

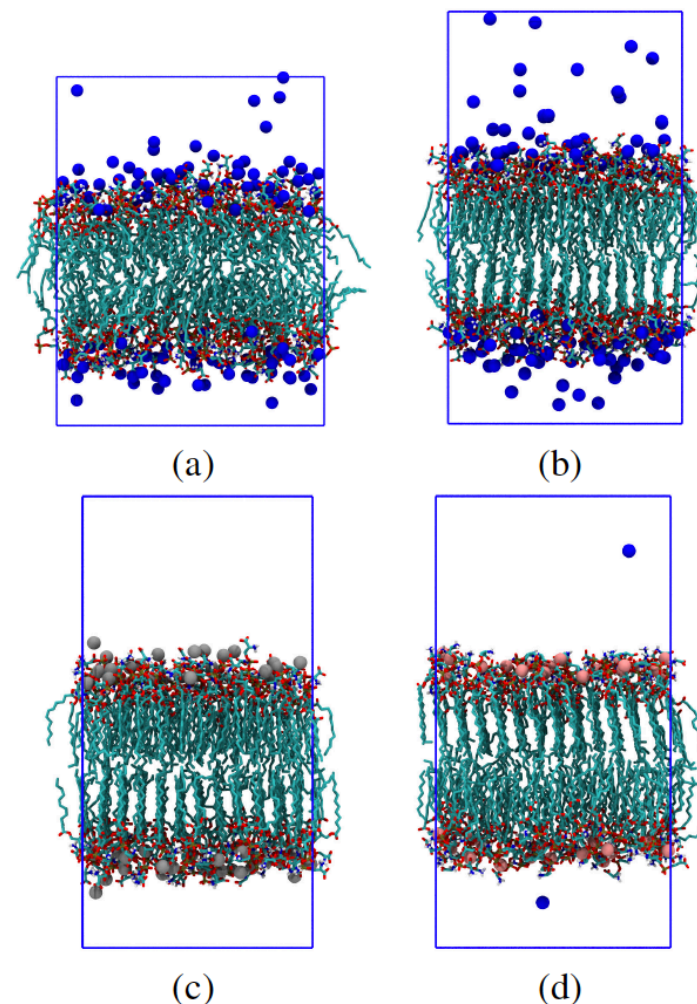
# The Driving Force for Crystallization of Anionic Lipid Membranes Revealed by Atomistic Simulations

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Crystalline vesicles are promising nanomaterials due to their mechanical stability in various environments. In order to control their fabrication, it is essential to understand the effects of different experimental conditions on crystallization. We performed atomistic molecular dynamics simulations of anionic lipid membranes composed of 1,2-dilauroyl-sn-glycero-3-phosphol-L-serine (DLPS).

- In the presence of  $\text{Na}^+$  monovalent counterions, we access the phase transition from the liquid-like disordered liquid-crystalline phase to the ordered gel phase by lowering the temperature of the system.
- The phase transition is conclusively evidenced by the scattering structure factor.
- Quantitative calculations show that the enhancement of the inter-tail van der Waals interaction (about  $-6 k_B T$ ) plays a dominant role in driving the phase transition, rather than the increase of the cohesive interaction ( $-0.5 k_B T$ ) between lipids and counterions.
- In the presence of multivalent counterions of  $\text{Zn}^{2+}$  or  $\text{La}^{3+}$  the gel phase is found throughout the temperature range investigated. Moreover, the van der Waals interaction per hydrocarbon group is about 20% stronger in the gel phase ( $-1.8 k_B T$  regardless of the counterions) than in the liquid-crystalline phase ( $-1.5 k_B T$ ).



*Figure: Snapshots of the last simulation frames of (a) DLPS- $\text{Na}^+$  (317 K), (b) DLPS- $\text{Na}^+$  (310 K), (c) DLPS- $\text{Zn}^{2+}$  (310 K) and (d) DLPS- $\text{La}^{3+}$  (310 K). Order in the orientation of the hydrocarbon tails is evidently observed in (b) - (d), but not in (a). The counterions are highlighted using the VDW drawing method under VMD with waters omitted for clarity.*