Studies on the Bilayer Gel to Liquid Crystalline Transition: Influence of Polymer Grafting and Composition

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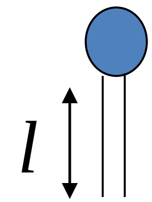
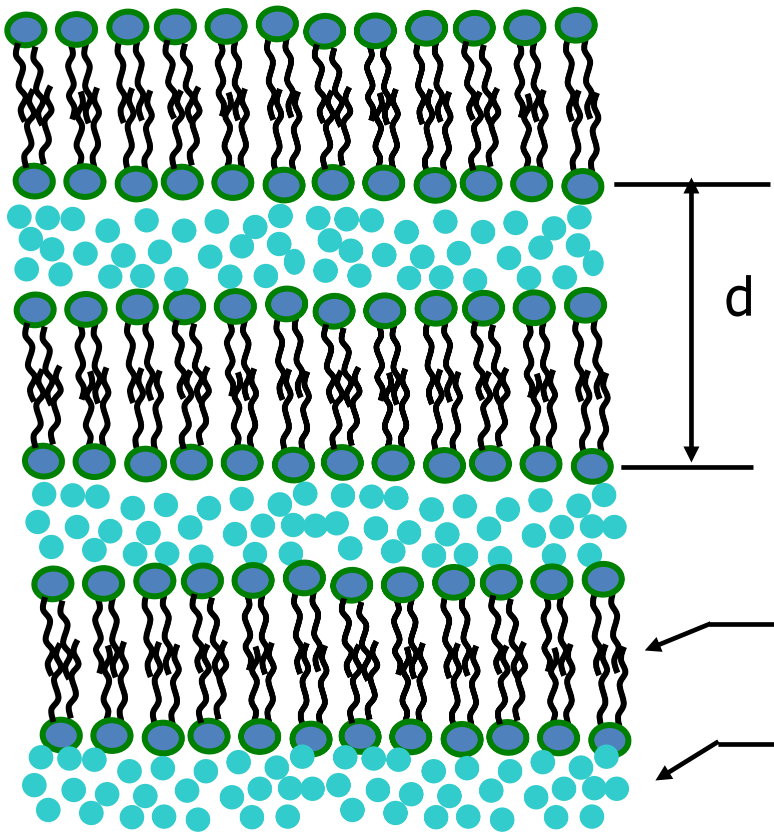
The Lamellar Phase

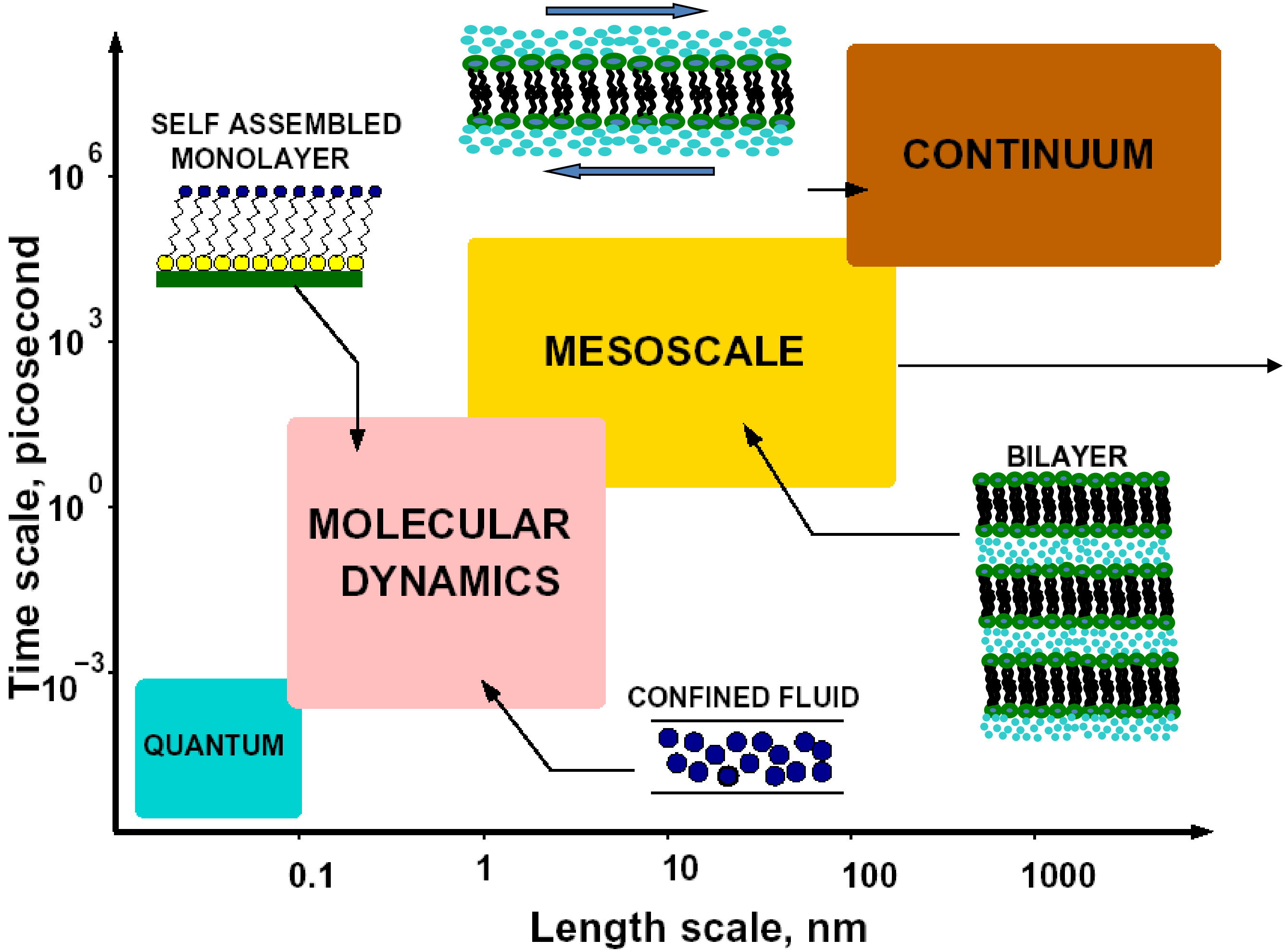


$$0.5 < \frac{A}{V_h / l} < 1$$

- Water-Surfactant Systems
- Cell Membrane - Lipid Bilayers
- Chain Lengths: C16-C18



Multiscaling:Bridging Length and Time Scales

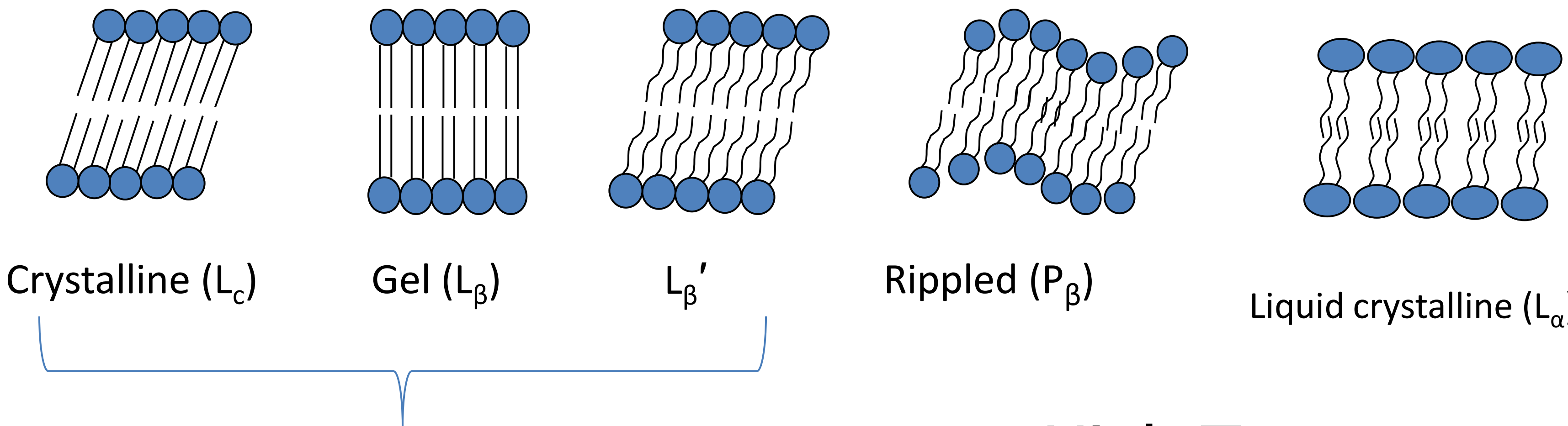


Lattice Boltzman
Simulations

Dissipative
Particle Dynamics
DPD

Lipid Bilayers

Phase Behaviour...



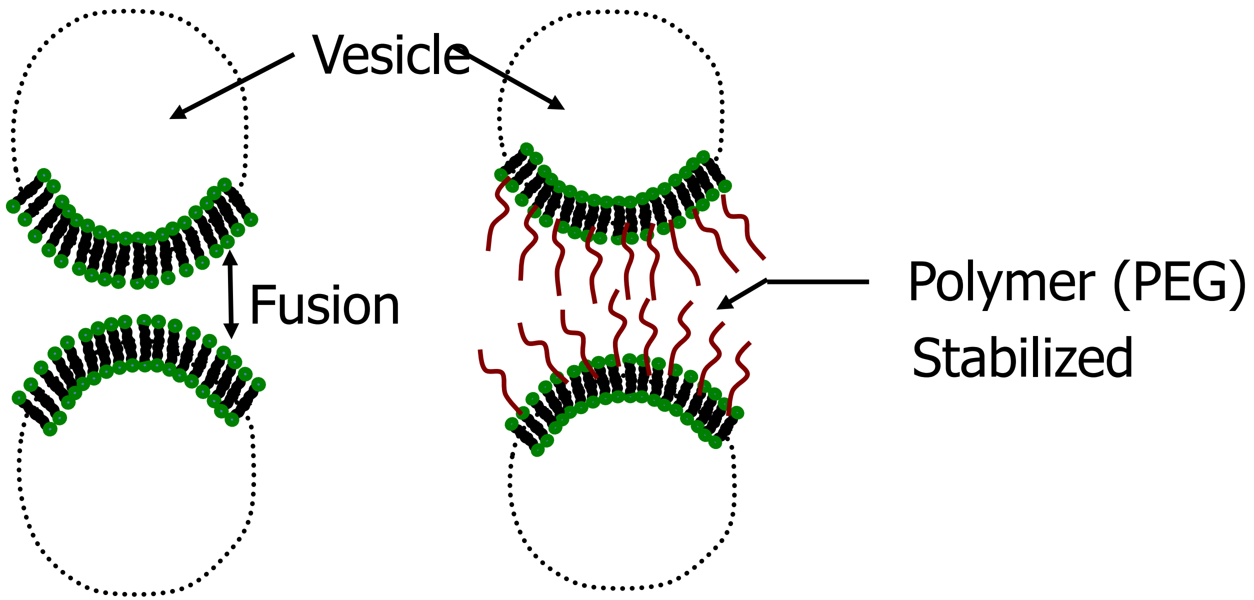
Low Temperature

High Temperature

- Chain Melting Transition
- Melting Temperatures : Saturation and Composition
- Polymer Grafted Bilayers

Polymer Grafted Membranes

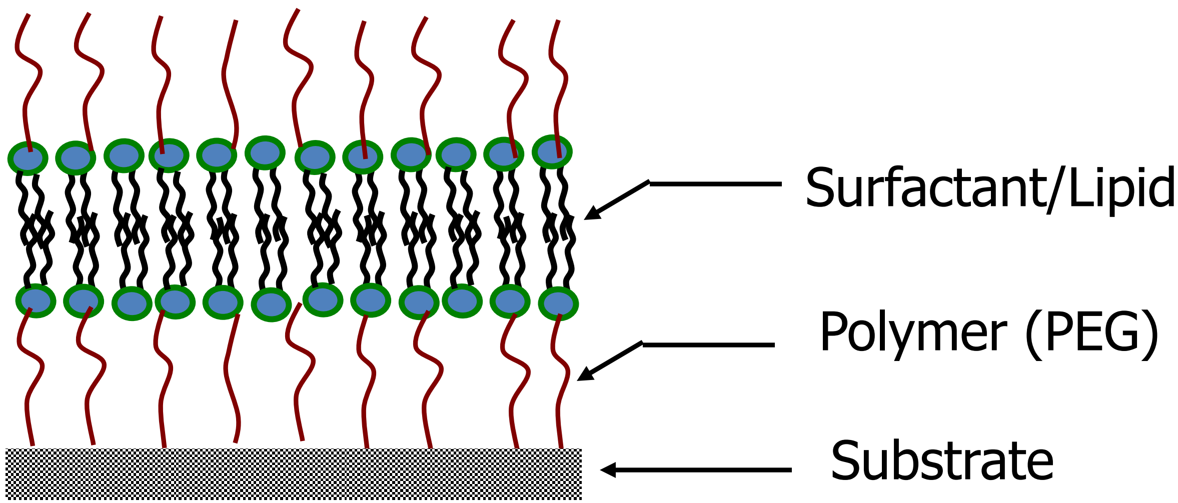
Polymer Stabilized Vesicles



Applications

- Drug delivery systems
- Precusors for supported membranes
- Cell mimicking systems
- Micropipette experiments

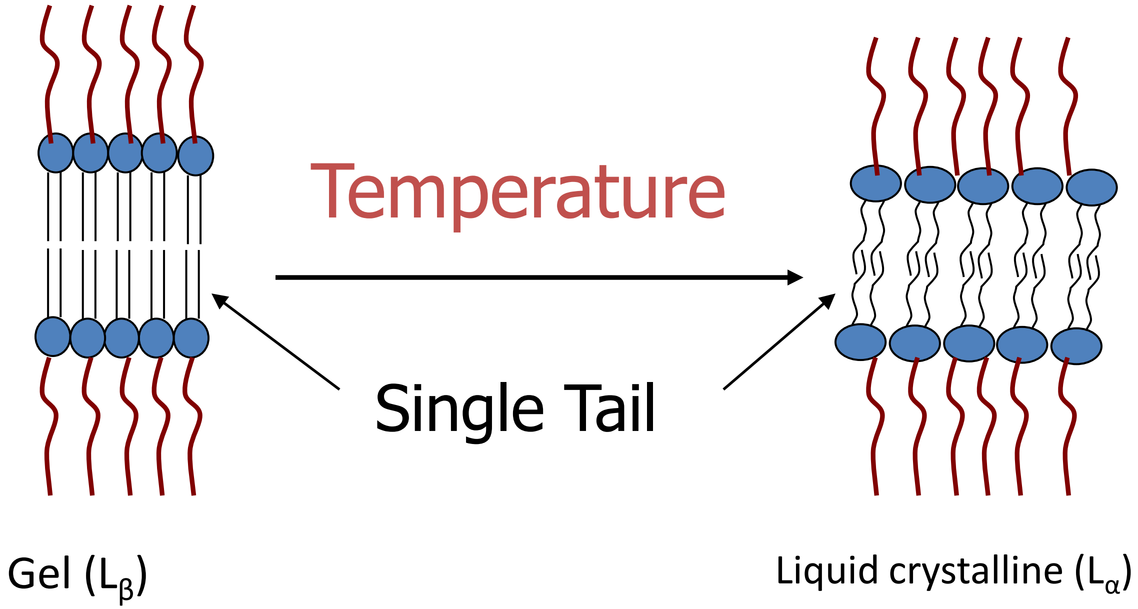
Polymer Supported Membranes



Applications

- Lipid protein interactions
- Interactions with cells
- Biosensors
- Surface forces: AFM, SFA Experiments
- Surface modification

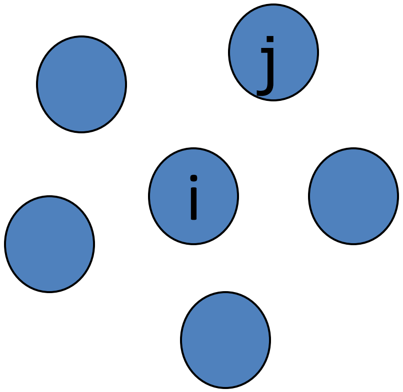
This Work:



- Influence on phase transition
- Bending modulus, d-spacing
- Polymer brush physics

Dissipative Particle Dynamics (DPD)

$$m_i \frac{d^2 \mathbf{r_i}}{dt^2} = F_i \qquad i = 1 \ldots N$$



$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R}$$

Conservative — Dissipative force — Random force

Hoogerbrugge and Koelman, Europhys. Lett., 19, 155 (1992)

Espanol and Warren, Europhys. Lett. 30, 191 (1995)

Achieving the Tensionless State

- Interfacial tension

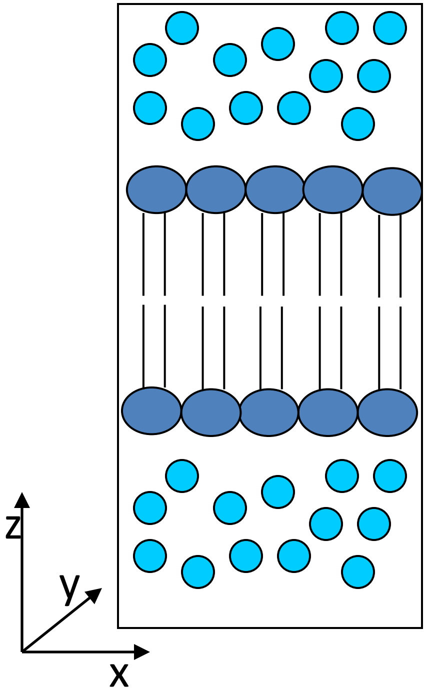
$$\gamma = \frac{1}{2}\int_{-\infty}^{\infty}[p_N(z) - p_T(z)]dz$$

Normal pressure

Lateral pressure

$$p_N(z) = p_{ZZ}(z)$$

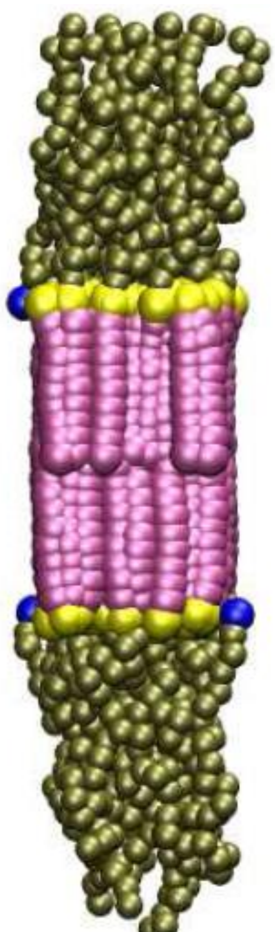
$$p_T(z) = \frac{p_{XX}(z) + p_{YY}(z)}{2}$$

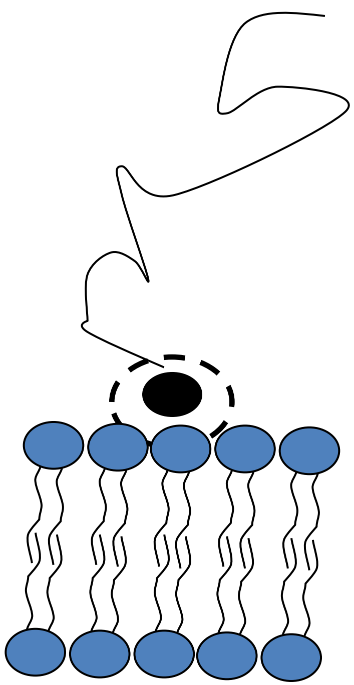


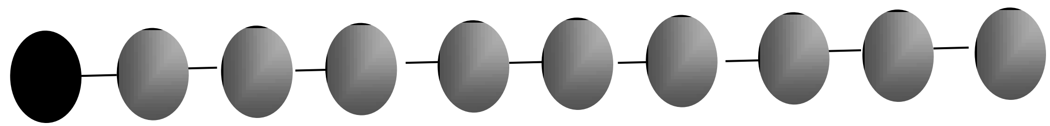
  – Andersen Barostat
  – Volume fluctuates to achieve desired pressure
  – Previous methods : Monte Carlo moves to change the area

Polymer Grafting

- First bead of polymer attached to the bilayer surface







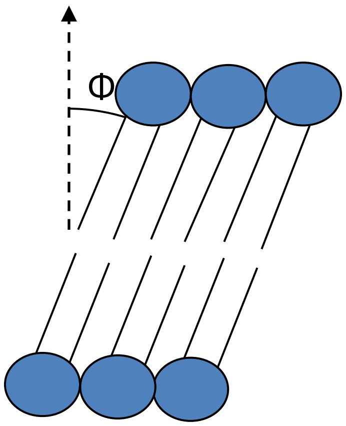
20 BEADS

Grafting Fraction - G_f

$$= \frac{\text{Number of Polymer Chains}}{\text{Number of Lipid Molecules (800)}}$$

G_f = 0, 0.04, 0.09, 0.16, 0.2

Order Parameter

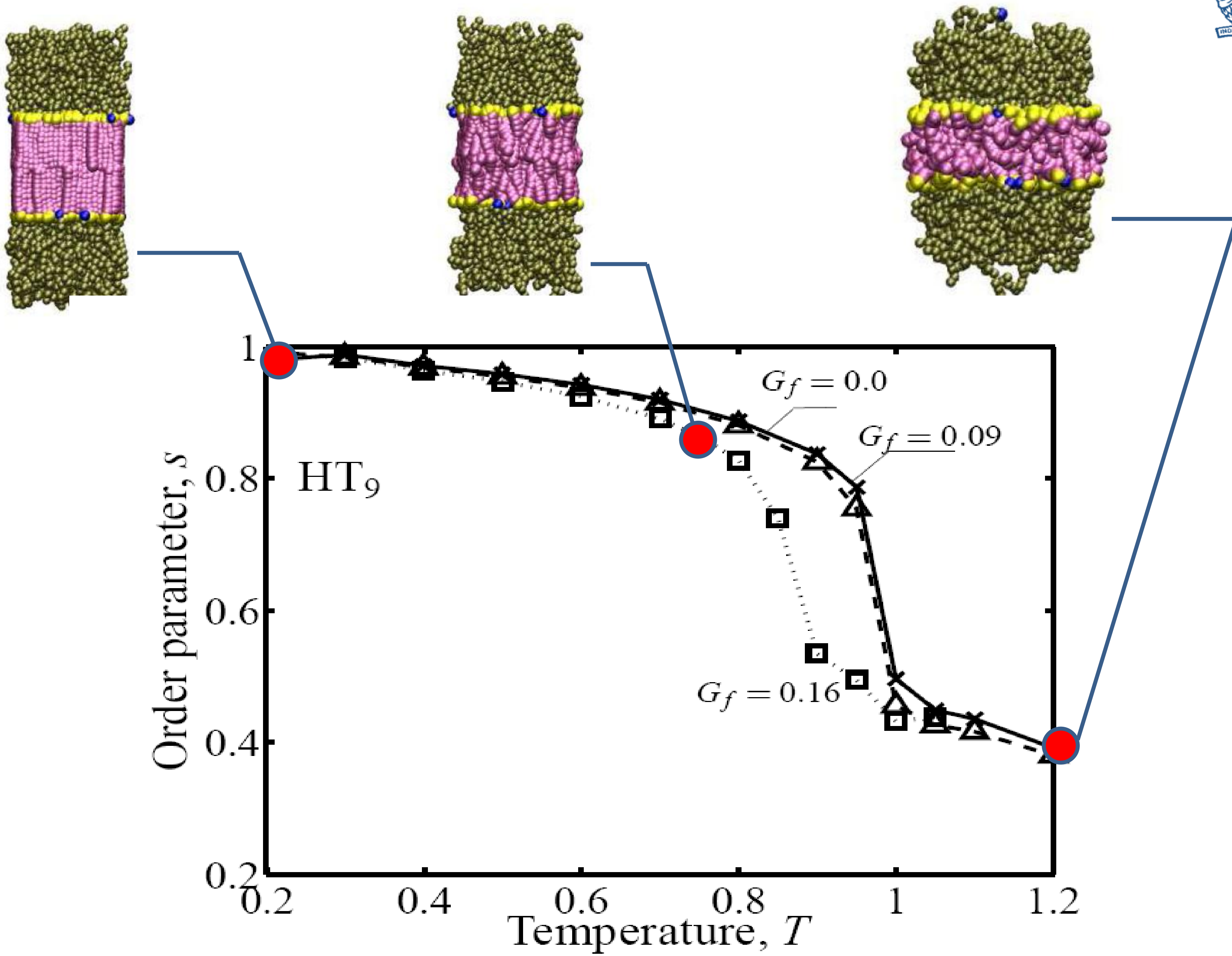


Orientational order parameter

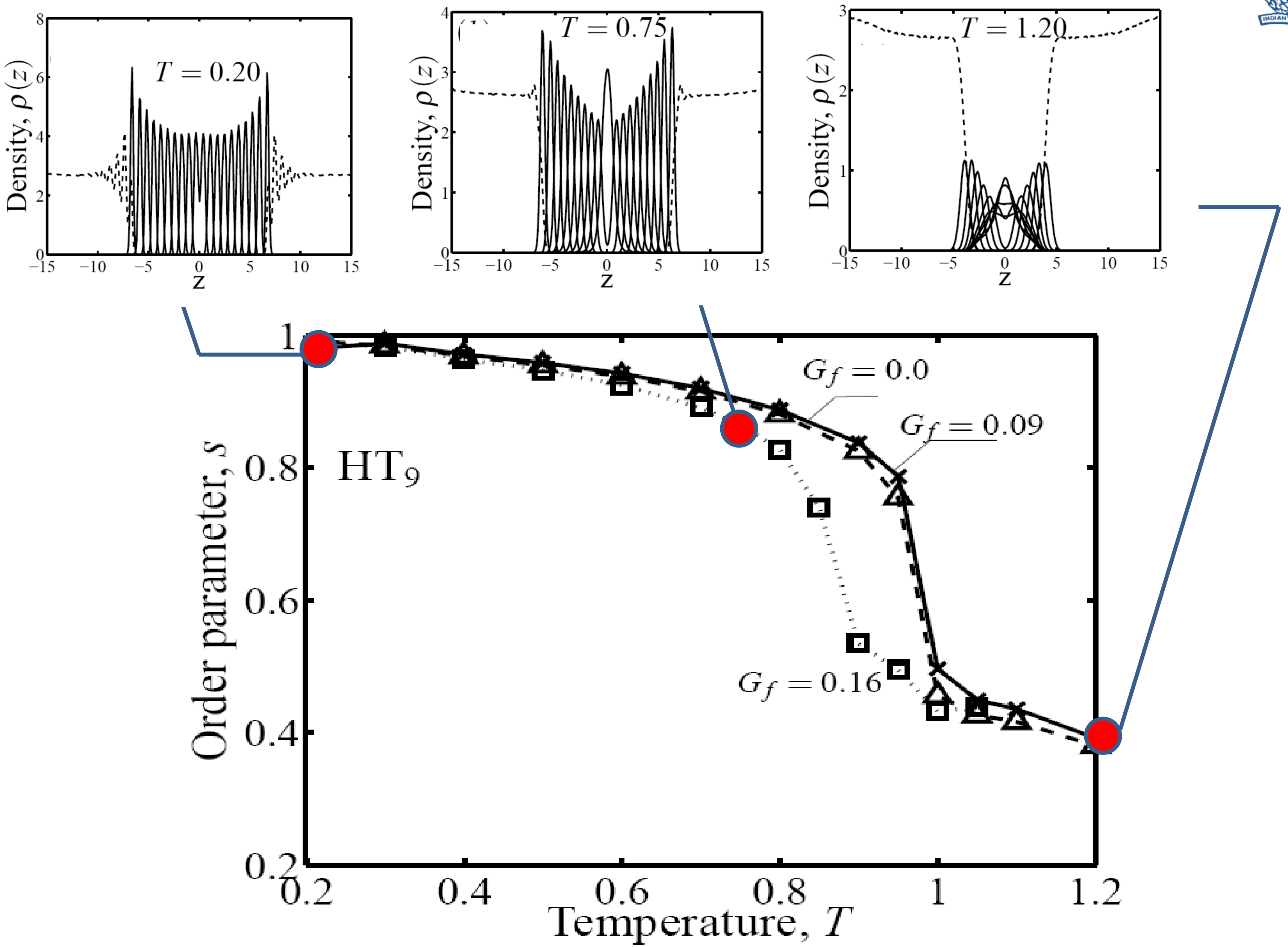
$$s = \frac{1}{2}\left\langle 3\cos^2\phi - 1 \right\rangle$$

Bilayer Melting Transition

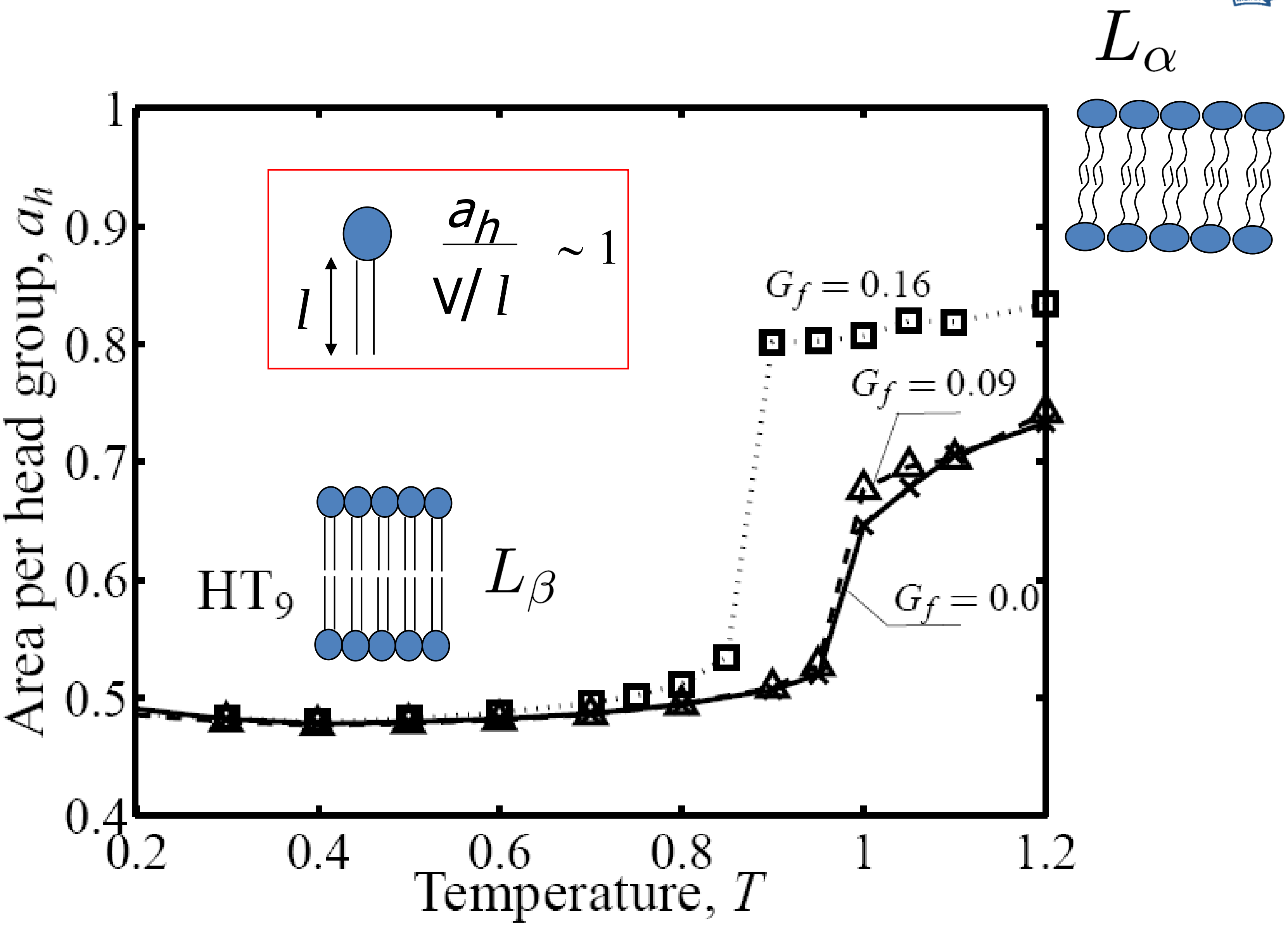
Melting Transition: Low Grafting Fraction



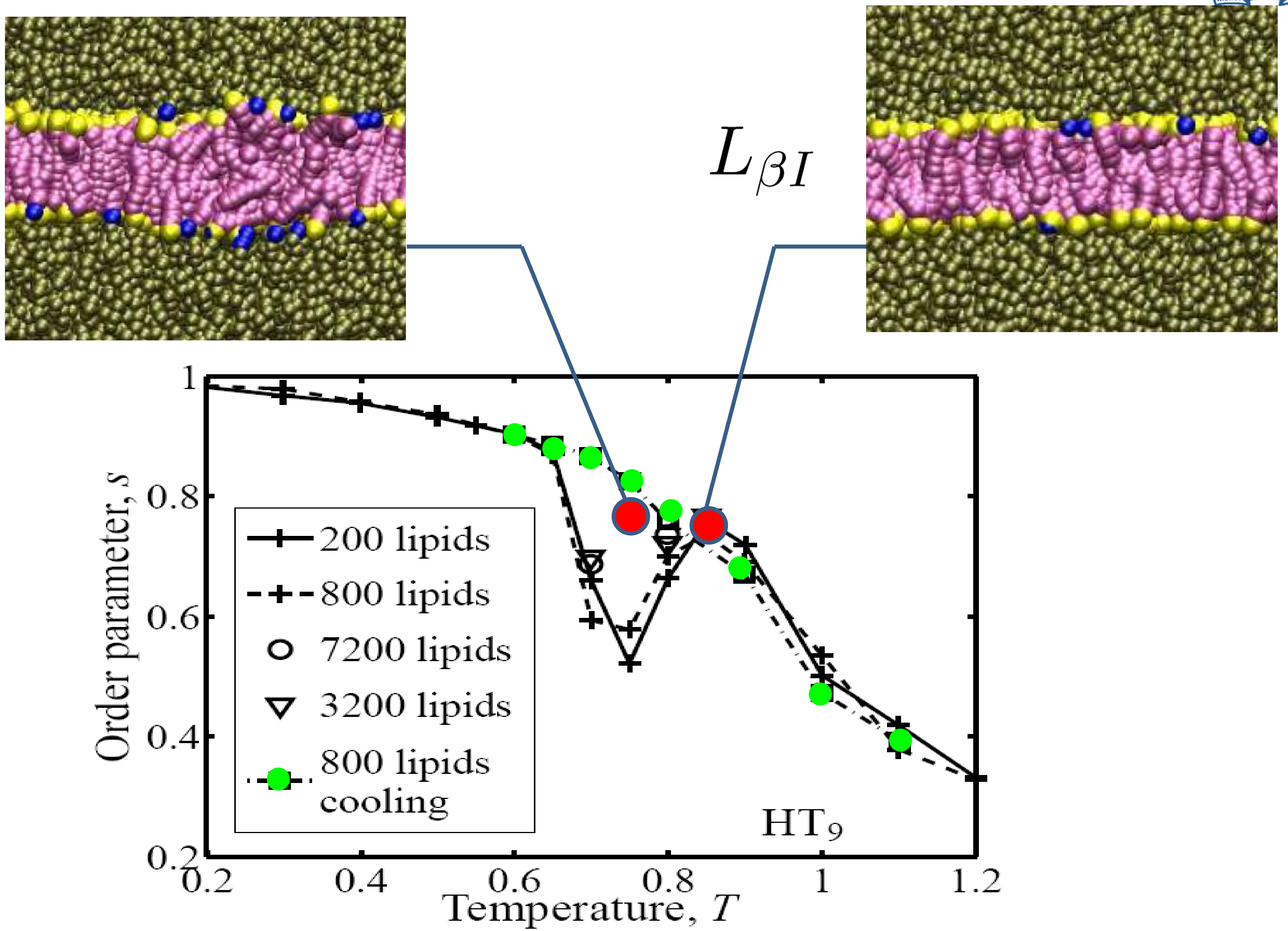
Density Distributions: Low Grafting Fraction



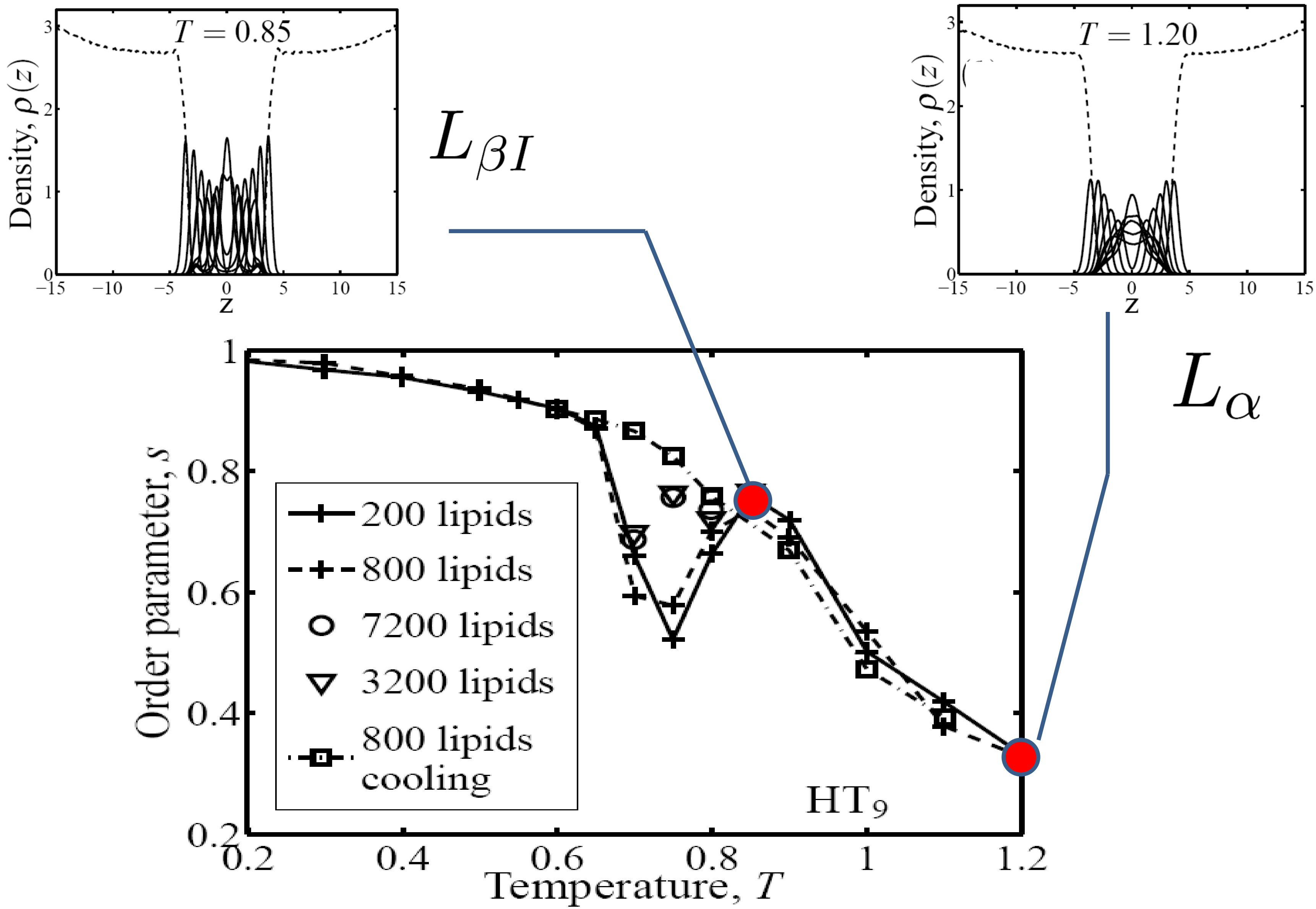
Head Group Area: Low Grafting Fraction



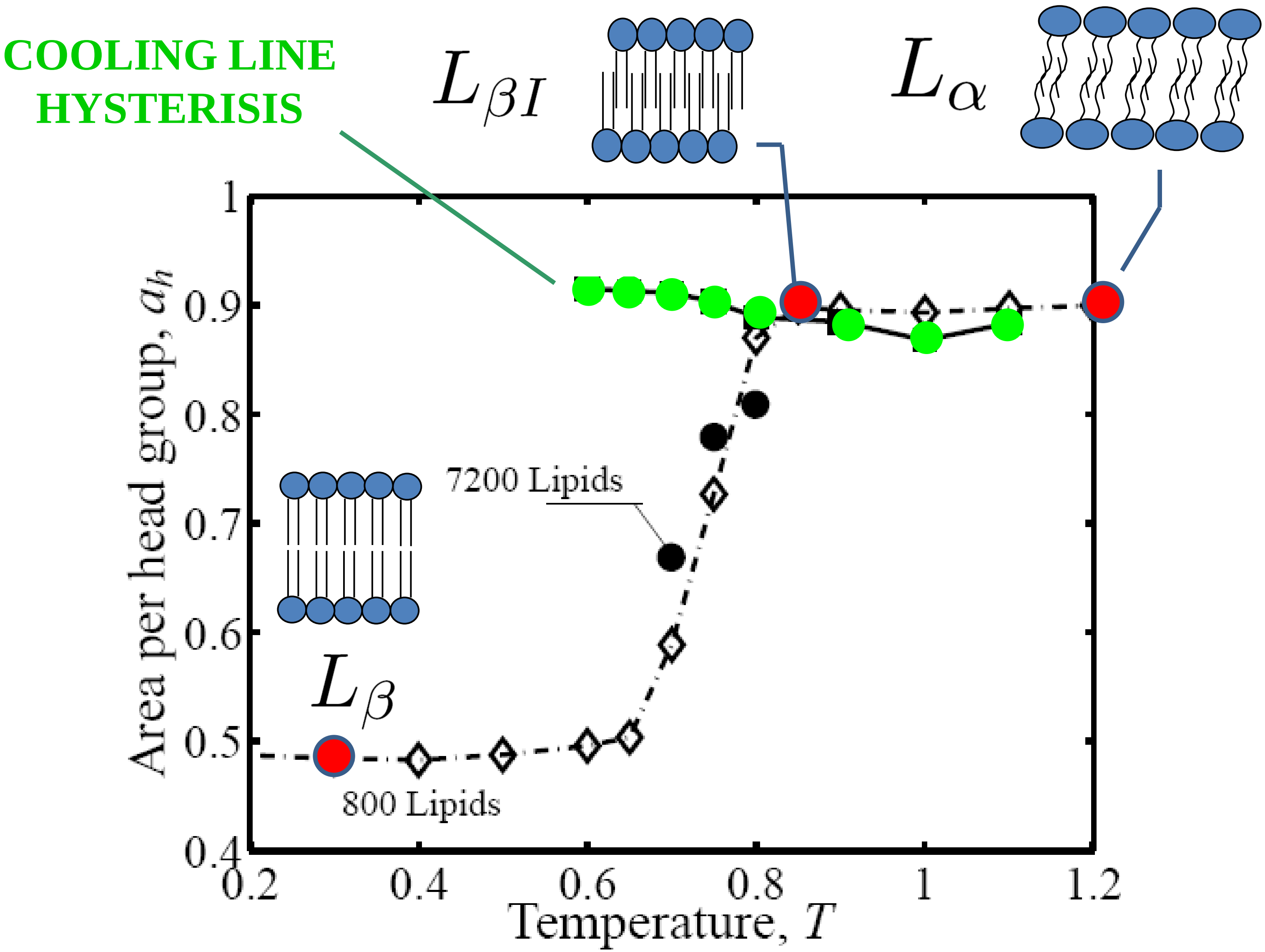
Melting Transition: High Grafting Fraction (0.2)



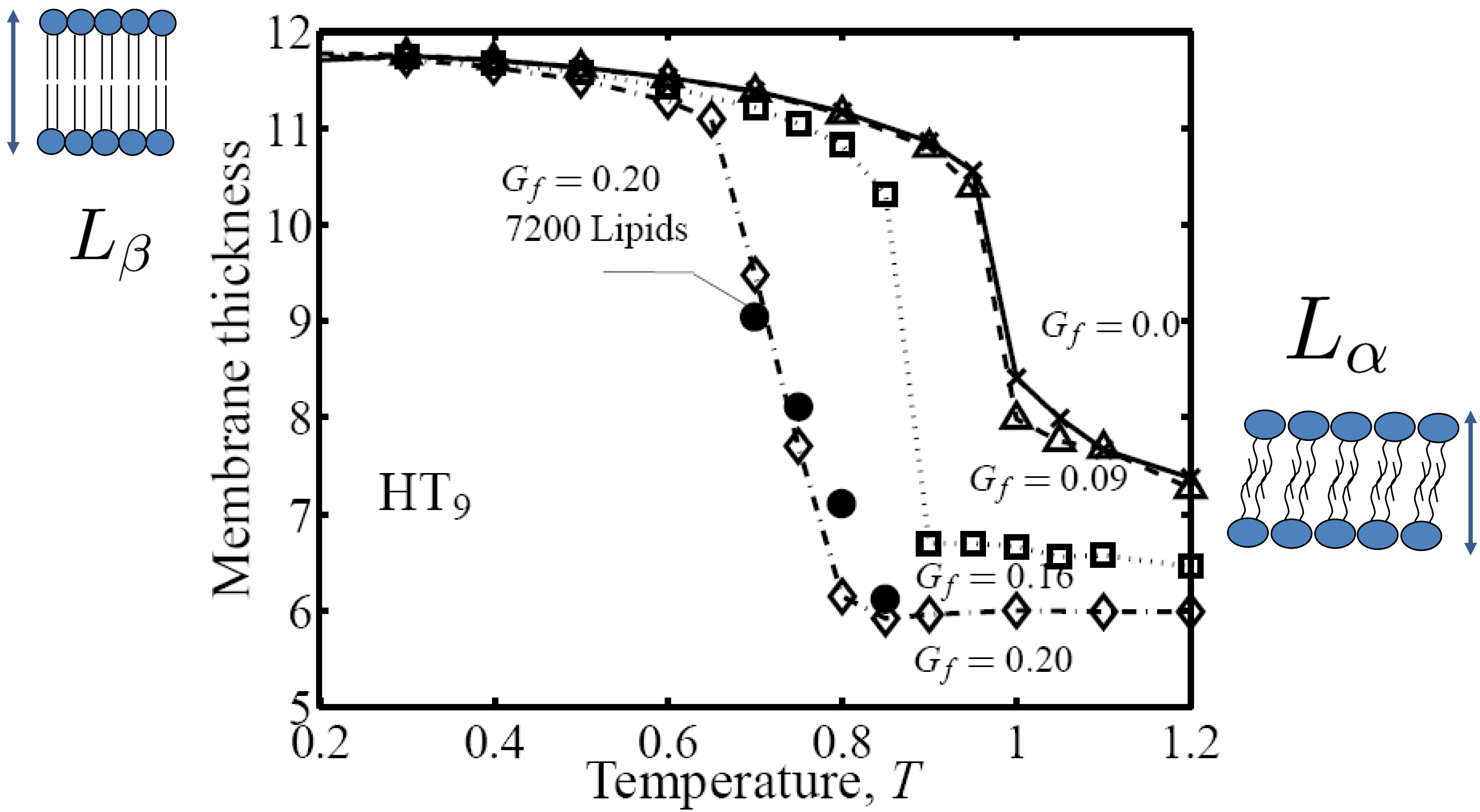
Melting Transition: High Grafting Fraction (0.2)



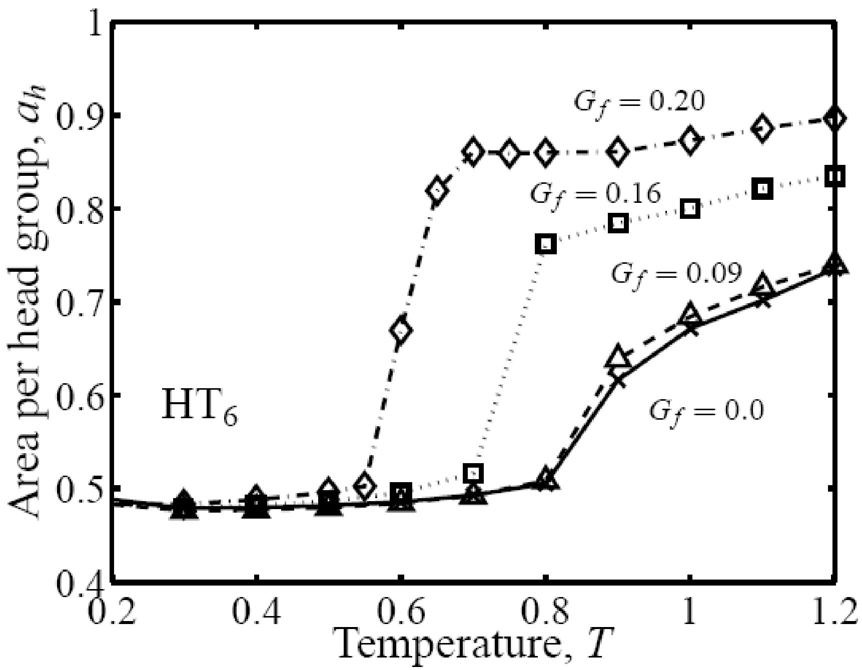
Head Group Area: High Grafting Fraction

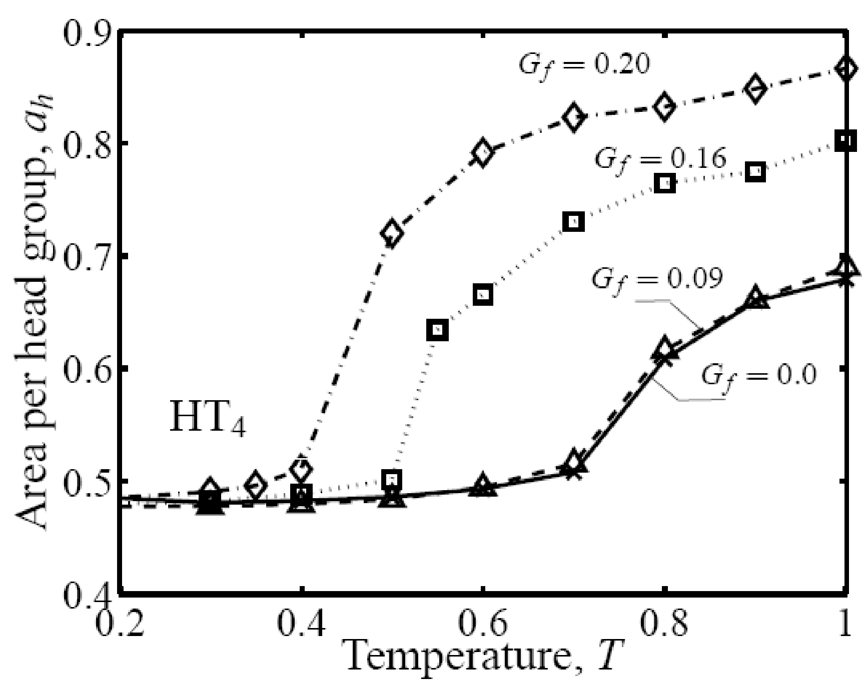


Membrane Thickness



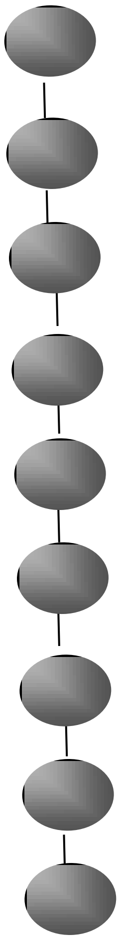
Shorter Lipids: HT6 and HT4

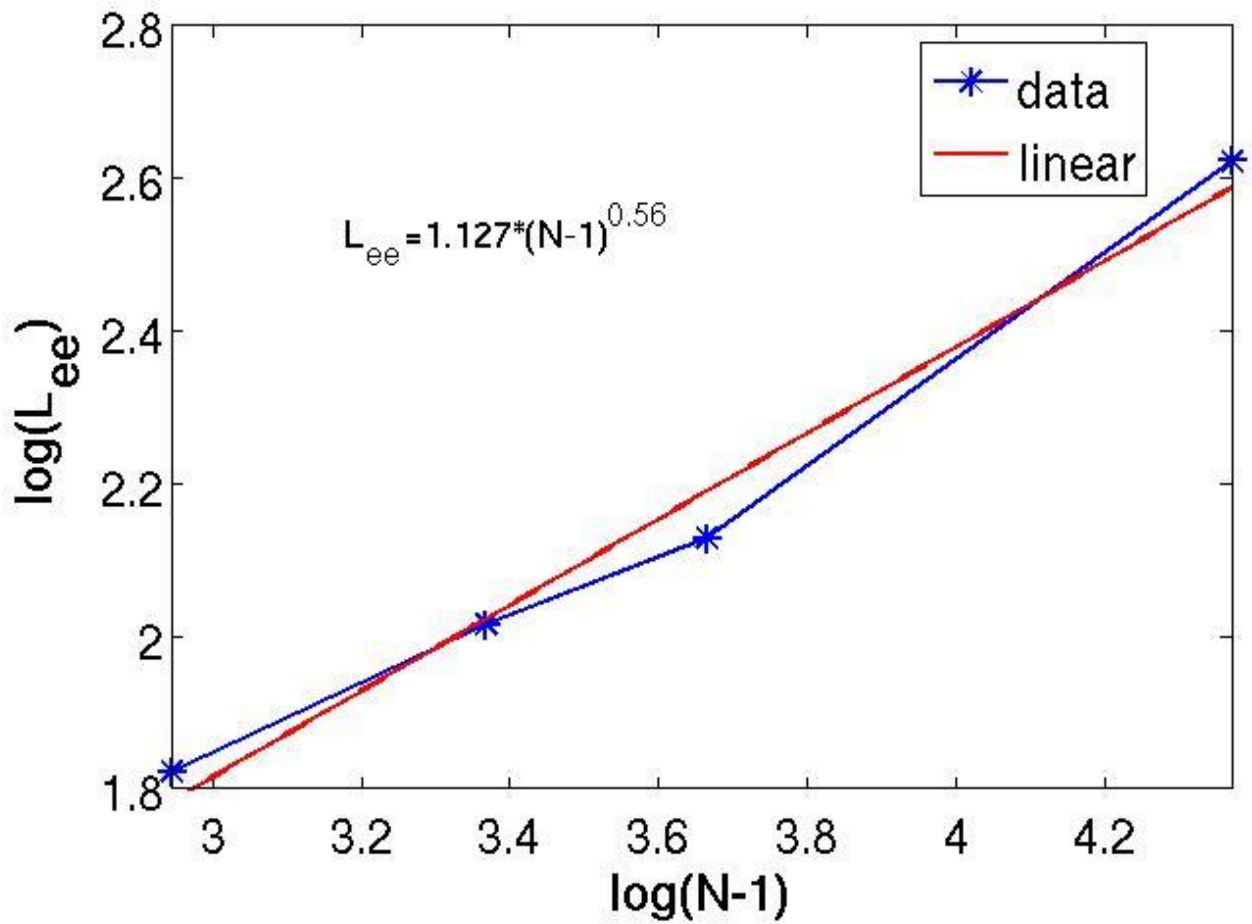




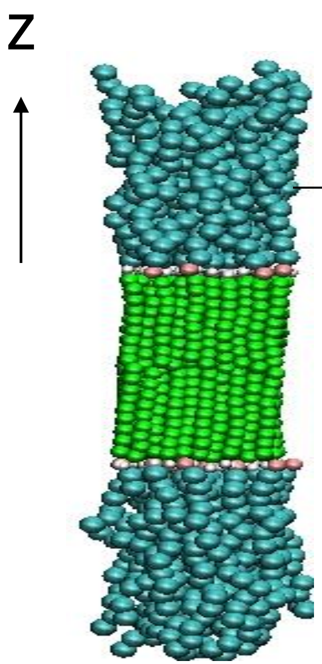
Polymer Scaling Relations

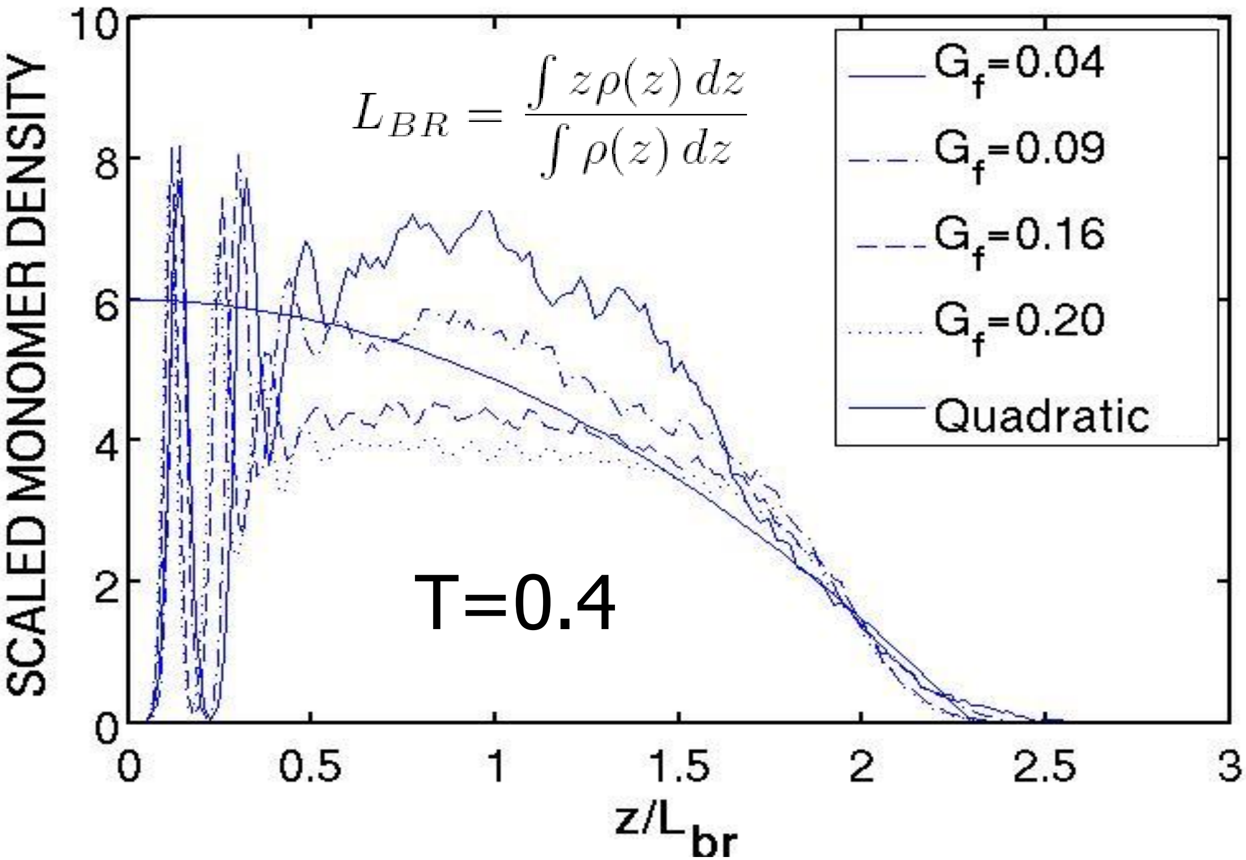
Bulk Polymer Scalings: Bead Spring Model



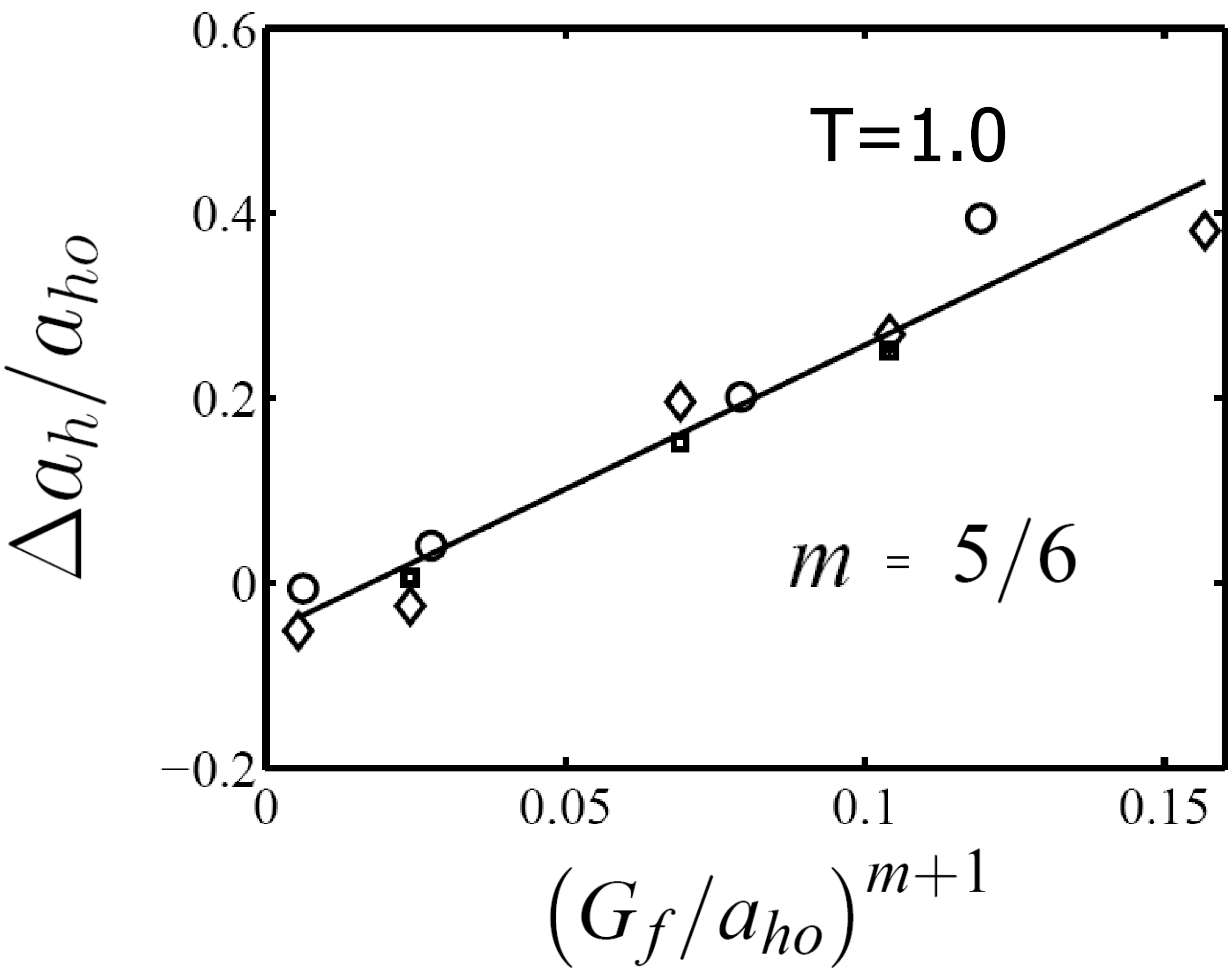


Monomer Density Scaling





Scalings for Area per Head Group: Single Tail Lipids

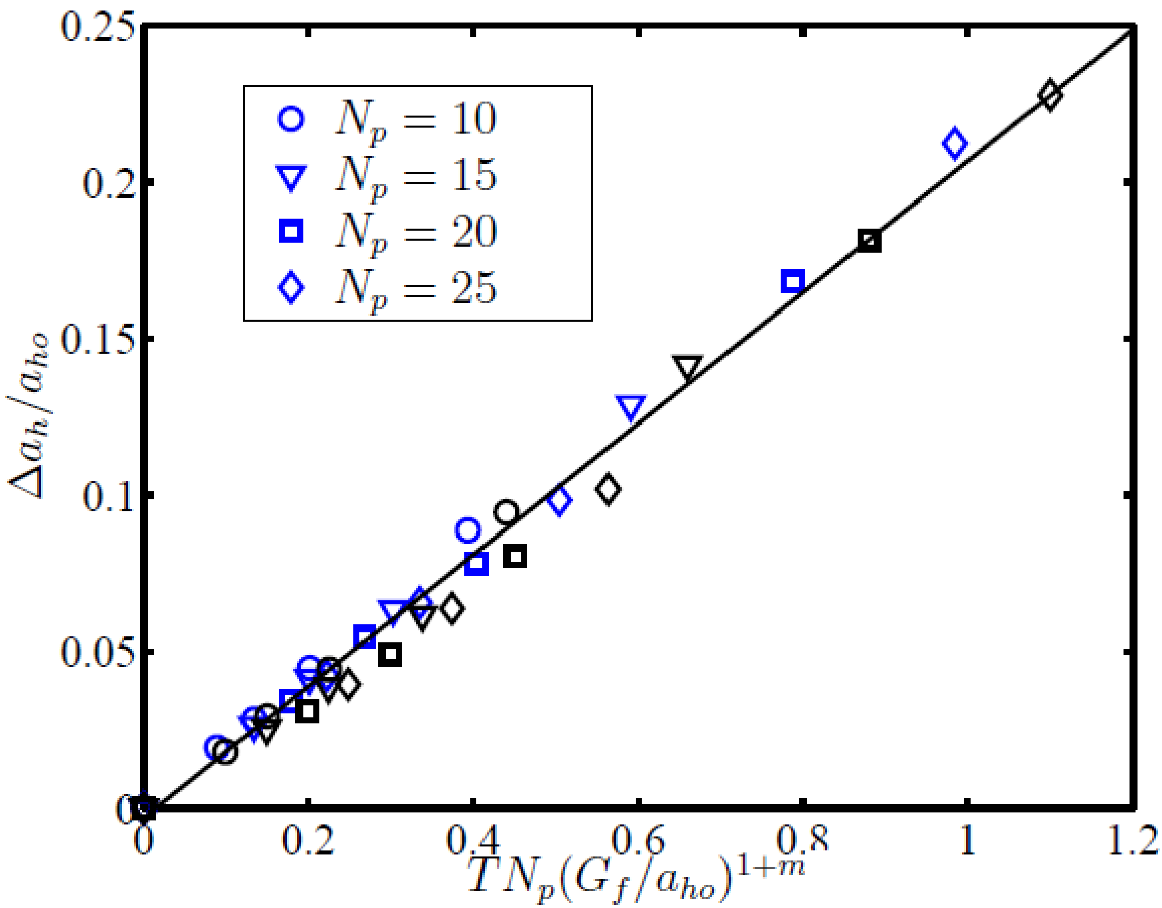


$$\frac{\Delta a_h}{a_{ho}} \approx (G_f / a_{ho})^{m+1}$$

$$\Delta a_h = a_h - a_{ho}$$

Polymer free membrane

Scalings for Area per Head Group: Two Tailed Lipids



$$\Delta a_h = a_h - a_{ho}$$

Polymer free membrane

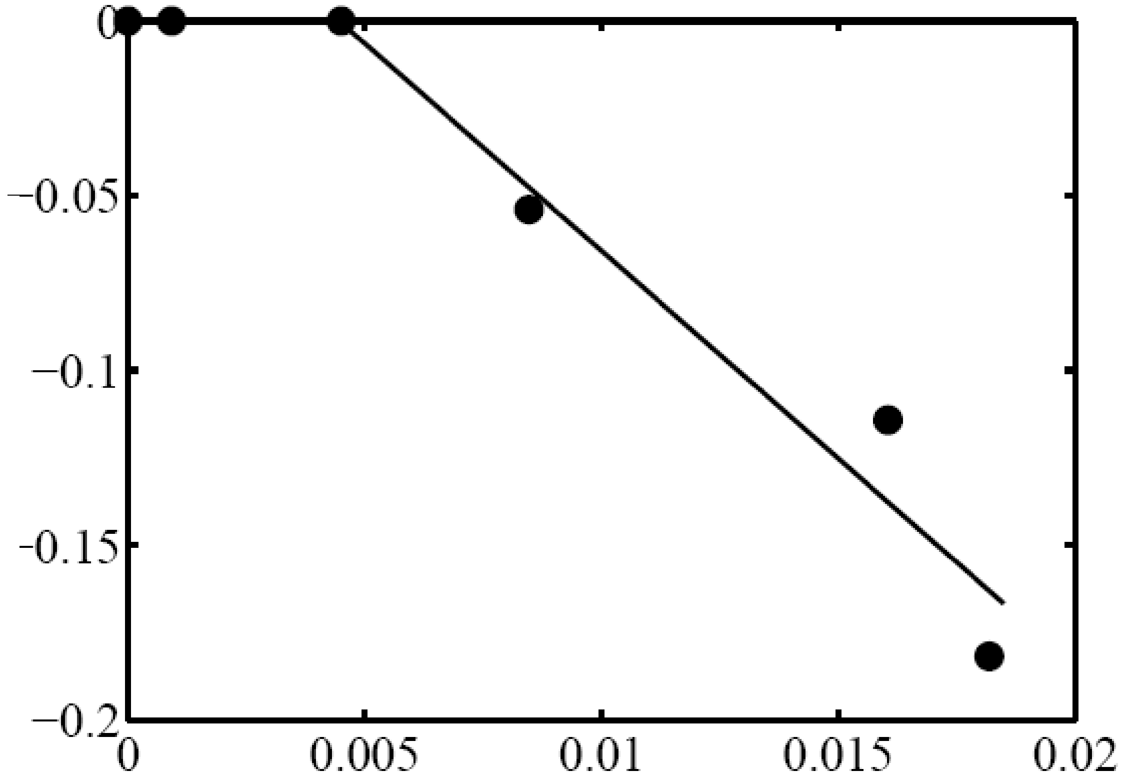
Two tail lipids

Within the experimental range(~0.3)

Marsh, Biochim. Biophys. Acta, 1615, 33 (2003)

Scalings for Decrease in Transition Temperature

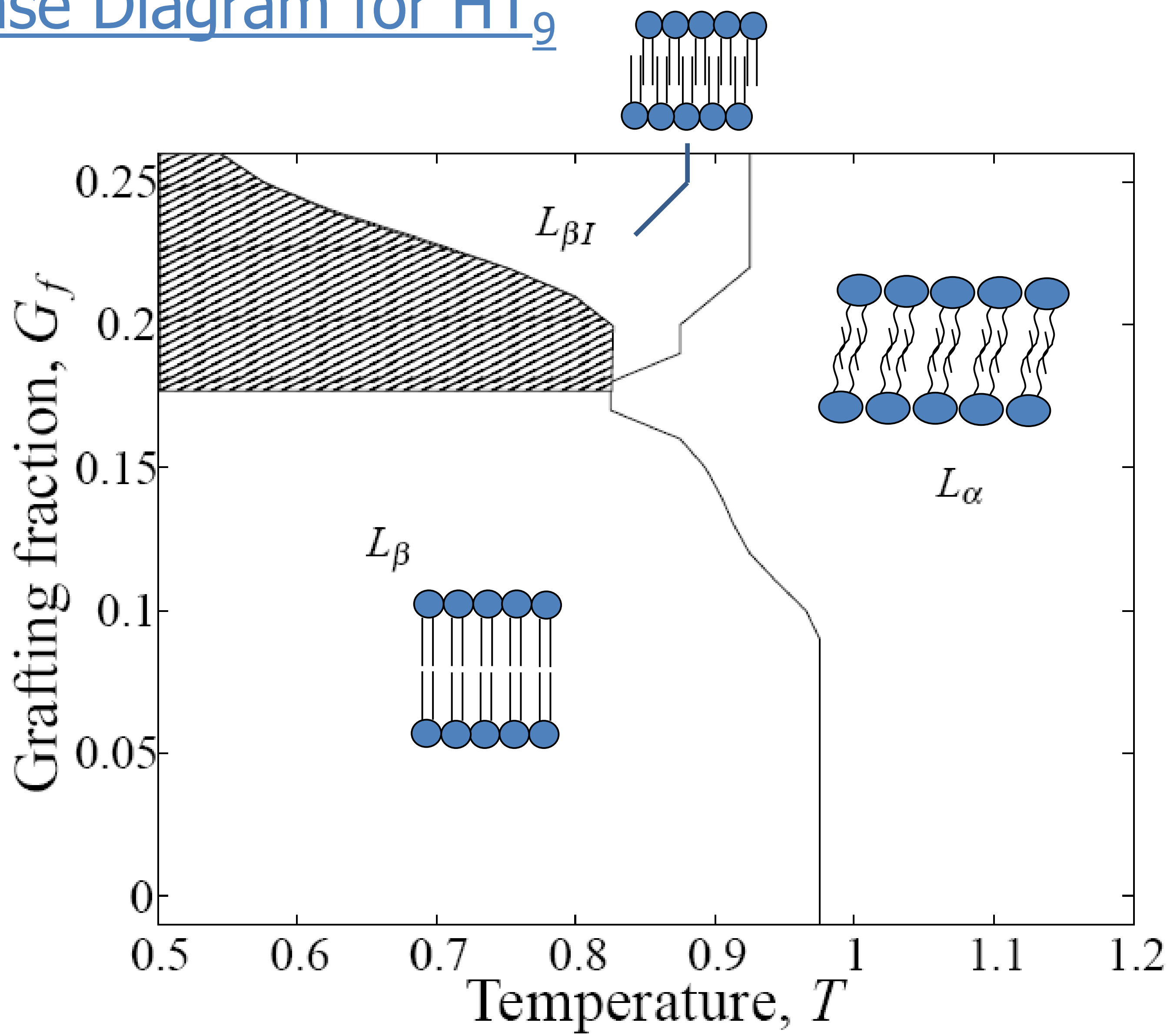
$$\Delta T = T - T_o$$



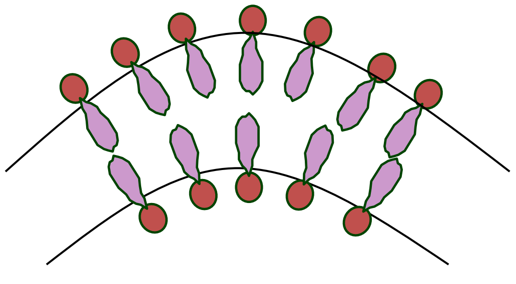
$\Delta T/T$

$\Delta a_h (G_f/a_h)^{1+m}$

Phase Diagram for HT_9



Bending Modulus



Bending Modulus: Theoretical Background

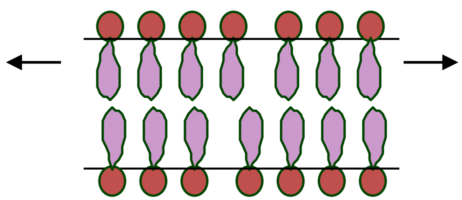
- Energy of the lipid bilayer

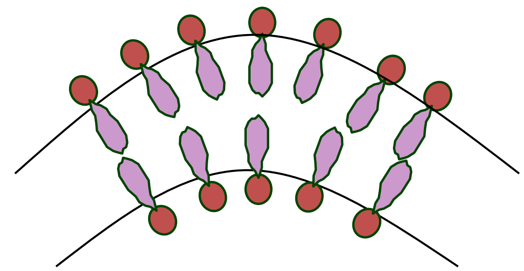
$$E = \int dA \left(\gamma + \frac{\kappa}{2}\left(c_1 + c_2 - 2c_0\right)^2 + \bar{\kappa} c_1 c_2 \right)$$

Interfacial tension

Bending modulus

Saddle-splay modulus





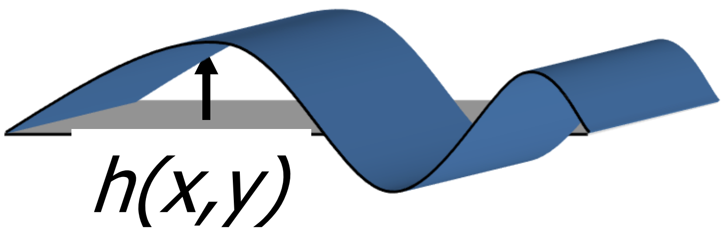
- For a flat bilayer

$$E = \int dA \left(\gamma + 2\kappa \bar{c}^2 \right)$$

Theoretical Background contd…

- Expressing in terms of fluctuations

$$e(h) = \frac{\gamma}{2}(\nabla h)^2 + \frac{\kappa}{2}(\nabla^2 h)^2$$



- Final equation, after Fourier transform and using equipartition theorem

$$[h(x,y) \rightarrow h(q)]$$

$$S(q) = A\langle |h(q)|^2 \rangle = \frac{kT}{\kappa q^4 + \gamma q^2}$$

0

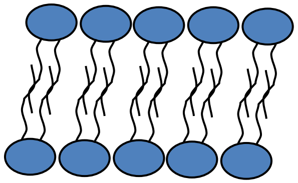
Valid only at low $q=2\pi/L$ ⟶ Large simulation Box needed

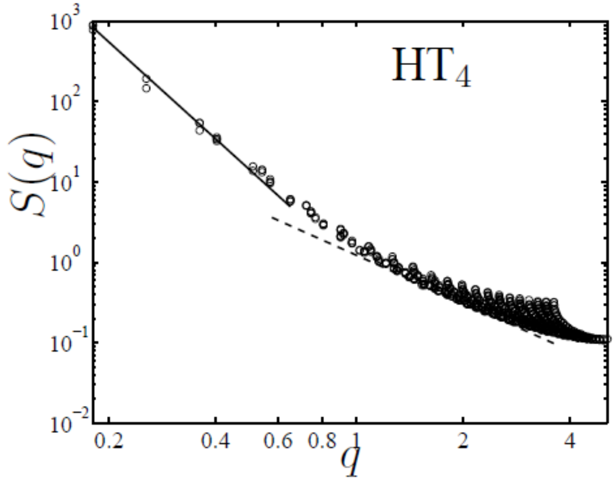
- At high q(L< membrane thickness)

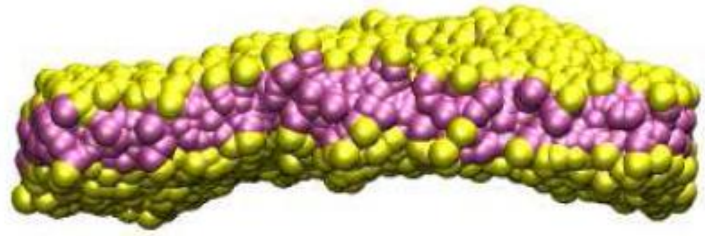
$$S(q) = \frac{kT}{\gamma_p q^2}$$

γ_p- protrusion tension

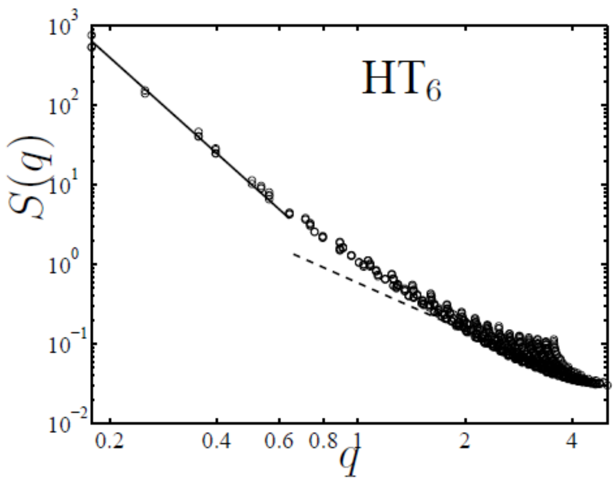
Frequency Spectrum: High T

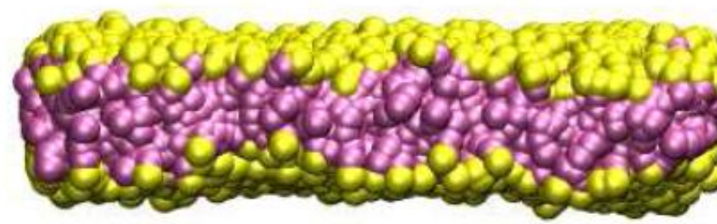






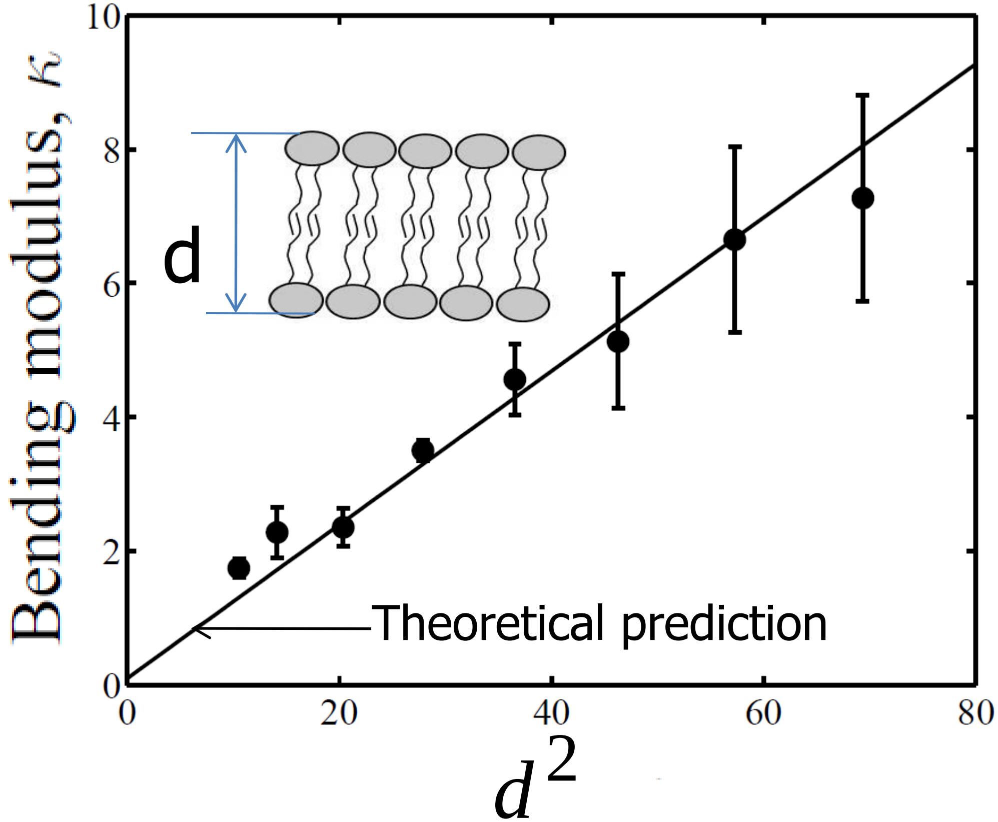
HT$_4$

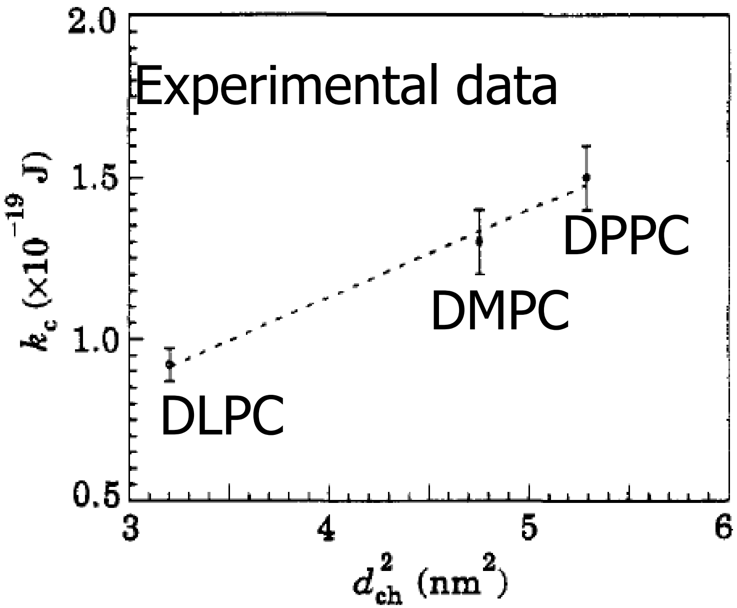




HT$_6$

Effect of Membrane Thickness

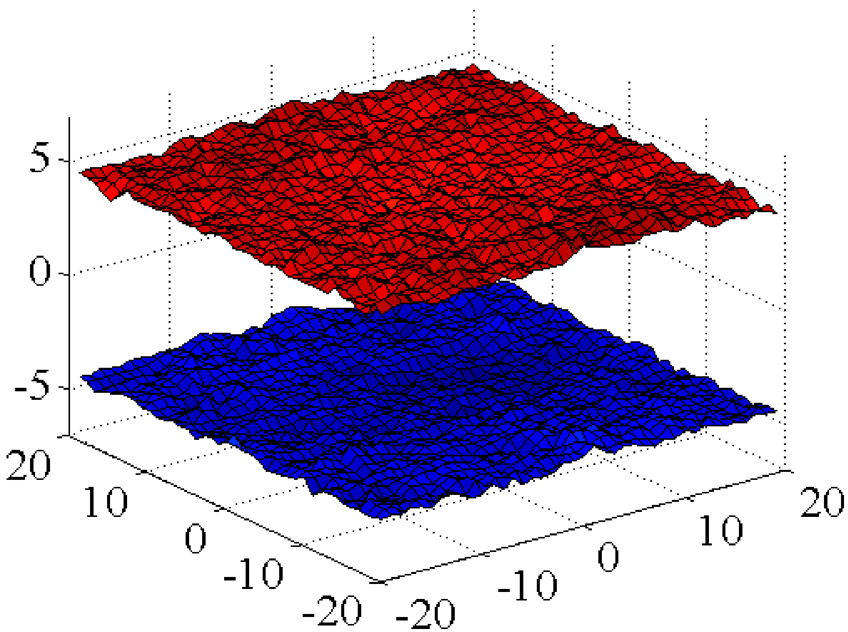


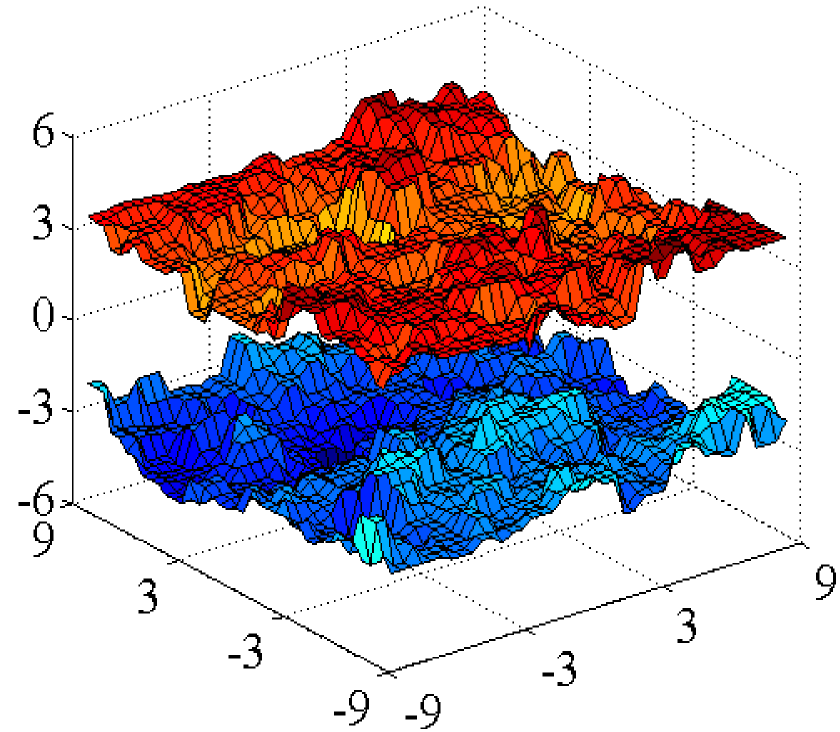


Continuum theory for elasitc sheets: $\kappa \propto d^2$

Fernandez-Puente et al., 1994

Bilayer Headgroup Surface (Delanuay Triangulation)

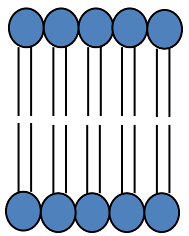


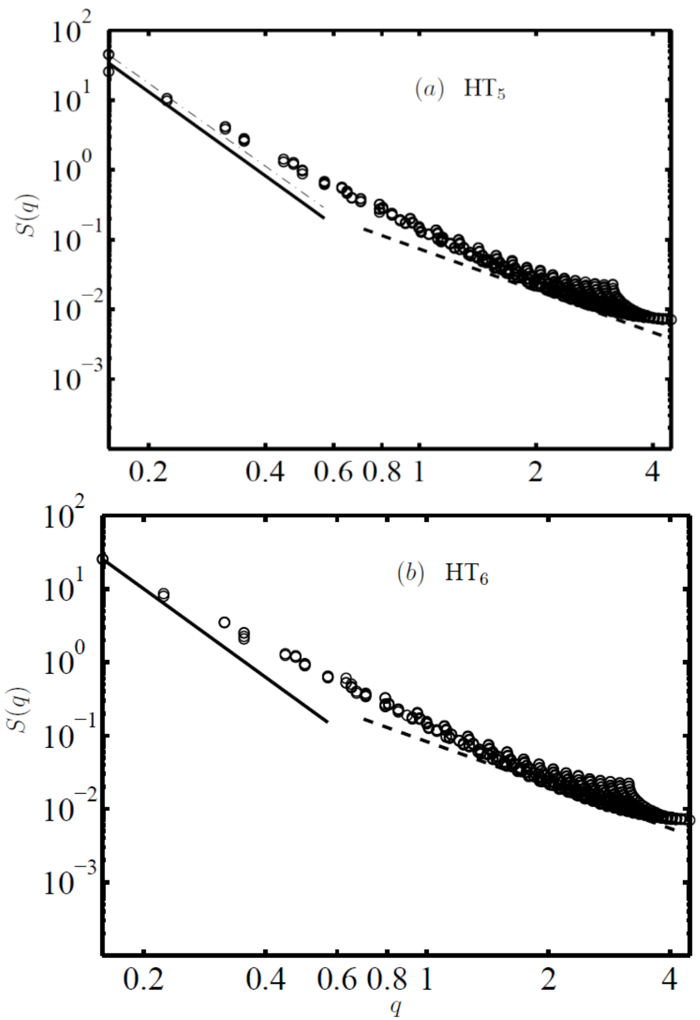


L_β phase: Very low fluctuations
Low temperature

L_α phase: High fluctuations
High temperature

Frequency Spectrum: Low T (GEL PHASE)





$$\kappa_{gel} / \kappa_{lc} = 12.5$$

$$\kappa_{gel} / \kappa_{lc} = 16.4$$

DPPC: $\kappa_{gel} / \kappa_{lc} \approx 10 \text{ to } 20$

Lee et al., PRE, 64, 020901 (2001)

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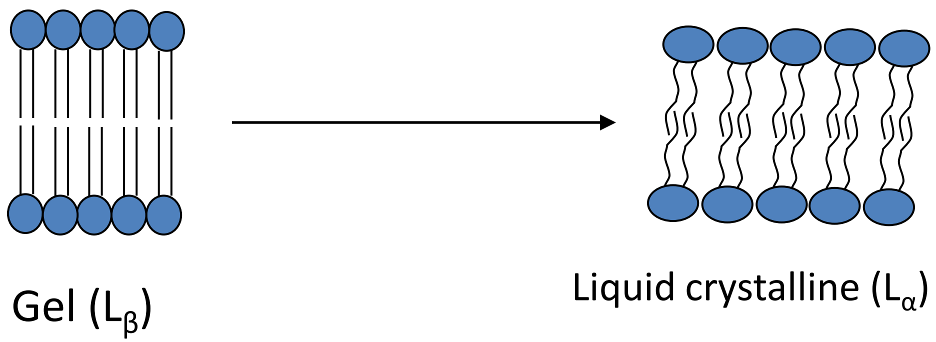
- Venkat Ganesan (U. T. Austin)
- Animesh Agarwal

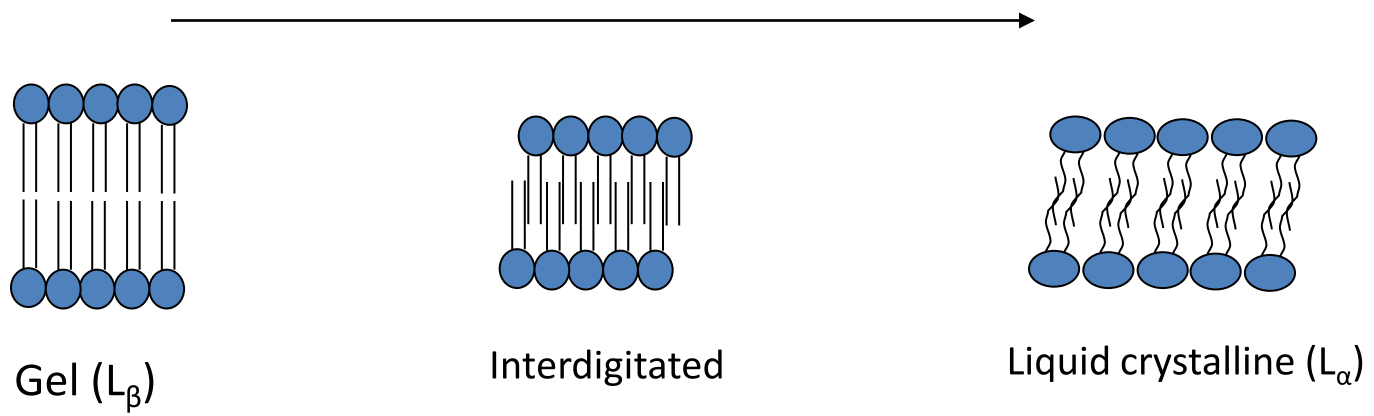
- Funding: Department of Science and Technology (DST) India, Procter and Gamble, USA

Summary

Low grafting density

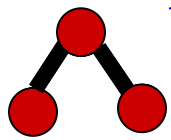


High grafting density



Surfactant Bilayers: Influence of Composition on Phase Behaviour

Bilayer Components

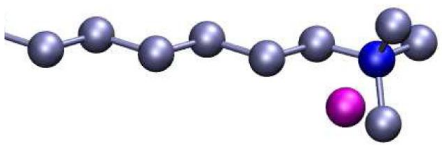


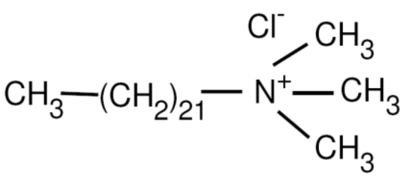
Explicit SPC

Water

Behenyl Trimethyl Ammonium Chloride (BTMAC)

Surfactant

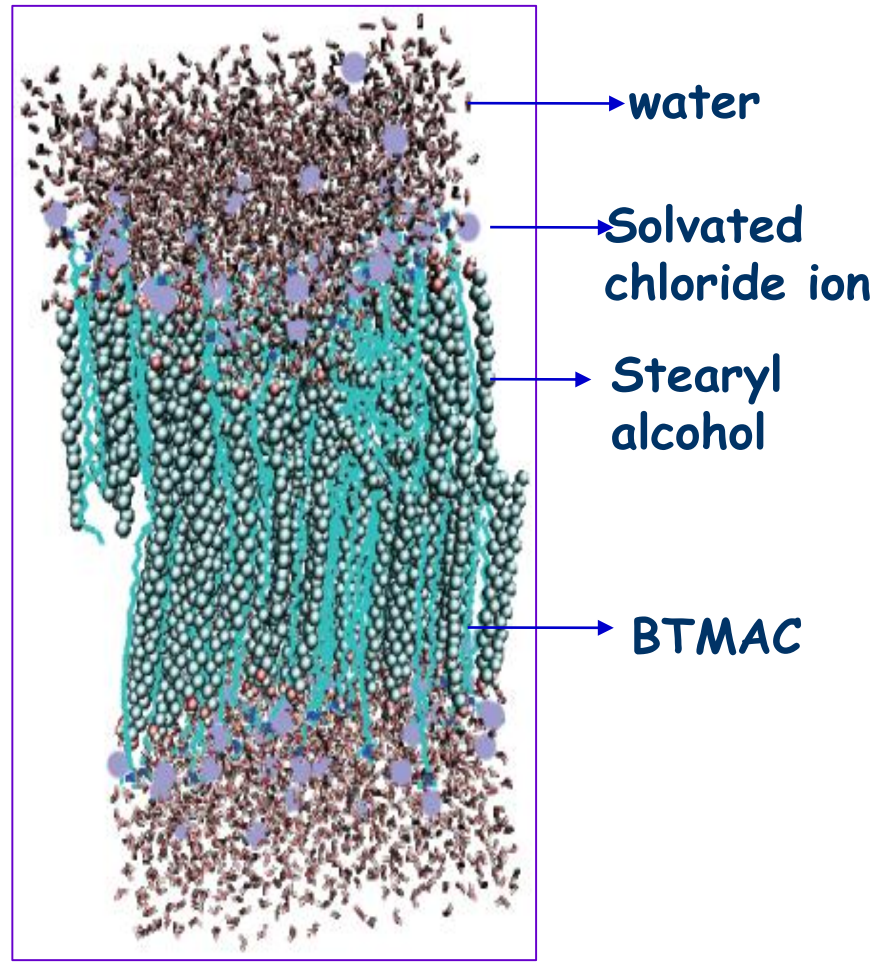




Stearyl Alcohol (SA)

Co-Surfactant

$CH_3 — (CH_2)_{17} — OH$



Membrane compositions investigated

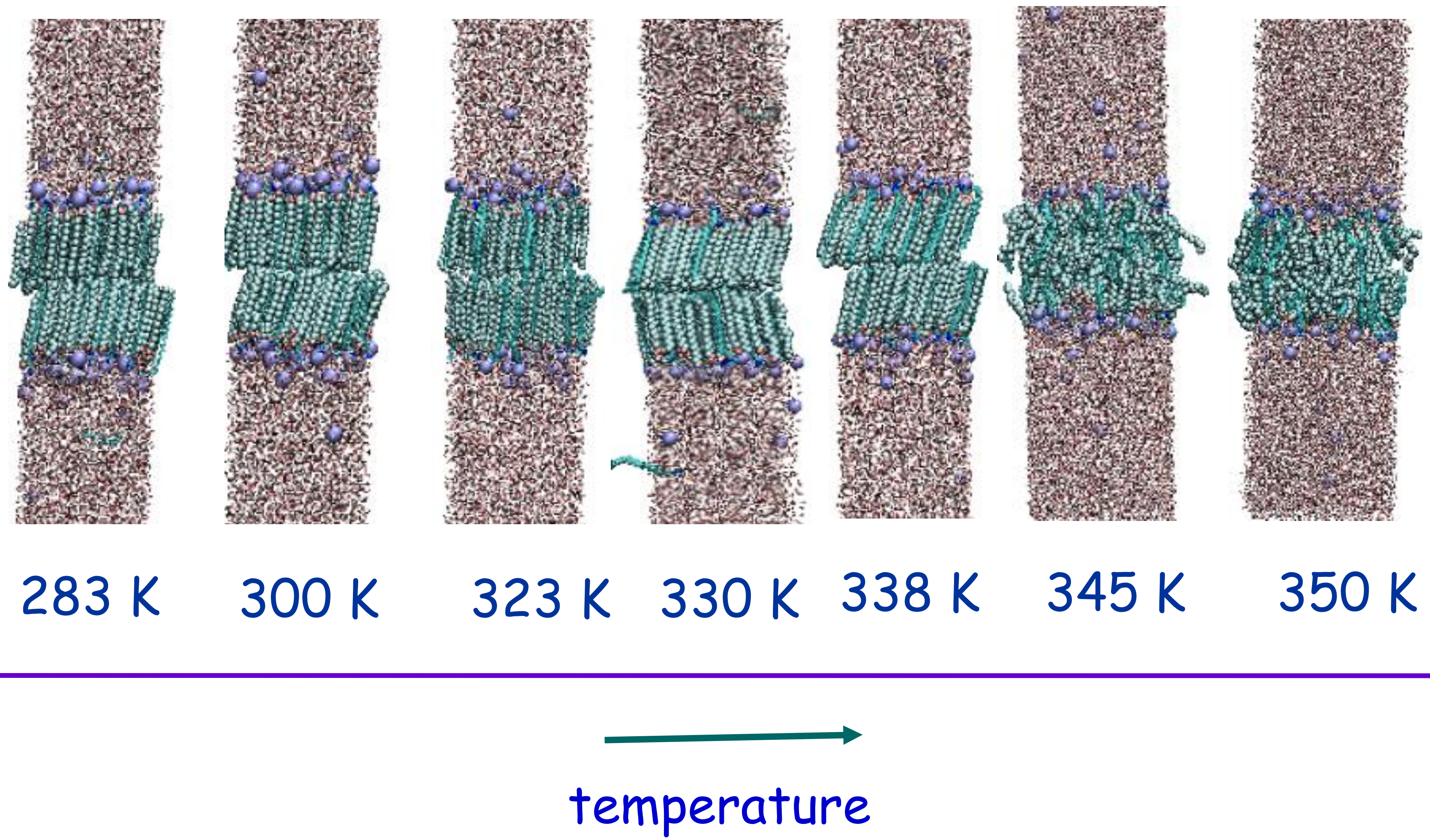
Bilayer	Number of molecules			NVT (ns)	NPT (ns)
	BTMAC	SA	Water		
S1	50	150	13484	1	25
S2	50	150	4000	1	25
S3	74	150	4000	1	25
S4	100	150	4000	1	25

Water effect (S1–S2)

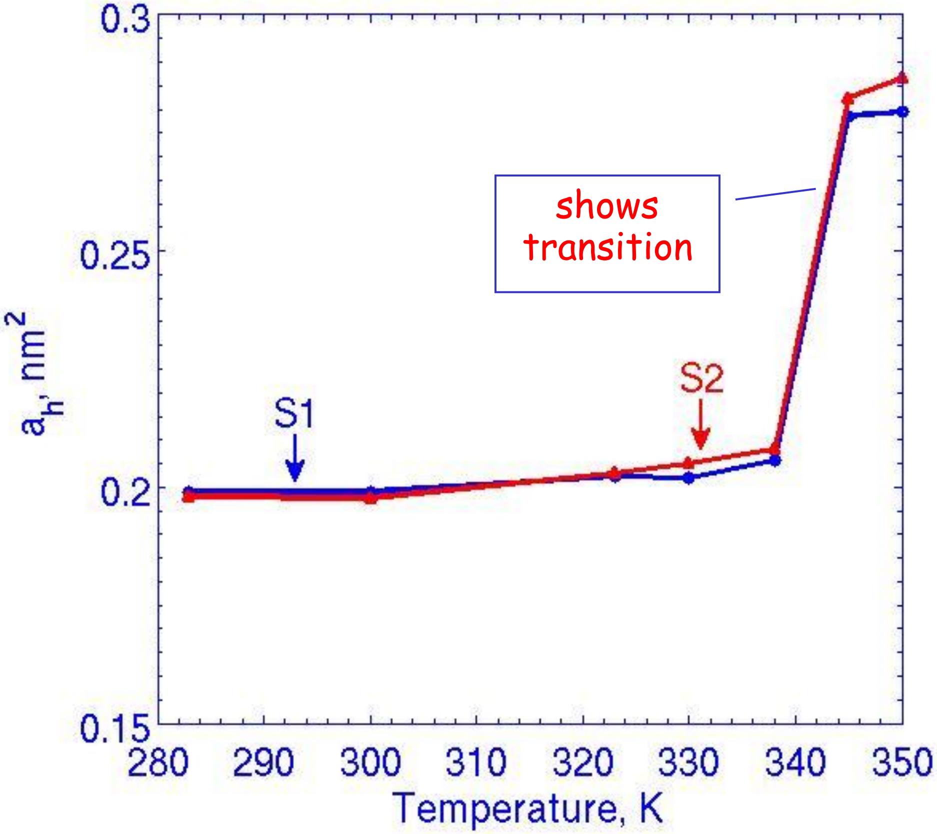
BTMAC effect (S2–S4)

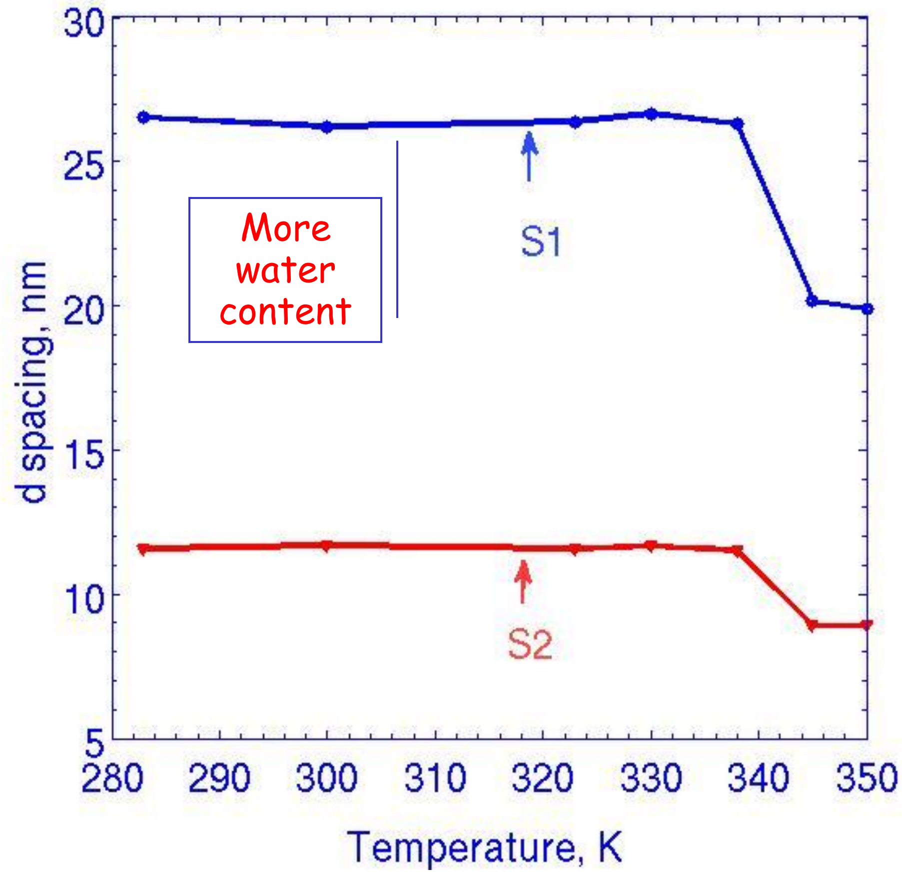
Semi-isotropic ensemble
Simulations run using **GROMACS**

Bilayer with high water content: S1



Area per head group (a_h) and d-spacing



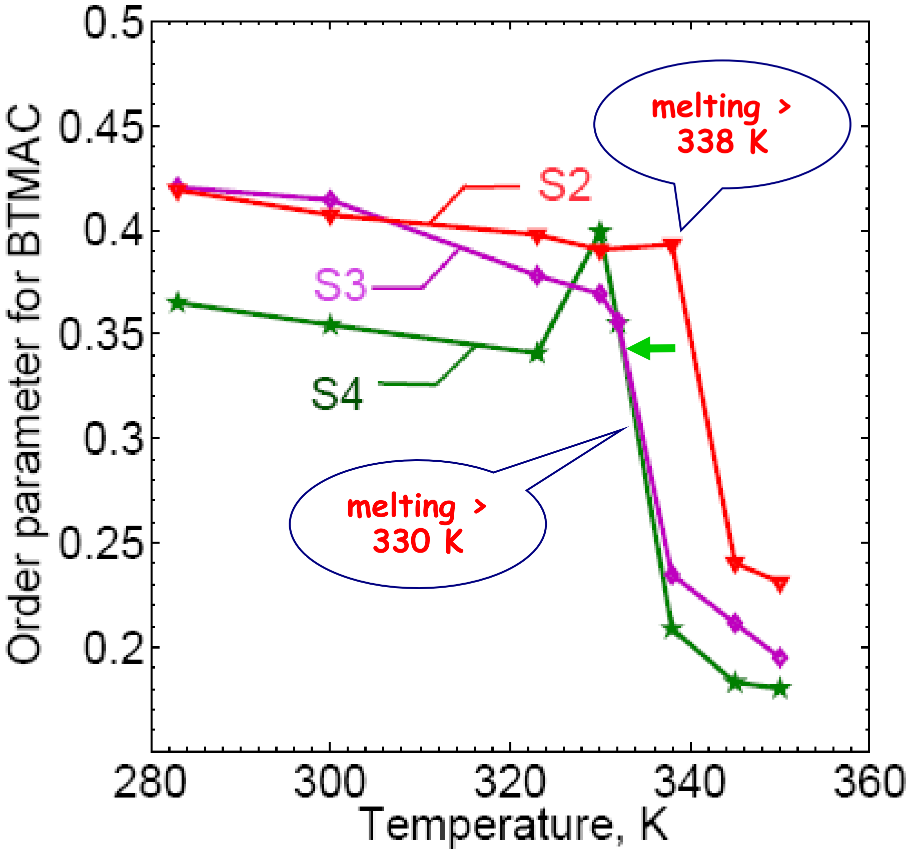


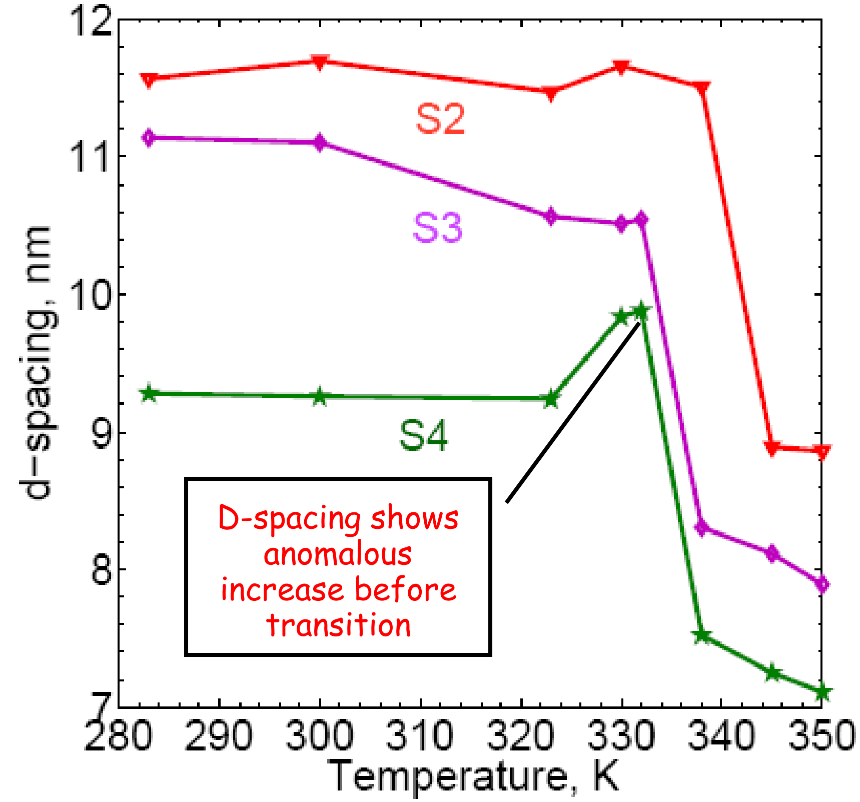
Water content does not influence the transition temperature

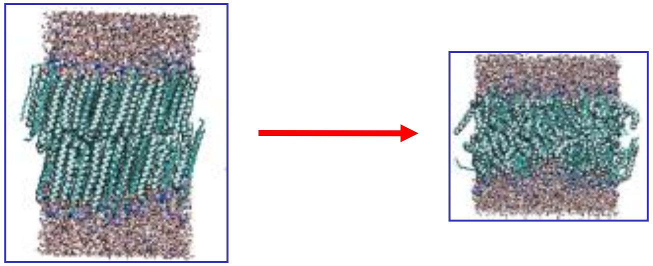
Influence of membrane composition

Larger BTMAC head groups affect transition

Order parameter and d-spacing

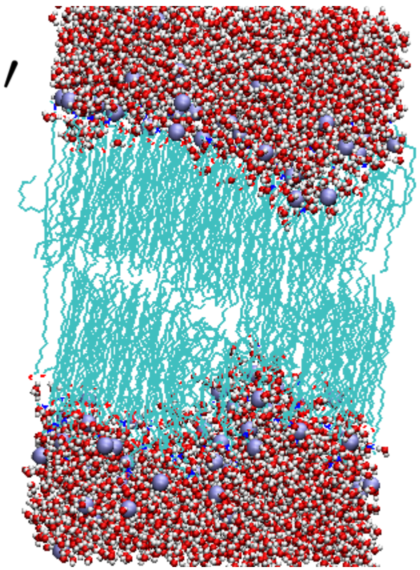




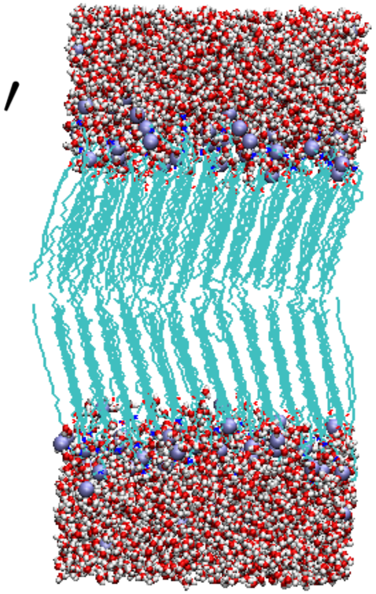


Density Distributions for S4

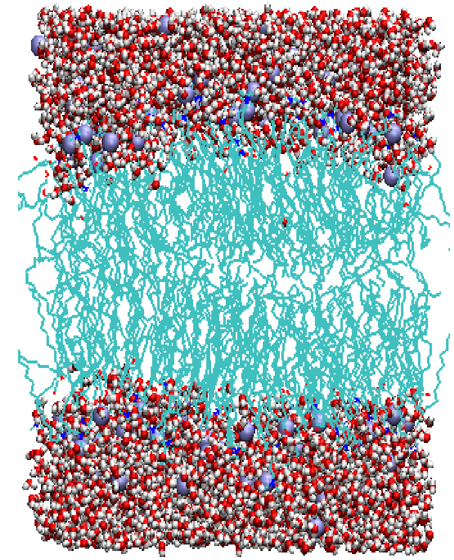
$P_{\beta'}$



$L_{\beta'}$

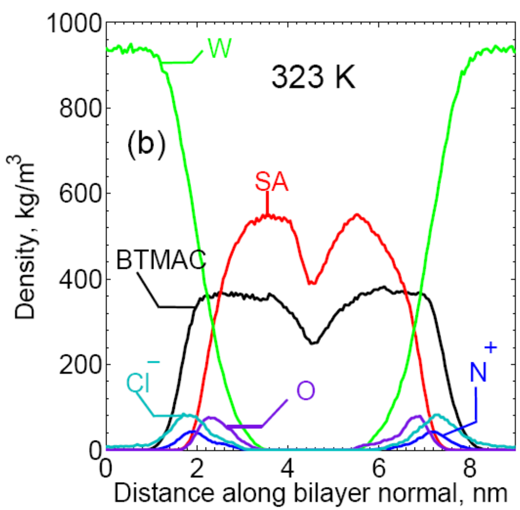


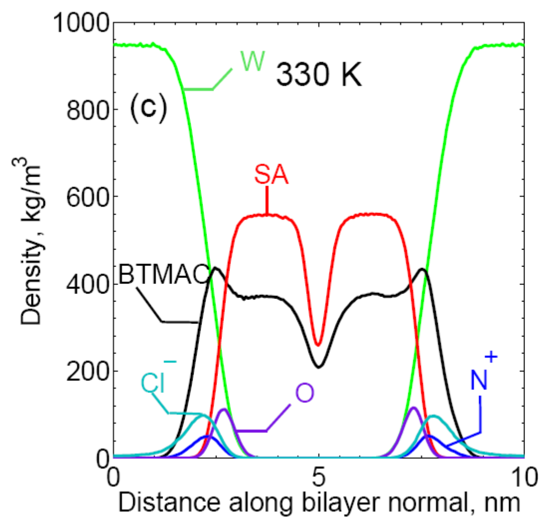
L_{α}

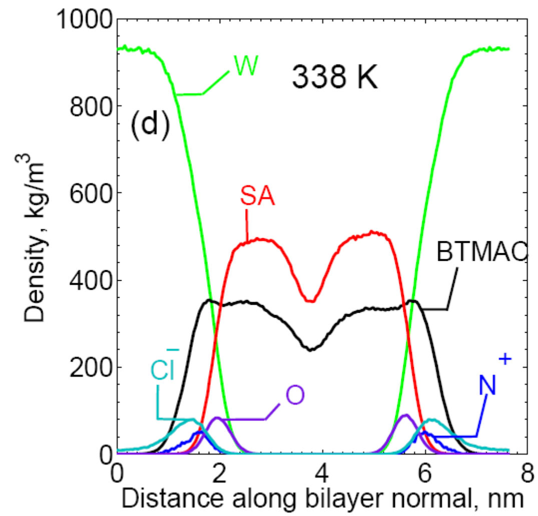


Diffuse Interface

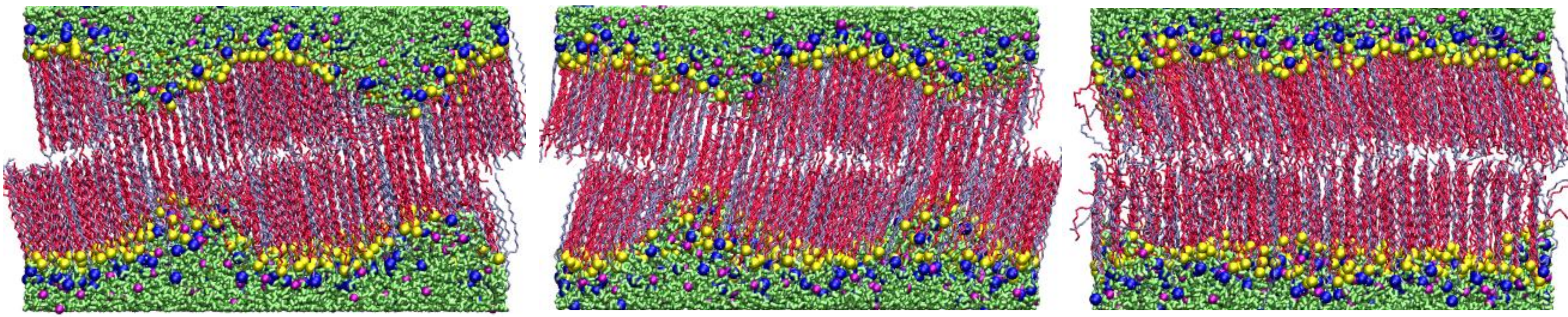
Sharp Interface







Bilayer S4, Larger System: Low Temperature Phases



283 K | 300 K | 330 K

Low Temperature Ripple Phase (283 K, 300 K)

$$P_{\beta'}$$

Gel Phase (330 K)

$$L_{\beta'}$$

Conclusions

For high and low water content bilayer main transition same, above 338 K, confirms water does not play role in transition.

BTMAC to SA ratio increases, transition temperature decreases from 338 K to 330 K, due to larger BTMAC head group: ensures the transition occurs due to chain melting.

Rippling observed in low temperature phases, water expulsion Accompanied by sharpening of interface, hydrophobic effect