Thermodynamics

of

Dissipative Self-Assembly

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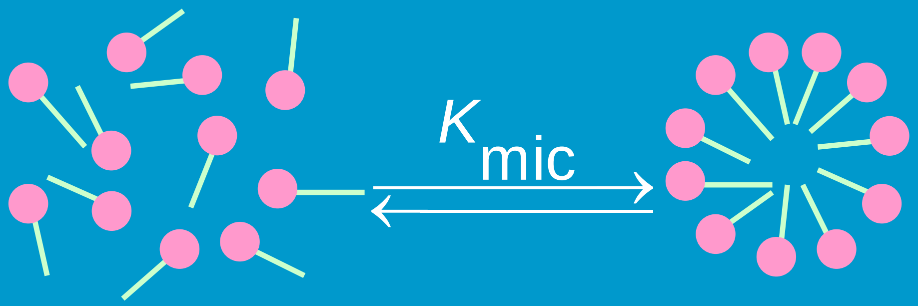
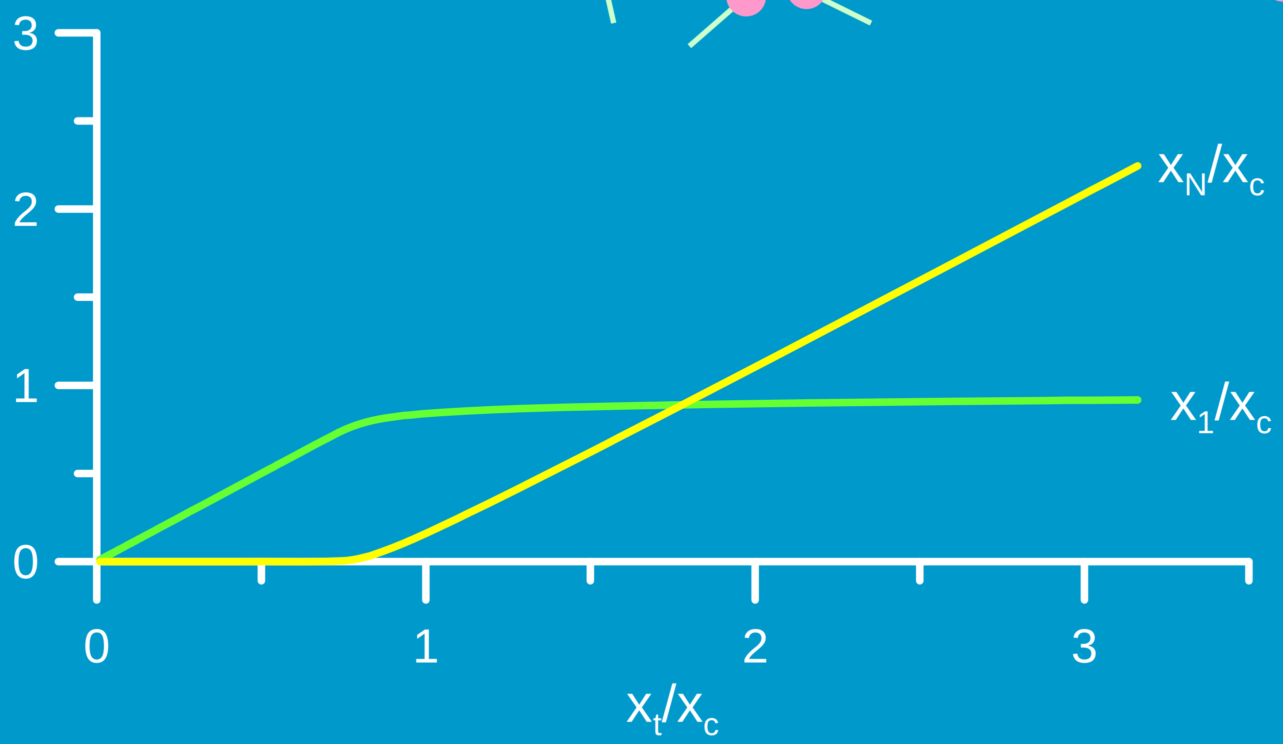
Classical Self Assembly

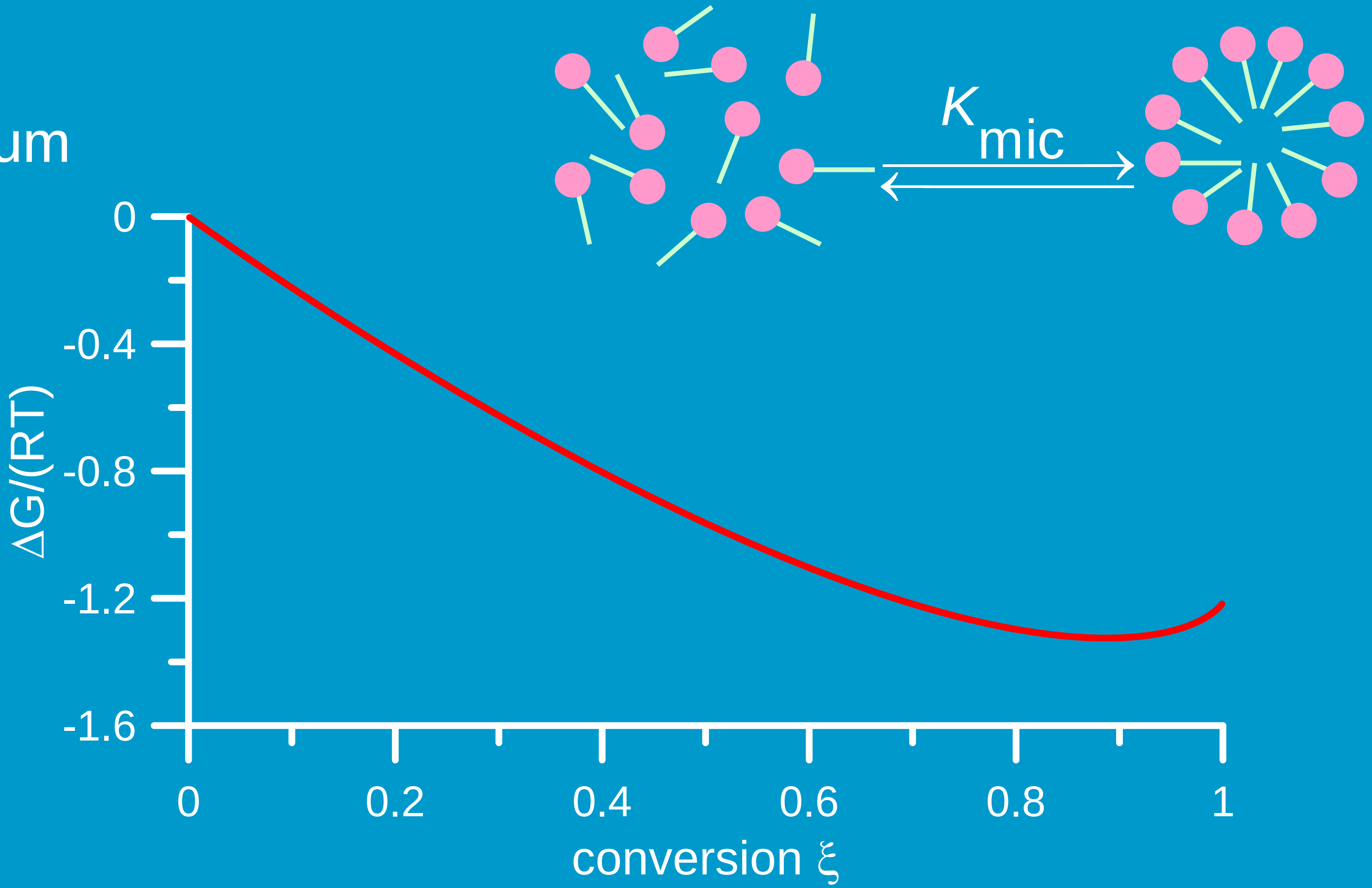
Law of mass action





Classical Self Assembly

Equilibrium



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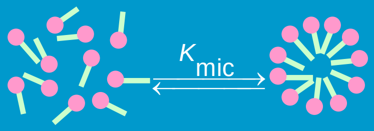
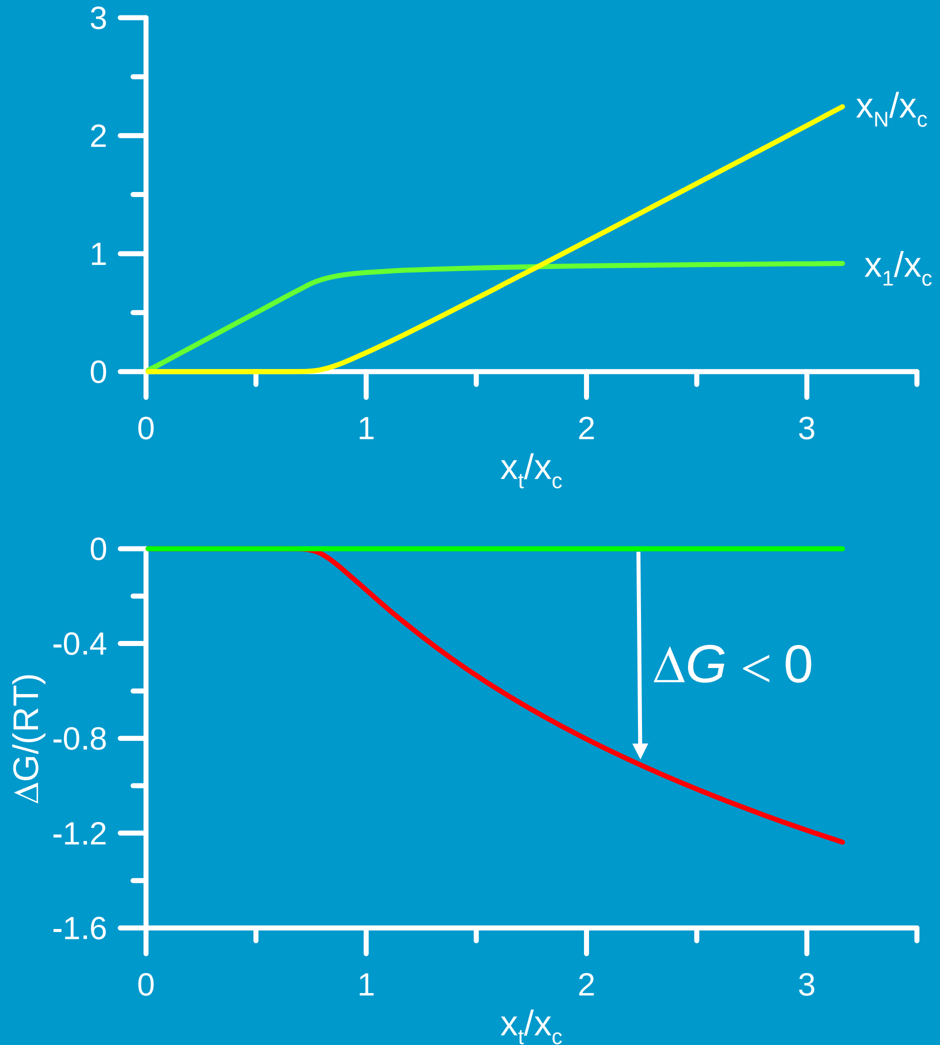
Classical Self Assembly

Spontaneous





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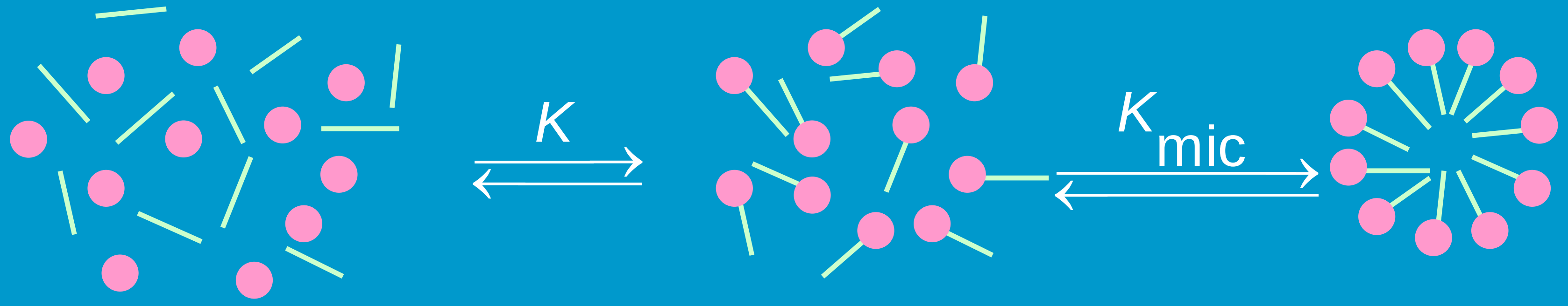
Controlled Self Assembly



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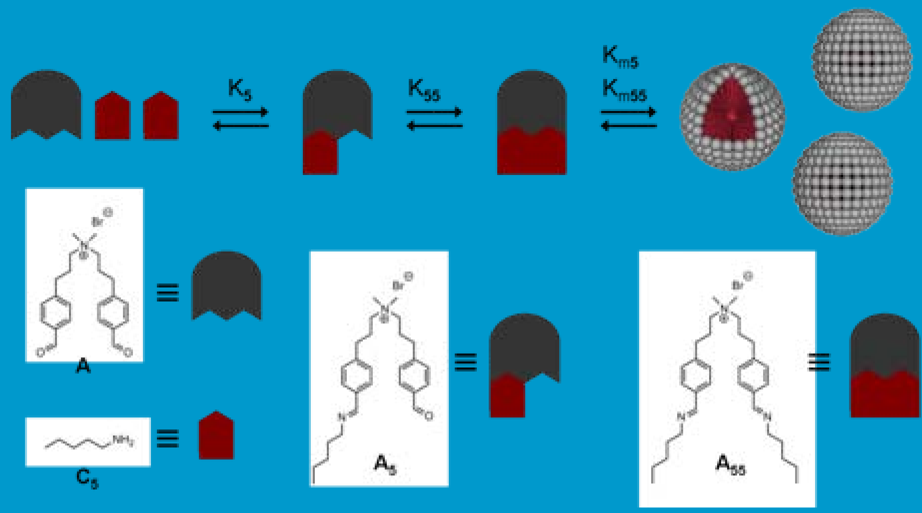
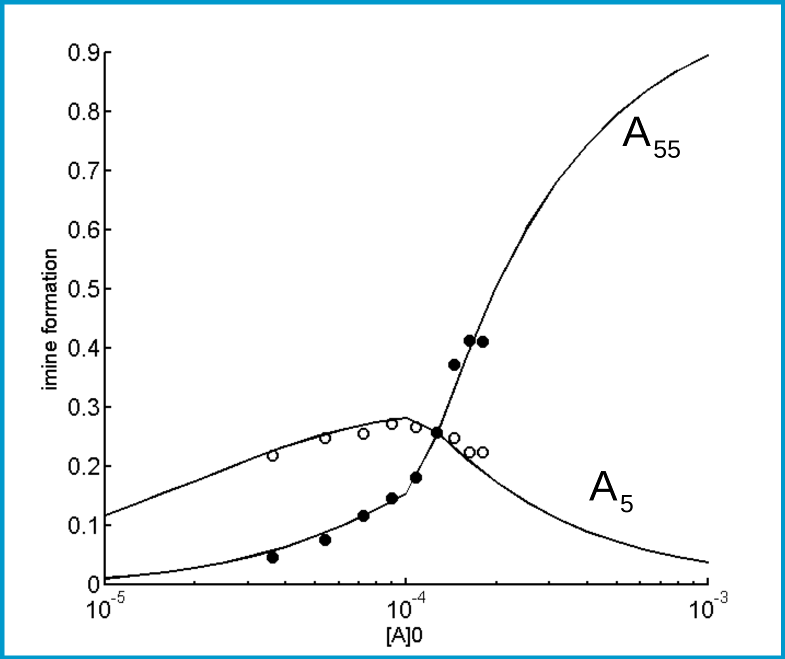
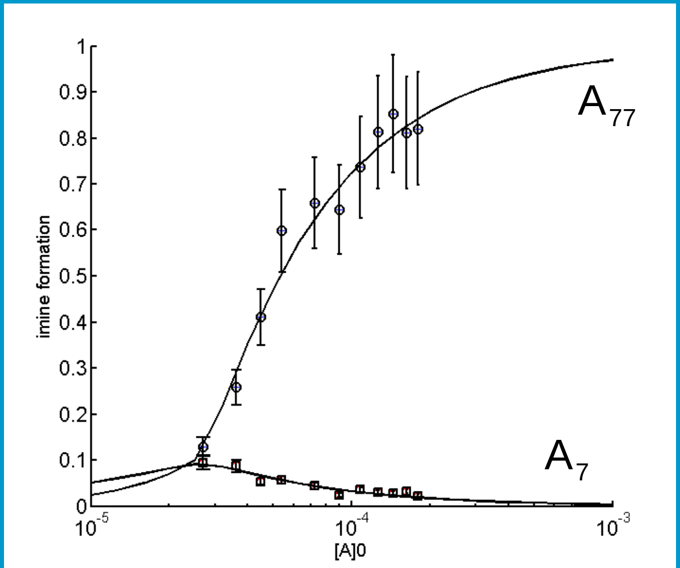
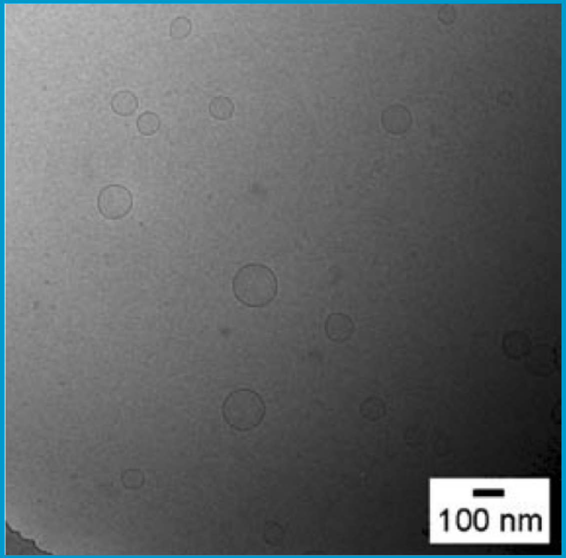
Example 1: micelles

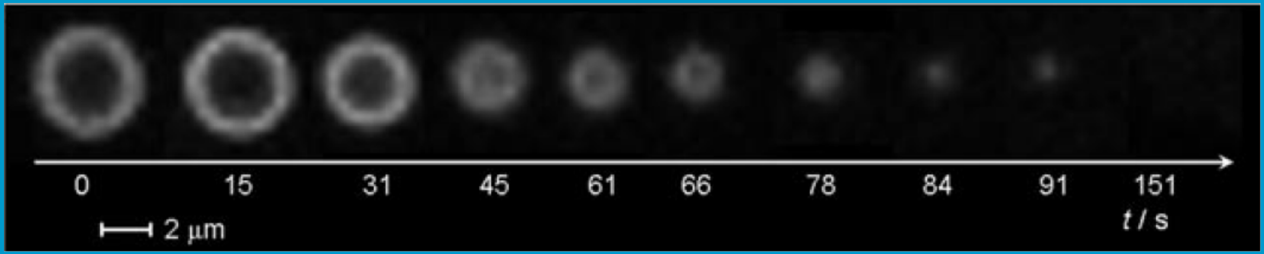




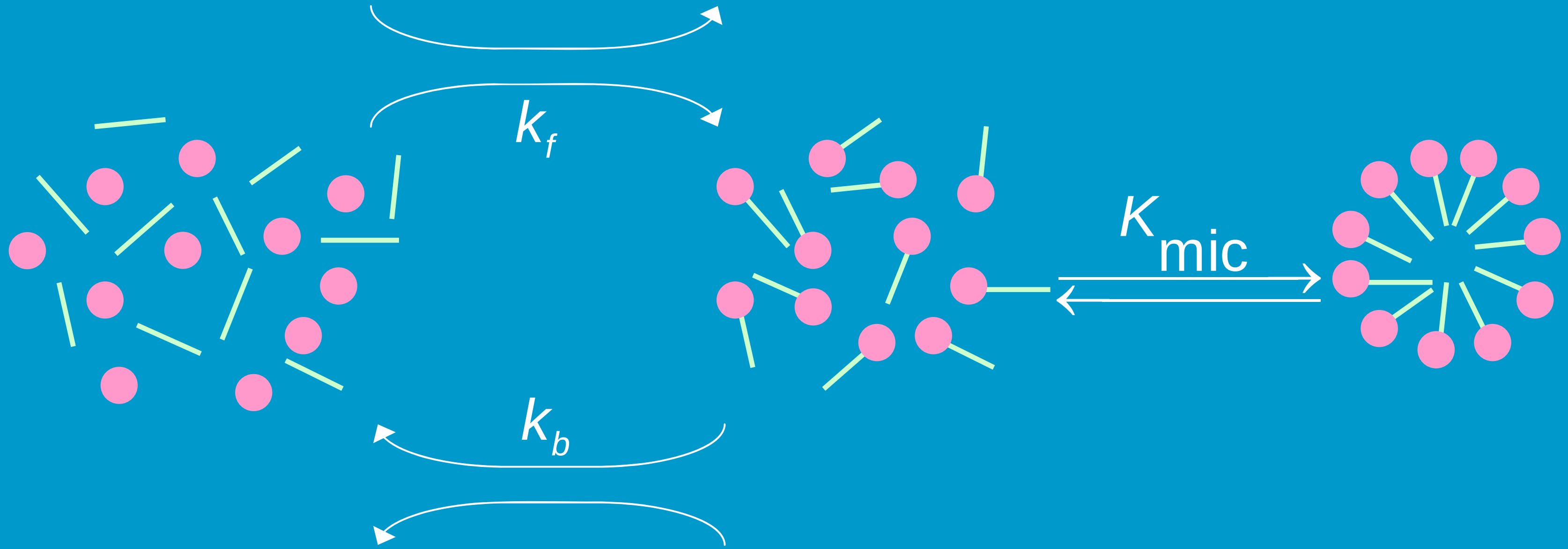
Example 2: responsive vesicles



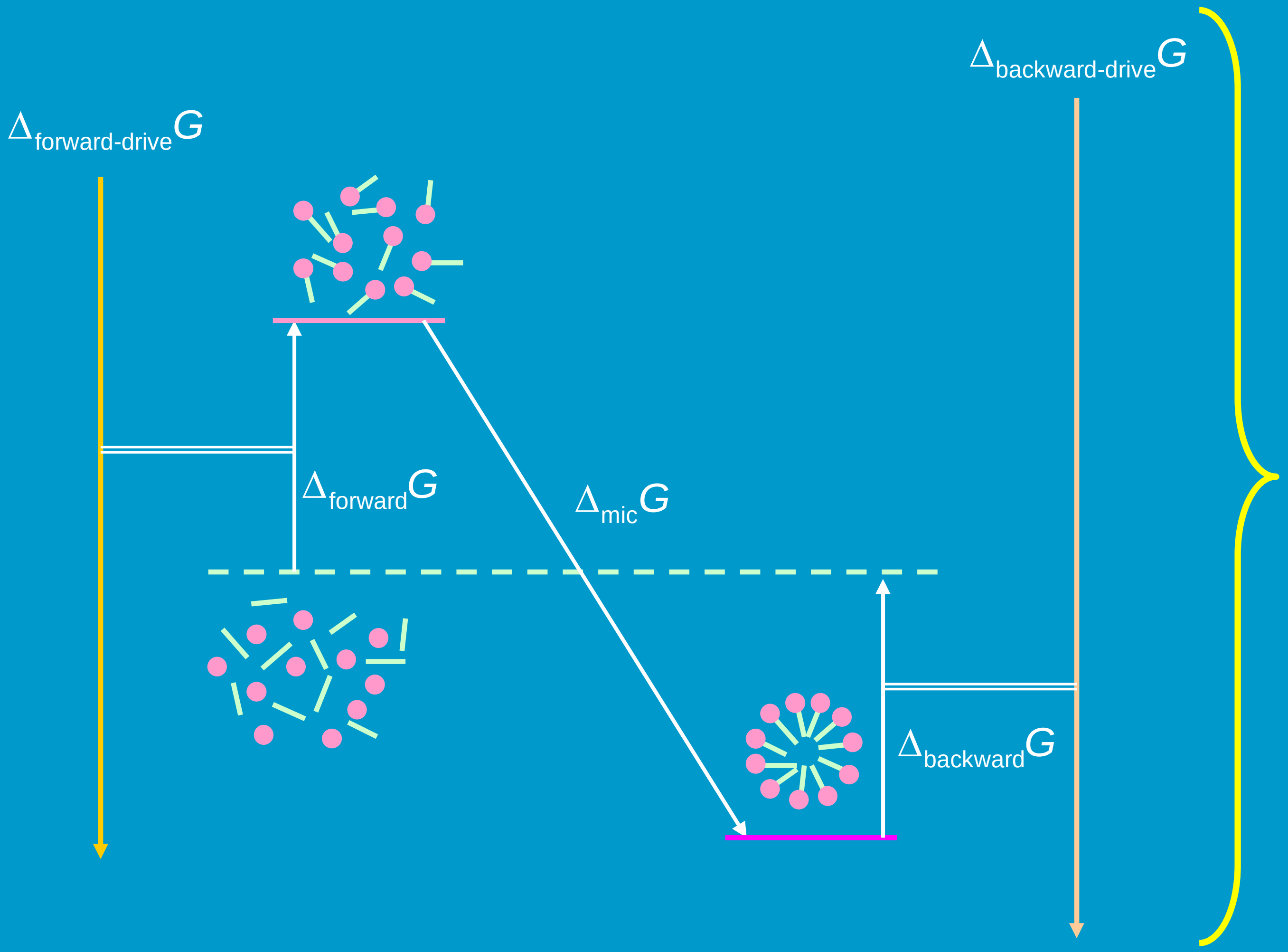




Enhanced Control of Self Assembly



Required work: driving reactions



$$\Delta_{\text{tot}}G = \sum_{\text{f,b}} \Delta_{\text{drive}}G$$

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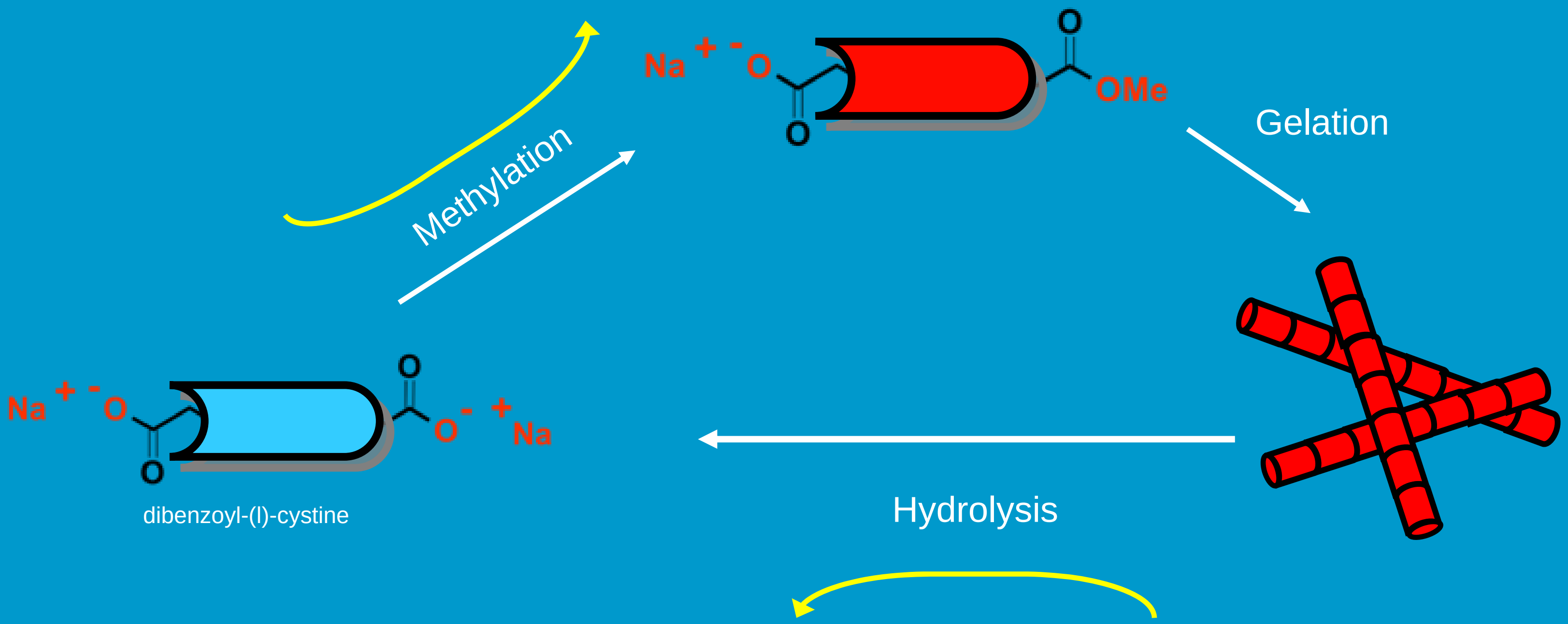
Example: gelation



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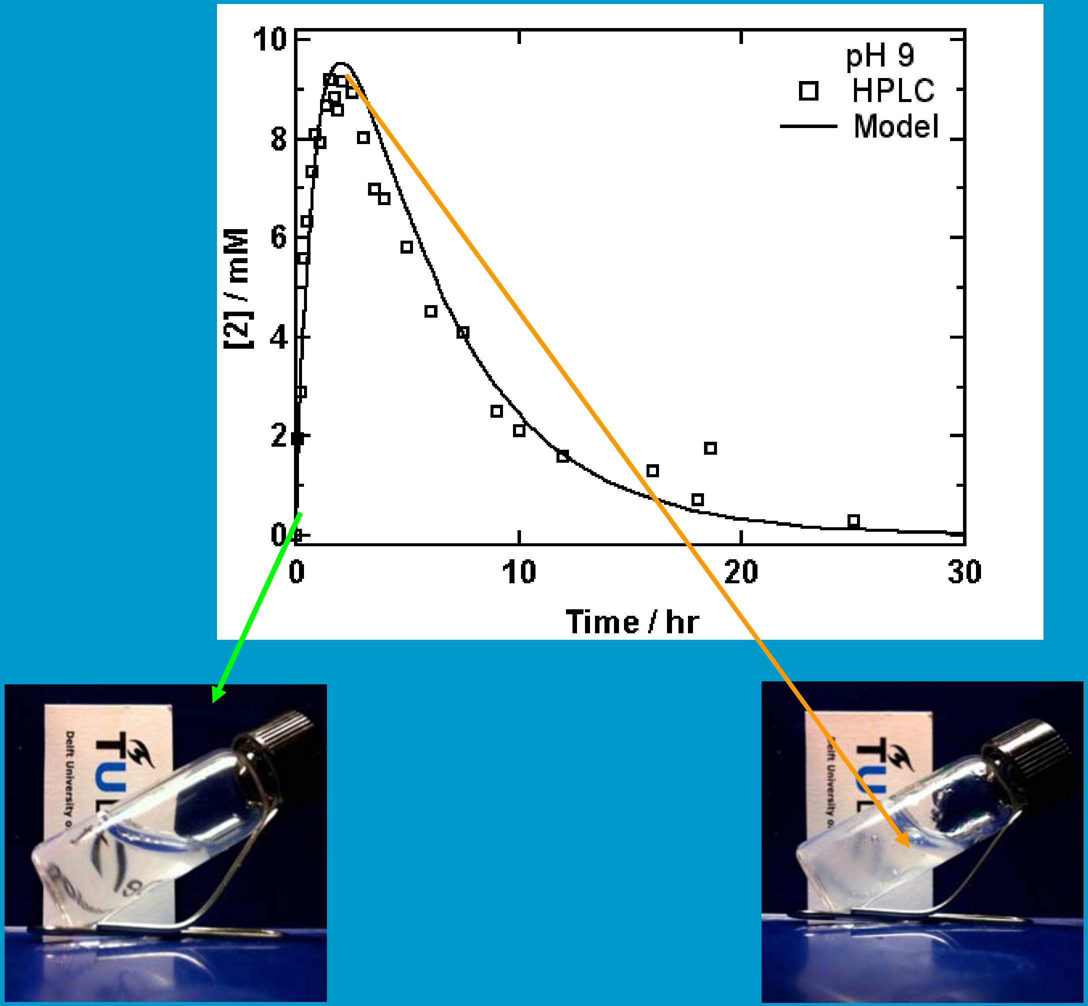
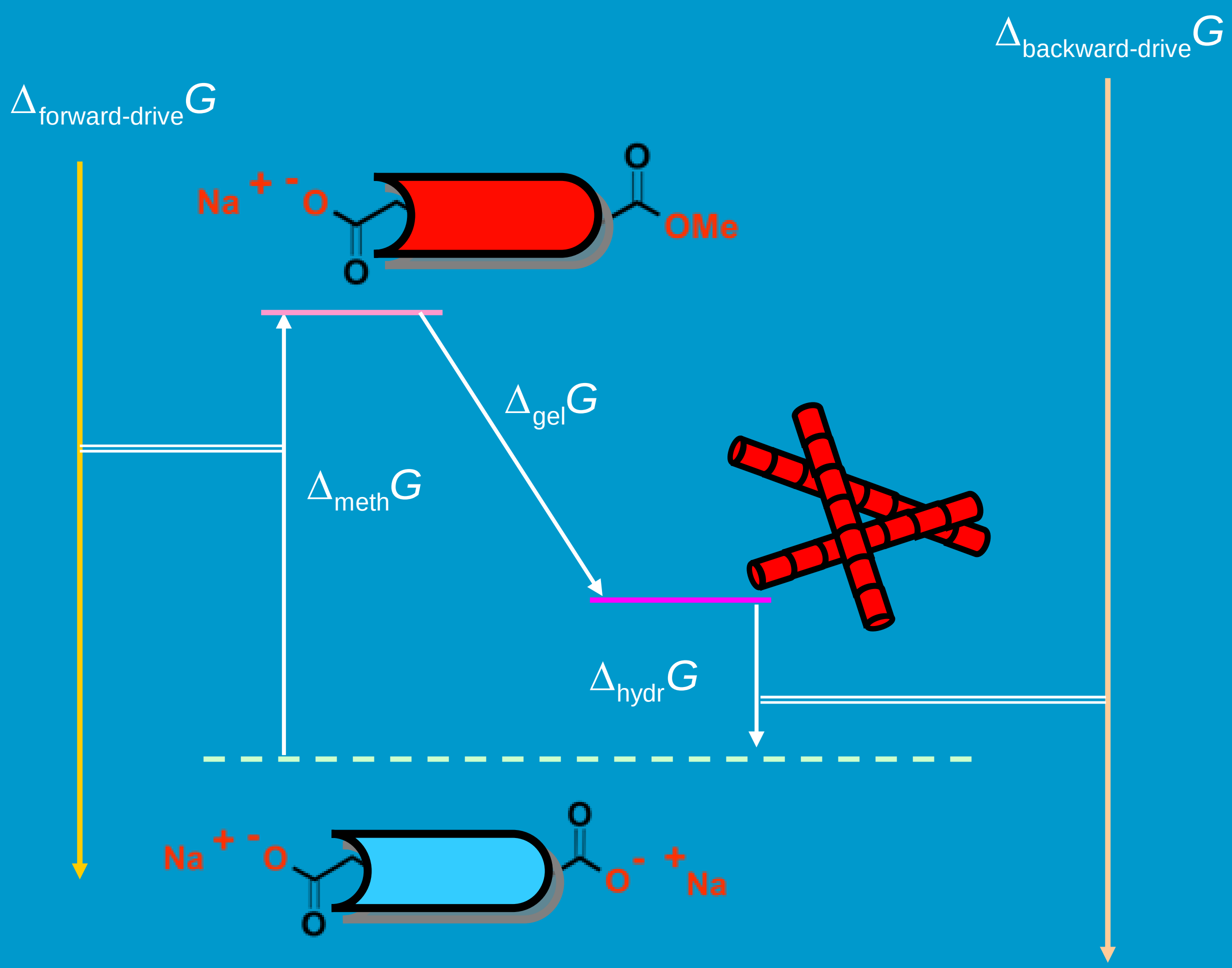
Transient gelation



Thermodynamic Analysis



Driving Reactions

- Methylation: $DMS + H_2O \rightarrow MMS^- + MeOH + H^+$
- Hydrolysis: $H^+ + OH^- \rightarrow H_2O$
- Net reaction: $DMS + OH^- \rightarrow MMS^- + MeOH$

Gibbs energy change of reaction $\Delta_r G^{\circ} = -398.4$ kJ/mol

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Efficiency of Driving Reactions

- Methylation reaction $\Delta_{\text{meth}}G^{\ominus} \approx 10$ kJ/mol
- Hydrolysis $\Delta_{\text{hydr}}G^{\ominus} = -\Delta_{\text{meth}}G^{\ominus} \approx -10$ kJ/mol

Efficiency of free energy transfer $\varepsilon \approx 3\%$

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Thermodynamic Analysis

- Stationary operation
  - Methylation/hydrolysis rate: $\dot{r} = 50$ mM/hr
  - Gibbs energy change of reaction $\Delta_r G^{\ominus} = -398.4$ kJ/mol
  - Lost work $W_{\text{lost}} = -\dot{r}\Delta_r G^{\ominus} \approx 20$ kJ/(L hr) ≈ 5.6 W/L
  - Entropy production $\dot{S} = \dfrac{W_{\text{lost}}}{T_{\text{amb}}} \approx 0.02$ J/(K L)

Conclusions

- Self-assembling systems
  - respond faster when driven
  - are dissipative when driven by irreversible reactions
  - can be used to store energy *!*

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