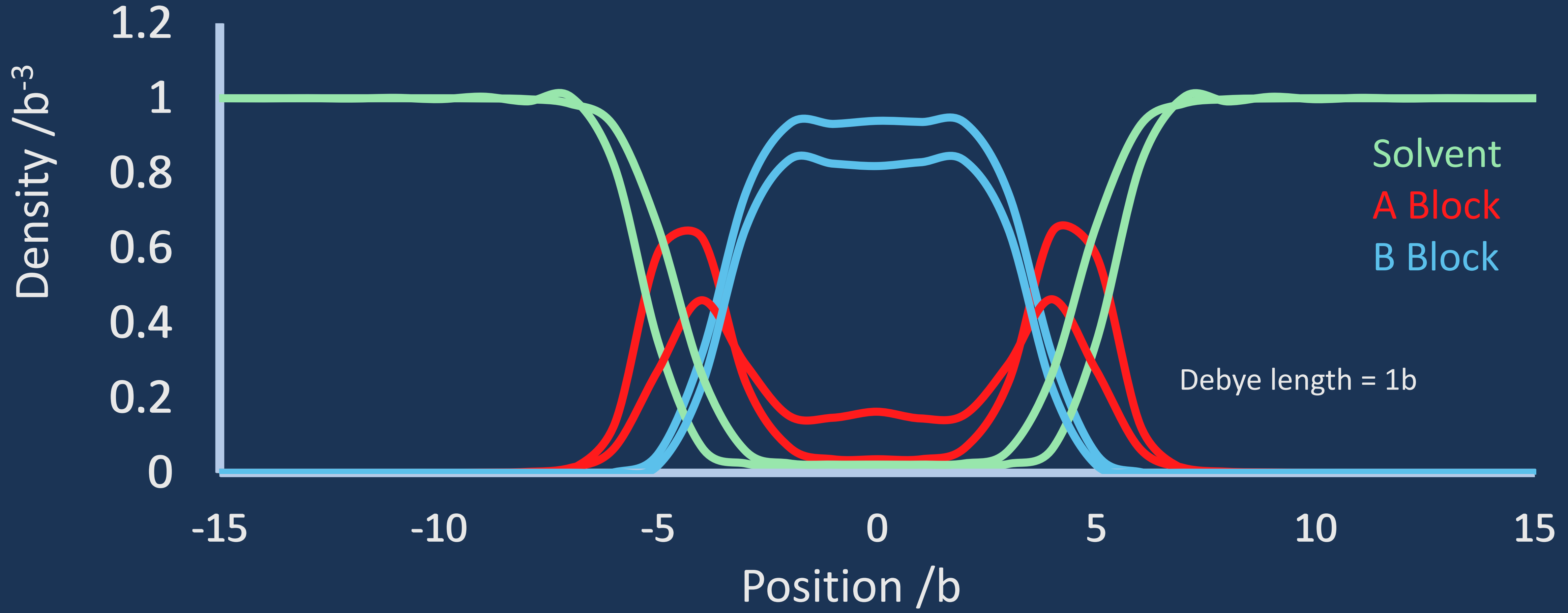


Charge	0.0e
ε_{AA}	0.075
ε_{AB}	0.075
ε_{AS}	0.09
ε_{BB}	0.085
ε_{BS}	0.09
ε_{SS}	0.075
N_{A1}-N_B-N_{A2}	8-32-8
n	220

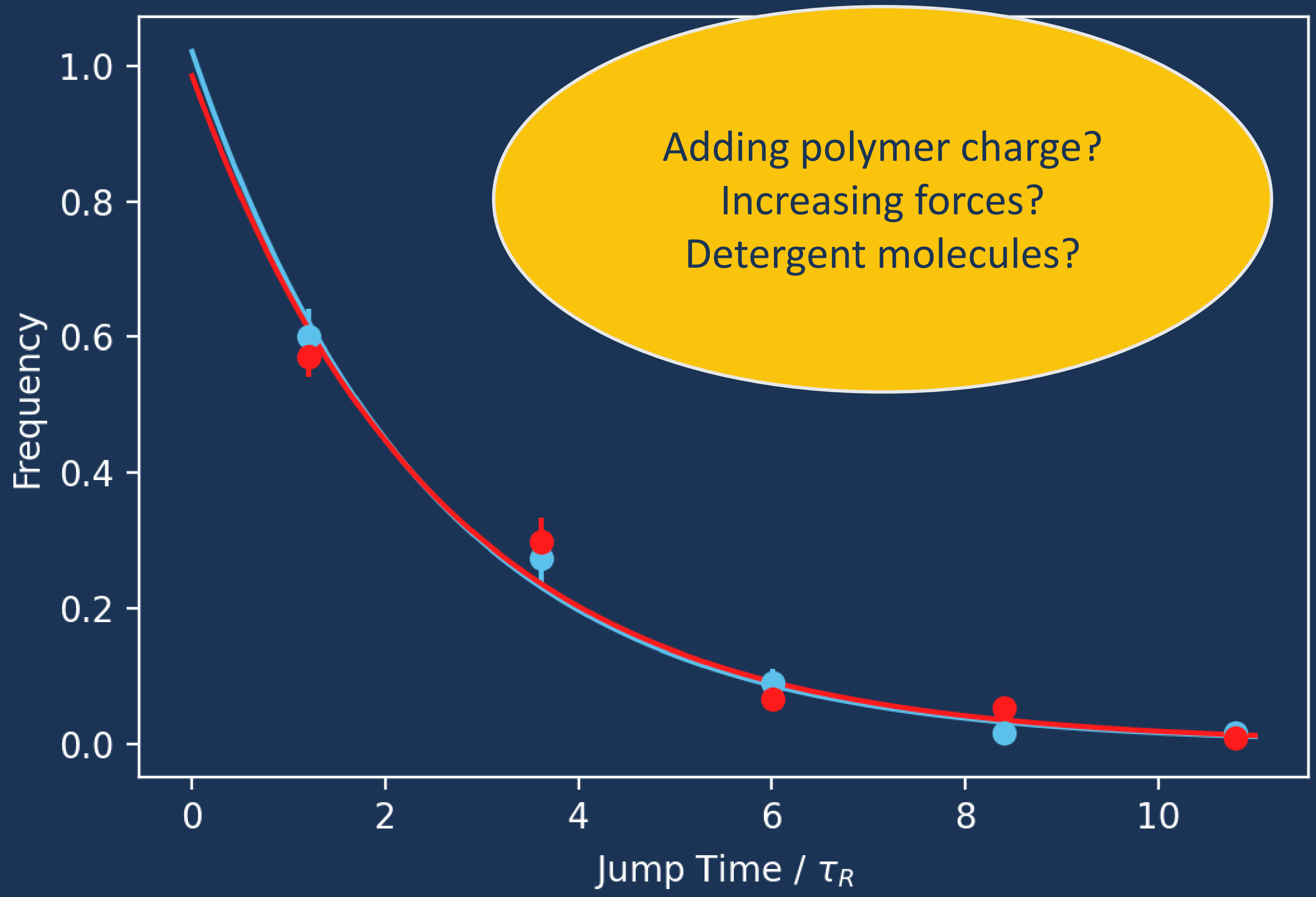
Neutral Membrane | Charged Membrane

0.0*e* / bead
0.173 chains/b^2

0.5*e* / bead
0.148 chains/b^2

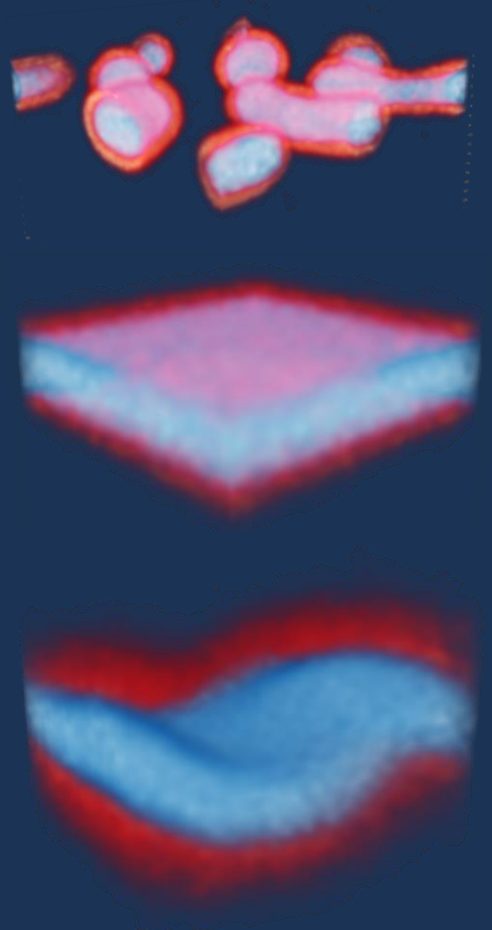


Jump Time Distribution



Charge	0.0*e* 0.5*e*
Total points	225 120
ε_{AA}	0.075
ε_{AB}	0.075
ε_{AS}	0.09
ε_{BB}	0.085
ε_{BS}	0.09
ε_{SS}	0.075
N_{A1}-N_B-N_{A2}	8-32-8

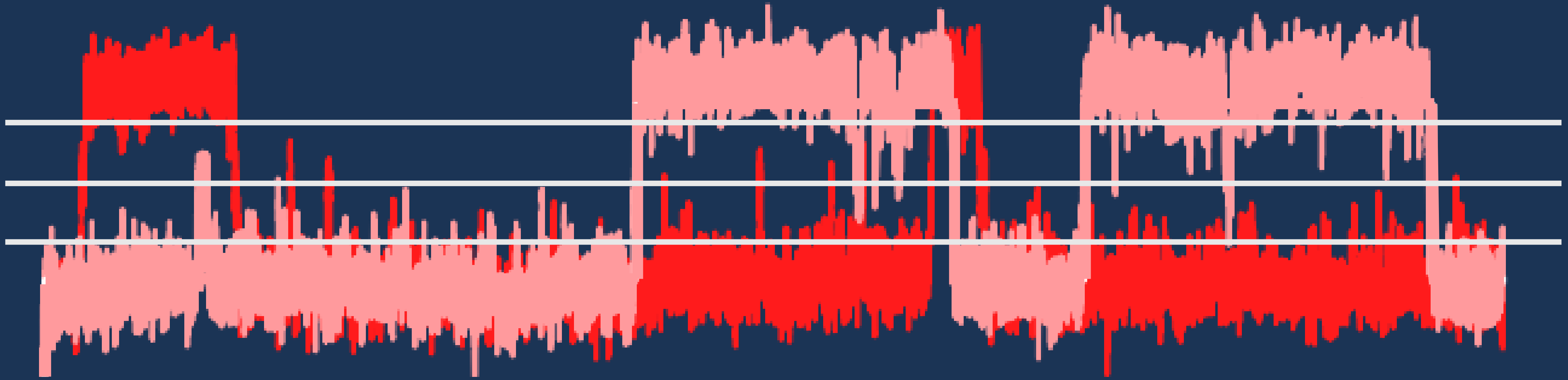
Conclusions



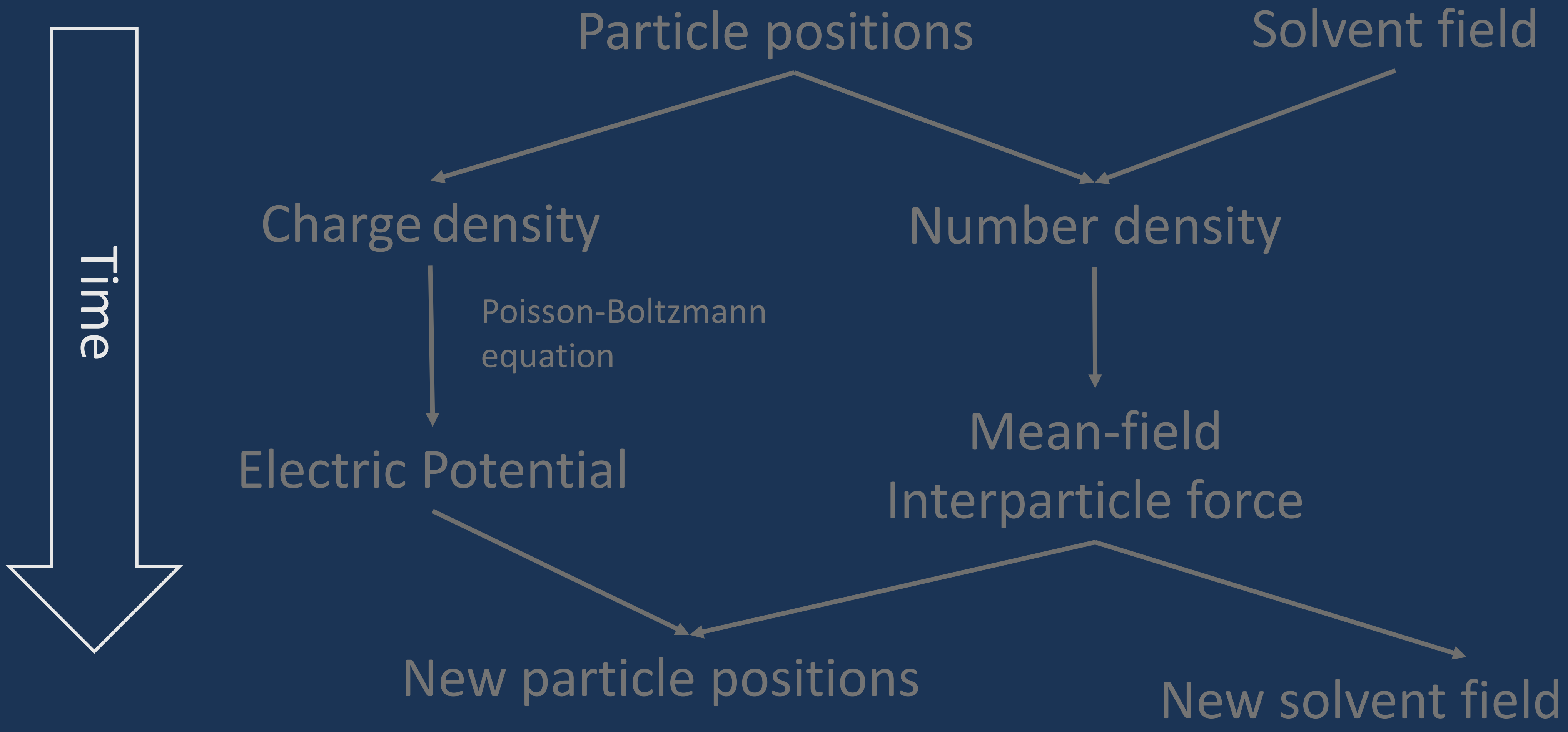
- Developed dynamical self consistent field theory for polyelectrolyte solutions
- Simulated stable membranes in different charge states
- Created a routine to categorize polymer conformations
- Analyzed jump time distribution for charged and neutral membranes

Questions?

Categorization: Directional Gating



Numerical Process



Mean Field Equations

$$\rho_\mu^{(\alpha)}(\boldsymbol{r},t) = \frac{1}{N}\sum_{k,m} \sigma_\mu^{(\alpha)}(m)\delta[\boldsymbol{r} - \boldsymbol{R}_k^{(m)}(t)]$$

$$\rho_\mu^{(Z)}(\boldsymbol{r},t) = \frac{1}{N}\sum_{k,m} z_\mu(m)\delta[\boldsymbol{r} - \boldsymbol{R}_k^{(m)}(t)]$$

$$\boldsymbol{\psi}^{(\alpha)}(\boldsymbol{r},t) = \sum_{\mu',\alpha'} \int dr' \boldsymbol{F}_{\alpha,\alpha'}(\boldsymbol{r} - \boldsymbol{r}')\rho_{\mu'}^{(\alpha')}(\boldsymbol{r}',t)$$

$$\nabla^2\phi(r,t) = \left(\frac{b}{\Lambda_D}\right)^2 \phi(\boldsymbol{r},t) - 4\pi\frac{\Lambda_B}{b}[\rho_M^{(Z)}(\boldsymbol{r},t) + \rho_P^{(Z)}(\boldsymbol{r},t)]$$

$$\frac{d\boldsymbol{R}_\mu^{(k,m)}}{dt} = \sigma_\mu^{(A)}(m)\boldsymbol{\psi}^{(A)}\left(\boldsymbol{R}_\mu^{(k,m)}(t),t\right) + \sigma_\mu^{(B)}(m)\boldsymbol{\psi}^{(B)}\left(\boldsymbol{R}_\mu^{(k,m)}(t),t\right) - z_\mu(m)\nabla\phi\left(\boldsymbol{R}_\mu^{(k,m)}(t),t\right) + \boldsymbol{S}_\mu^{(k,m)}(t) + \boldsymbol{f}_\mu^{(k,m)}(t)$$

$$\frac{dq_S(r,t)}{dt} = \nabla^2 q_S(\boldsymbol{r},t) - \nabla\cdot[\boldsymbol{\psi}^{(S)}(\boldsymbol{r},t)q_S(\boldsymbol{r},t)]$$

Stress:

let us quantify the stability of the membrane.

The stress, σ, in the β direction, due to a force in the α direction is measured by bond lengths

$$\sigma_{\alpha\,\beta} = \frac{1}{n(N-1)} \sum_{l=0}^{n} \sum_{m=0}^{N-1} B_{m,\alpha} B_{m,\beta}$$