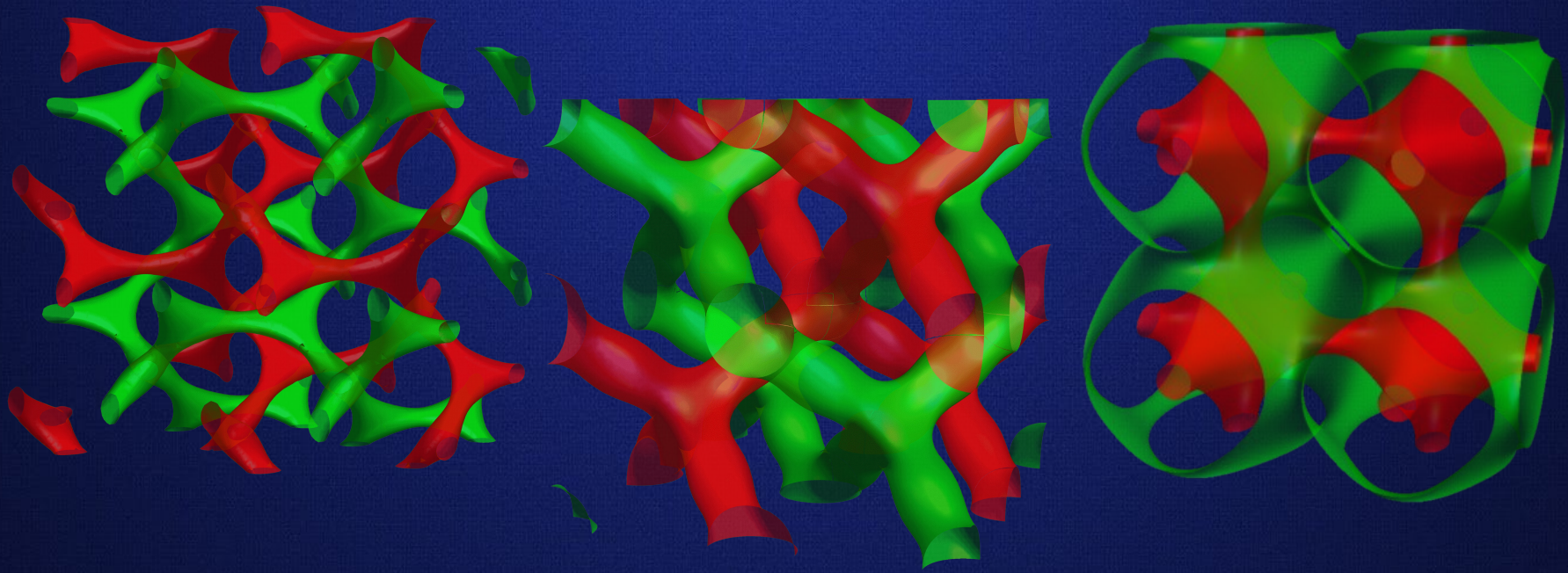
Binary Mixtures of Diblock Copolymers: A New Route to Novel Bicontinuous Phases



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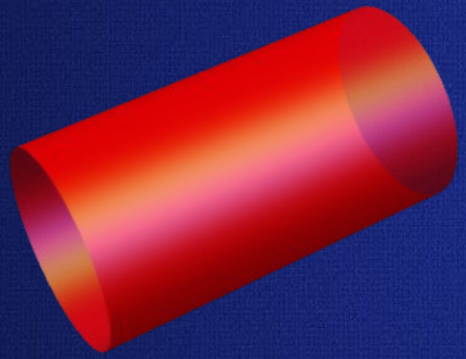
Acknowledgments

- Prof. An-Chang Shi for his support, supervision, and guidance
- Prof. Weihua Li for a very fruitful discussion
- SHARCNET for computational resources

- NSERC for funding

Cubic Bicontinuous Phases: Struts & Nodes

Struts



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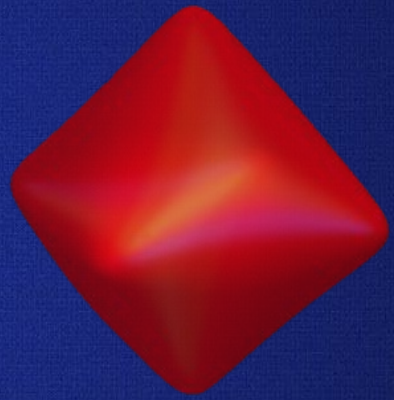
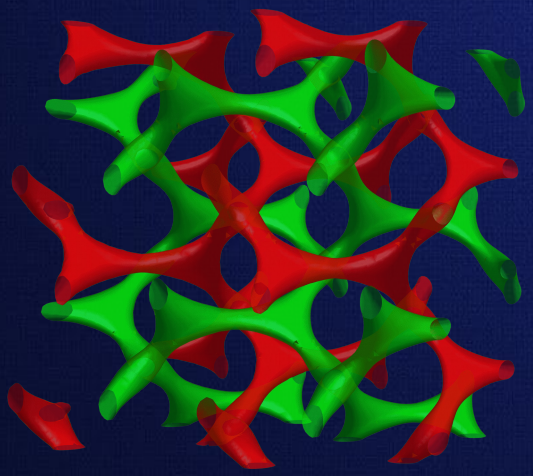
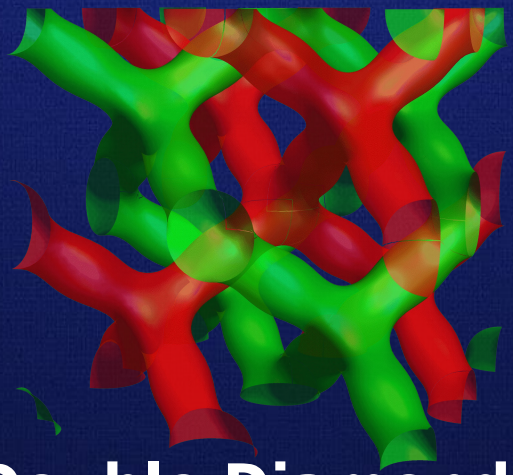


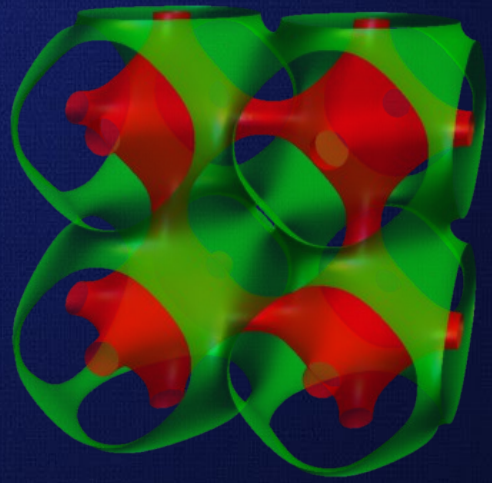
Nodes



Double Gyroid (G) ($Ia\bar{3}d$)

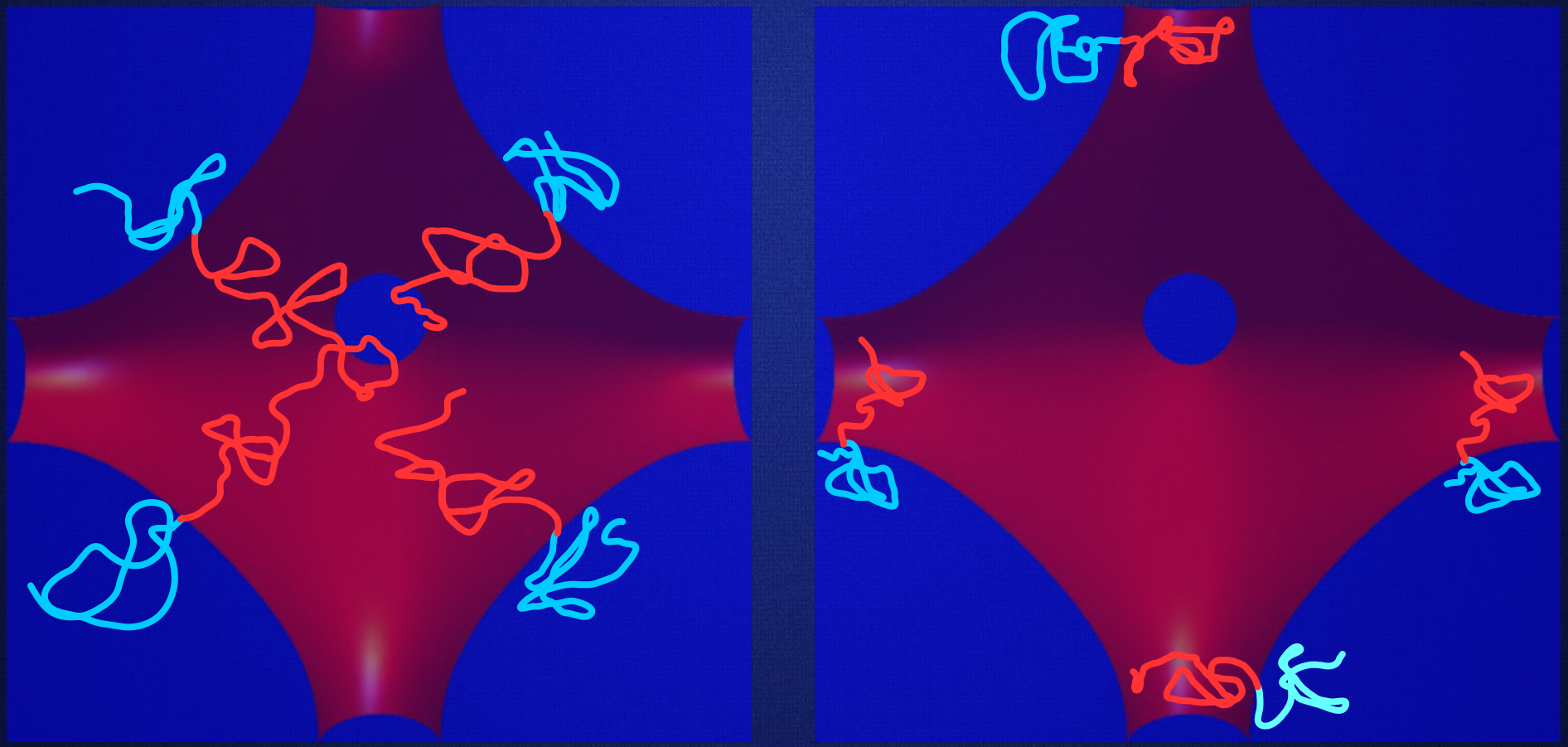


Double Diamond (DD) ($Pn\bar{3}m$)



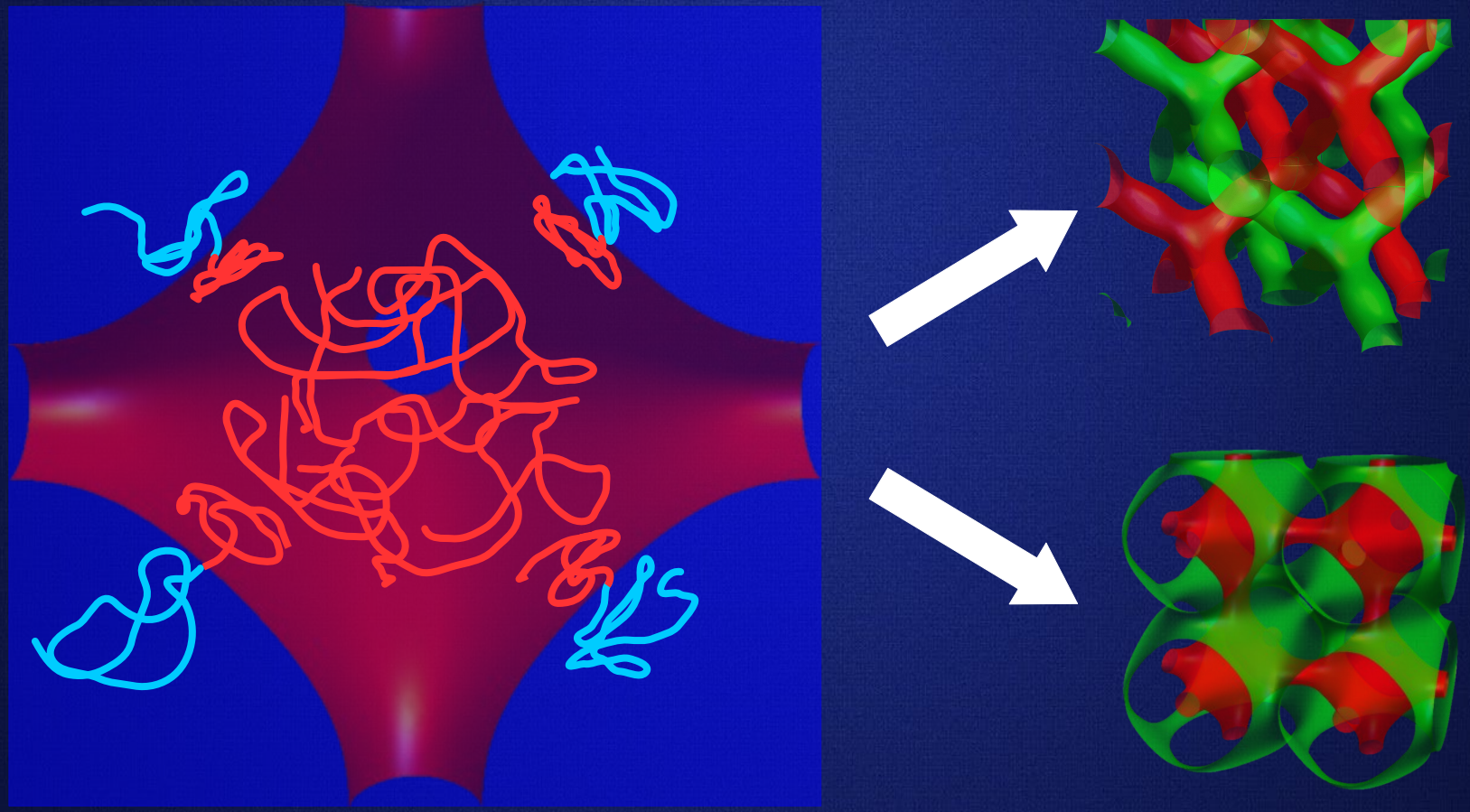
Plumber's Nightmare (P) ($Im\bar{3}m$)

Problem: Packing Frustration



Volume Difference between Struts and Nodes → **Unequal Stretching of Chains** → **Packing Frustration**

Solution: Space-filling Additives



Packing frustration can be reduced by including homopolymers to the blend [1-5].

[1] Macromolecules 1995 28 (17), 5765-5773
[2] Macromolecules 2007 40 (20), 7354-7365
[3] Macromolecules 2009 42 (5), 1775-1784
[4] Macromolecules 2009 42 (22), 9058-9062
[5] Macromolecules 2016 49 (14), 5232-5243

The New Route?

Task: To examine the possibility of stabilizing the novel bicontinuous phases, such as the double-diamond or P morphology, in the case where the additive is a second species of diblock copolymer.

We focus on binary blends of:

Gyroid-forming Species

$f_A = 0.34$

N_{DBC}

Homopolymer-like (HL) Chain

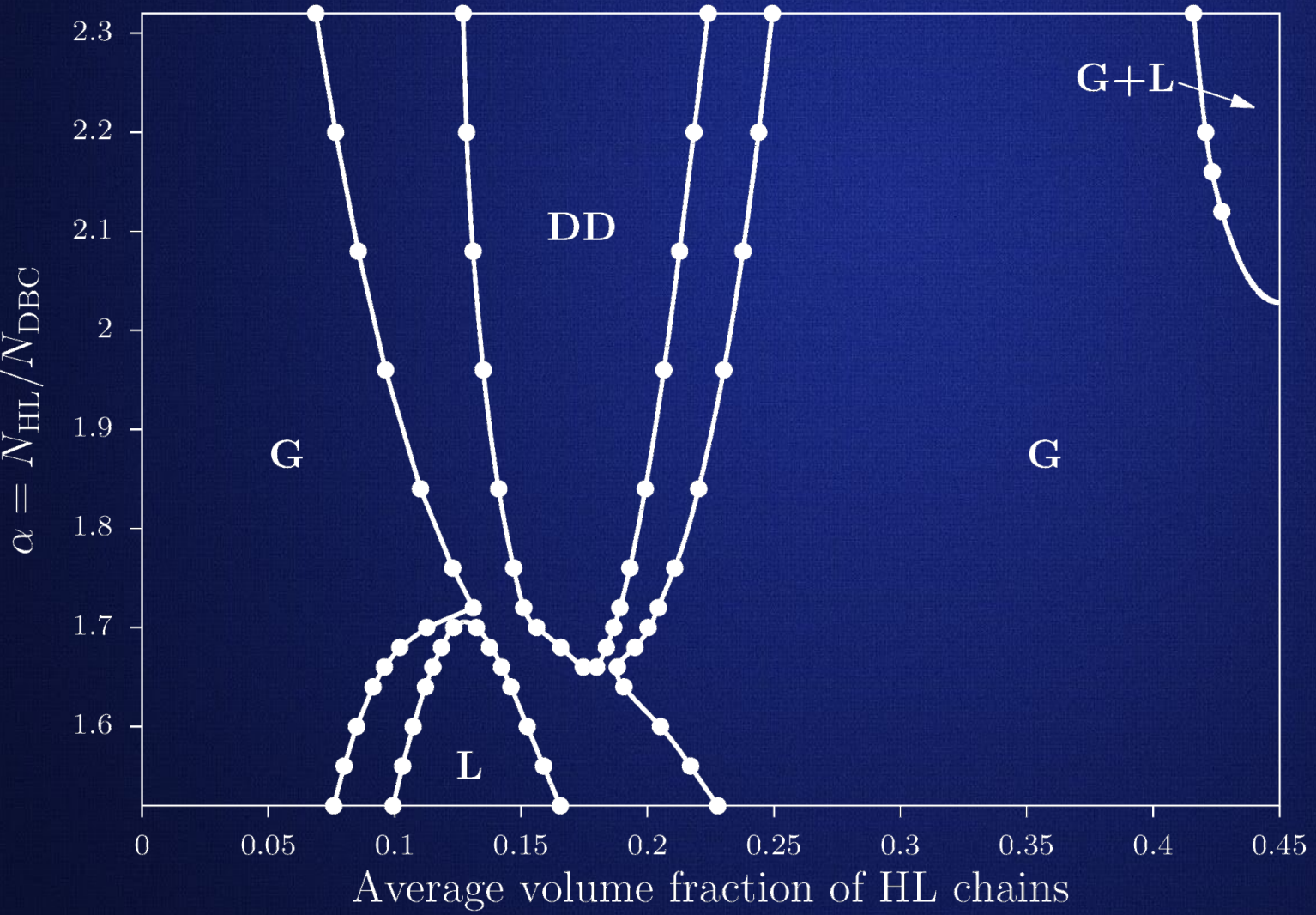
$f_A = 0.95$

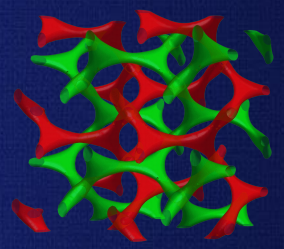
$N_{HL} = \alpha N_{DBC}$

Self-consistent field theory [1-3] is used to study to the resulting phase behavior.

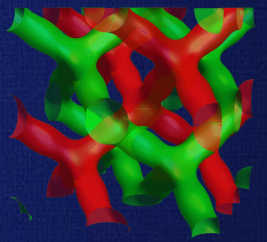
[1] Physical Review E 2002 65, 041806
[2] Journal of Polymer Science Part B: Polymer Physics 2002 40, 1777 (2002).
[3] Macromolecules 2006 39 (19), 6661-6671

Stabilization of the DD Phase





G



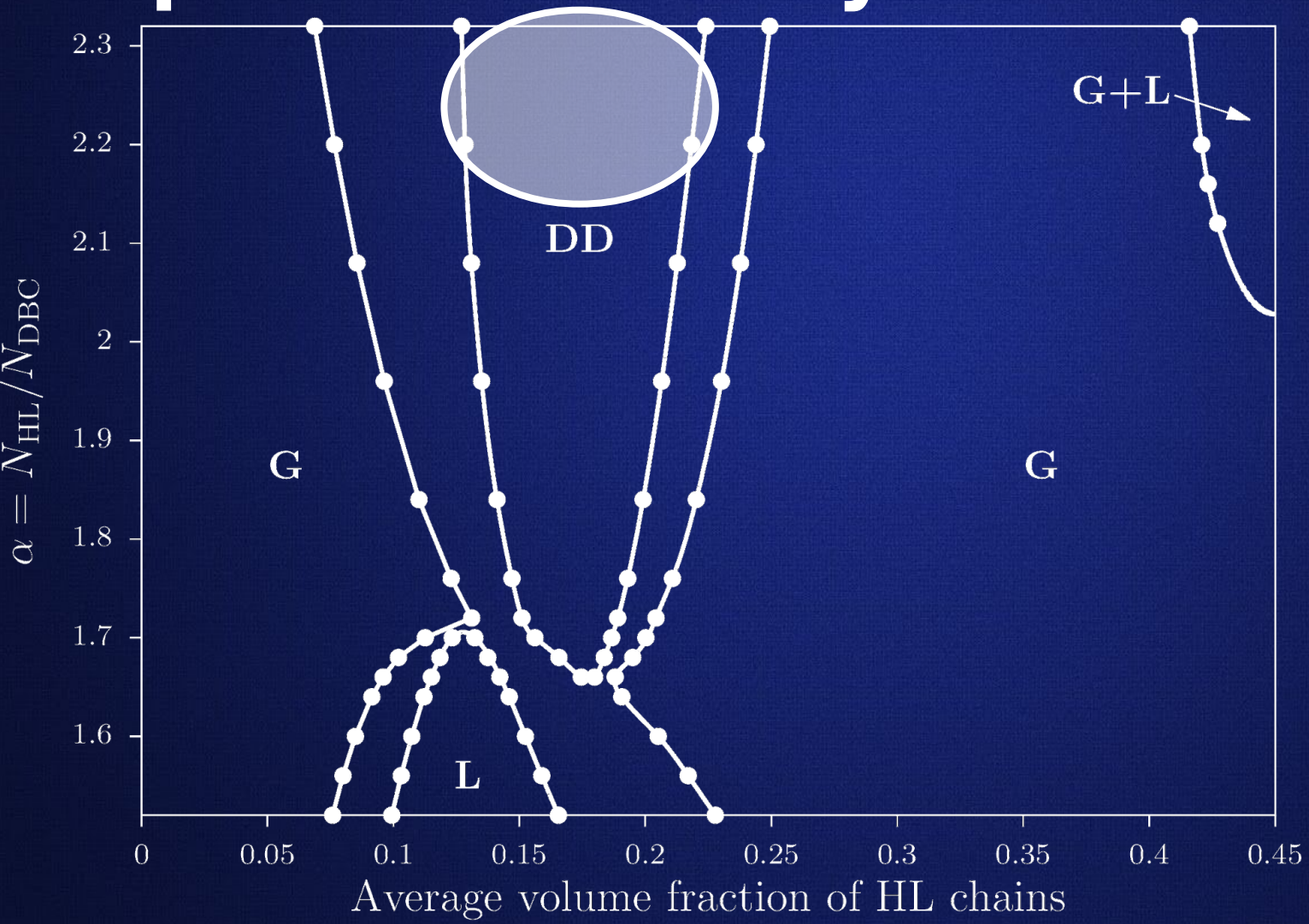
DD

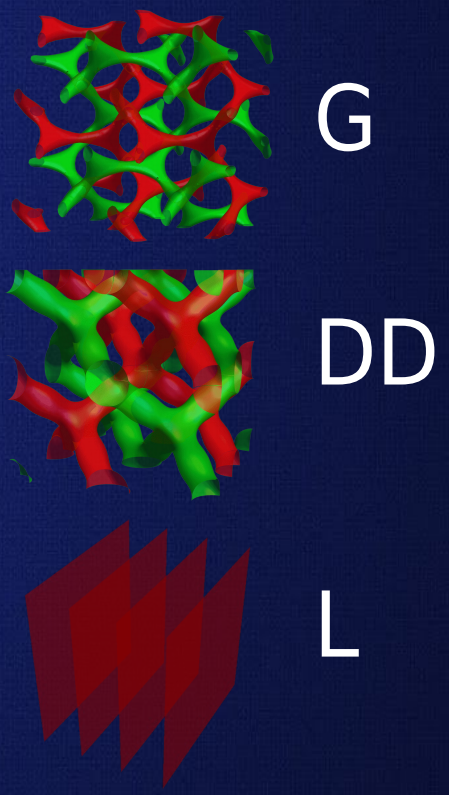
L

$\chi_{AB} N_{DBC} = 25.$

Gyroid-forming Species + **Homopolymer-like (HL) Chain**

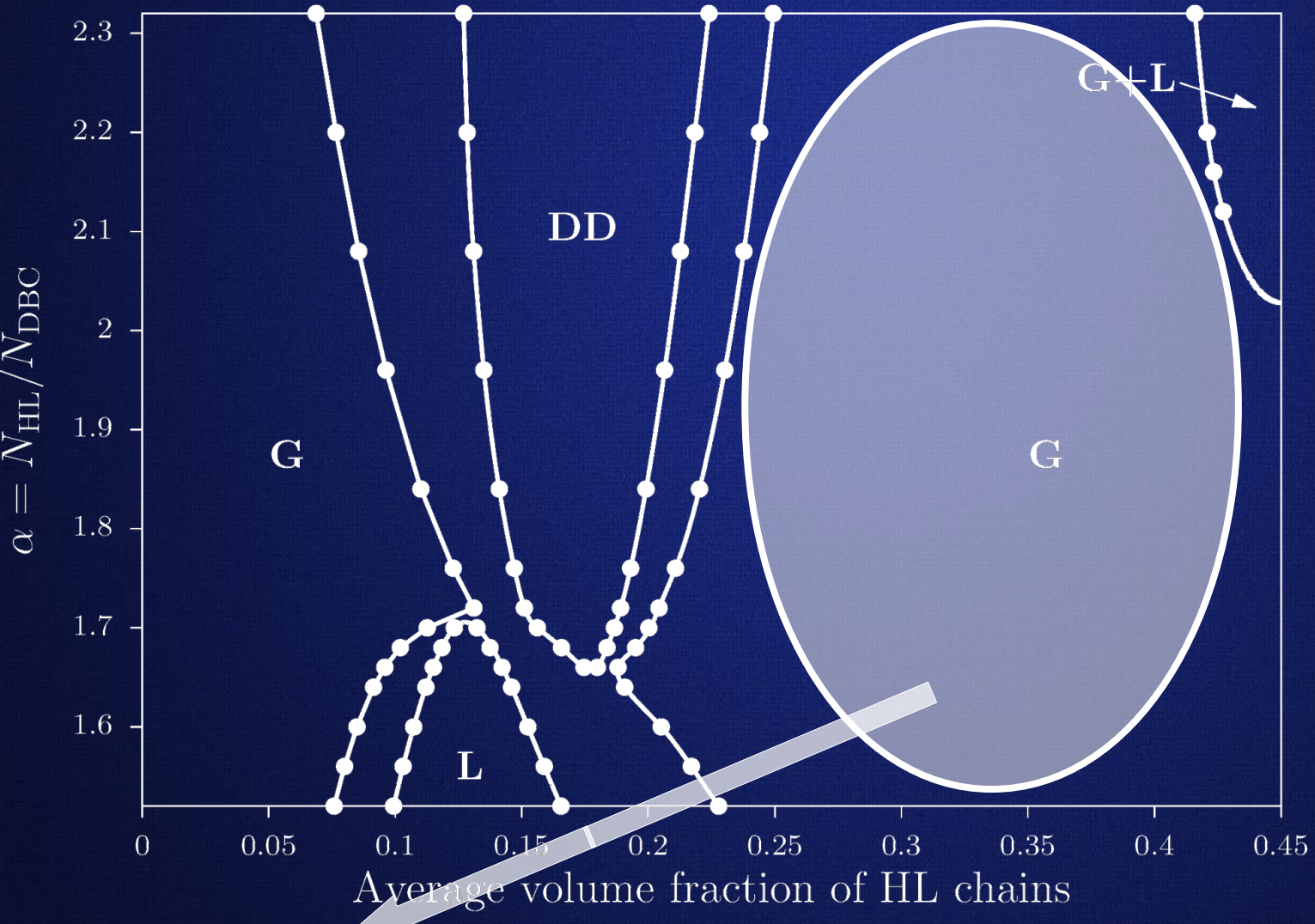
Improved Stability of DD Phase

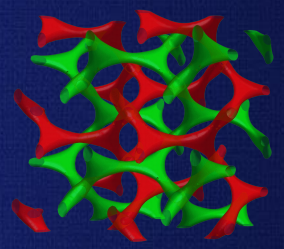




Stability region of the double-diamond phase spans ~10% in the average additive concentration at $\alpha = 2.32$

A-Majority Gyroid Phase





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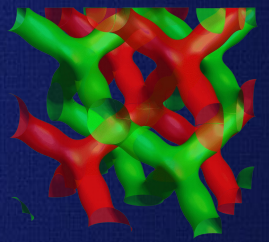
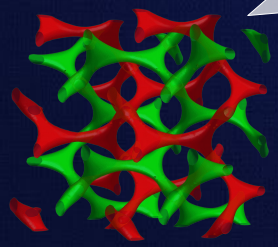


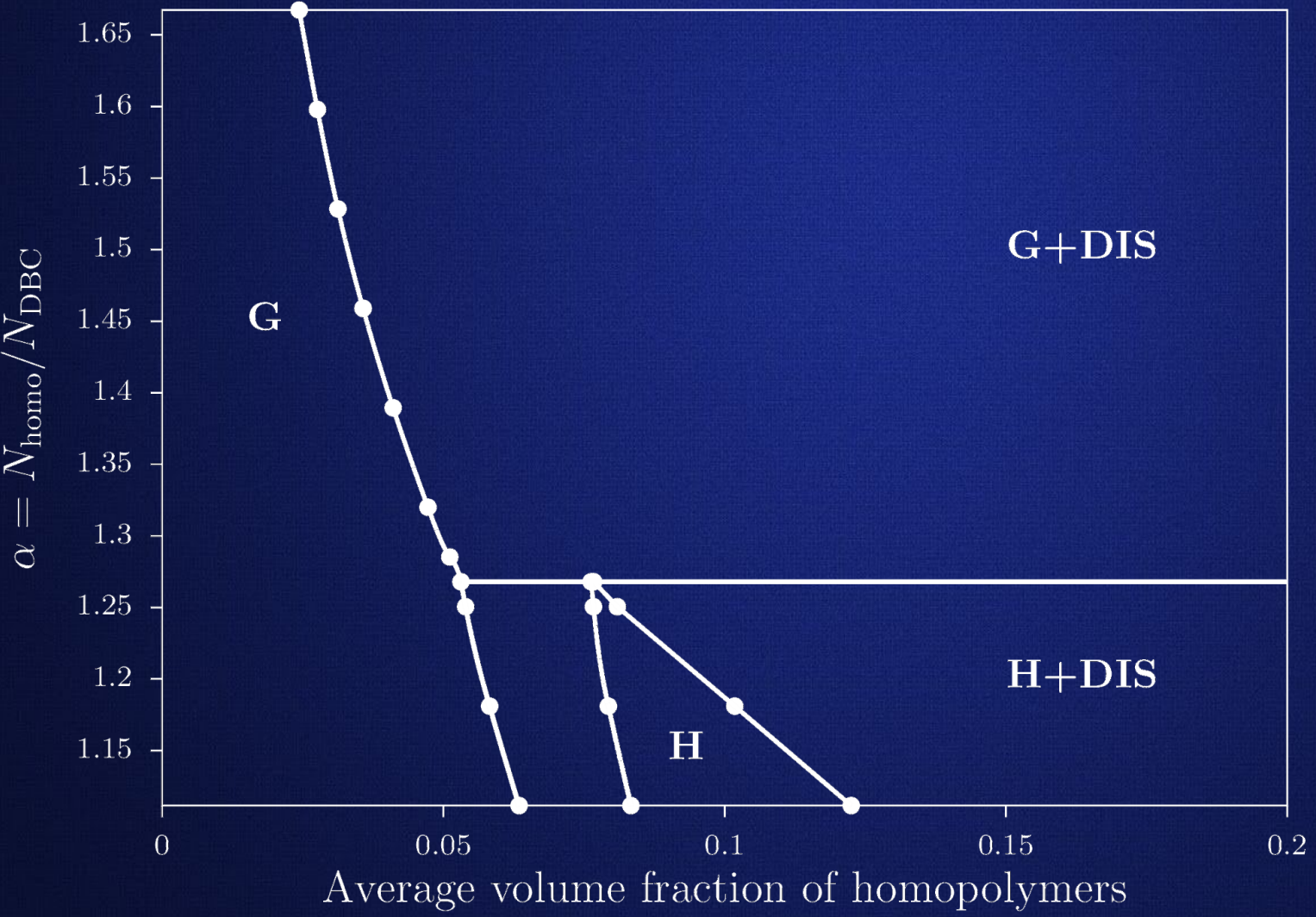
DD

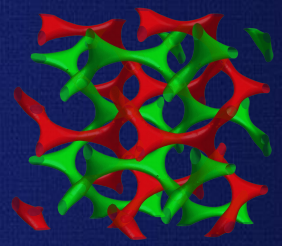
L



for an average A-monomer volume fraction, $\overline{\phi}_A$, ranging from 45% to 60%!

Return to Homopolymers





G

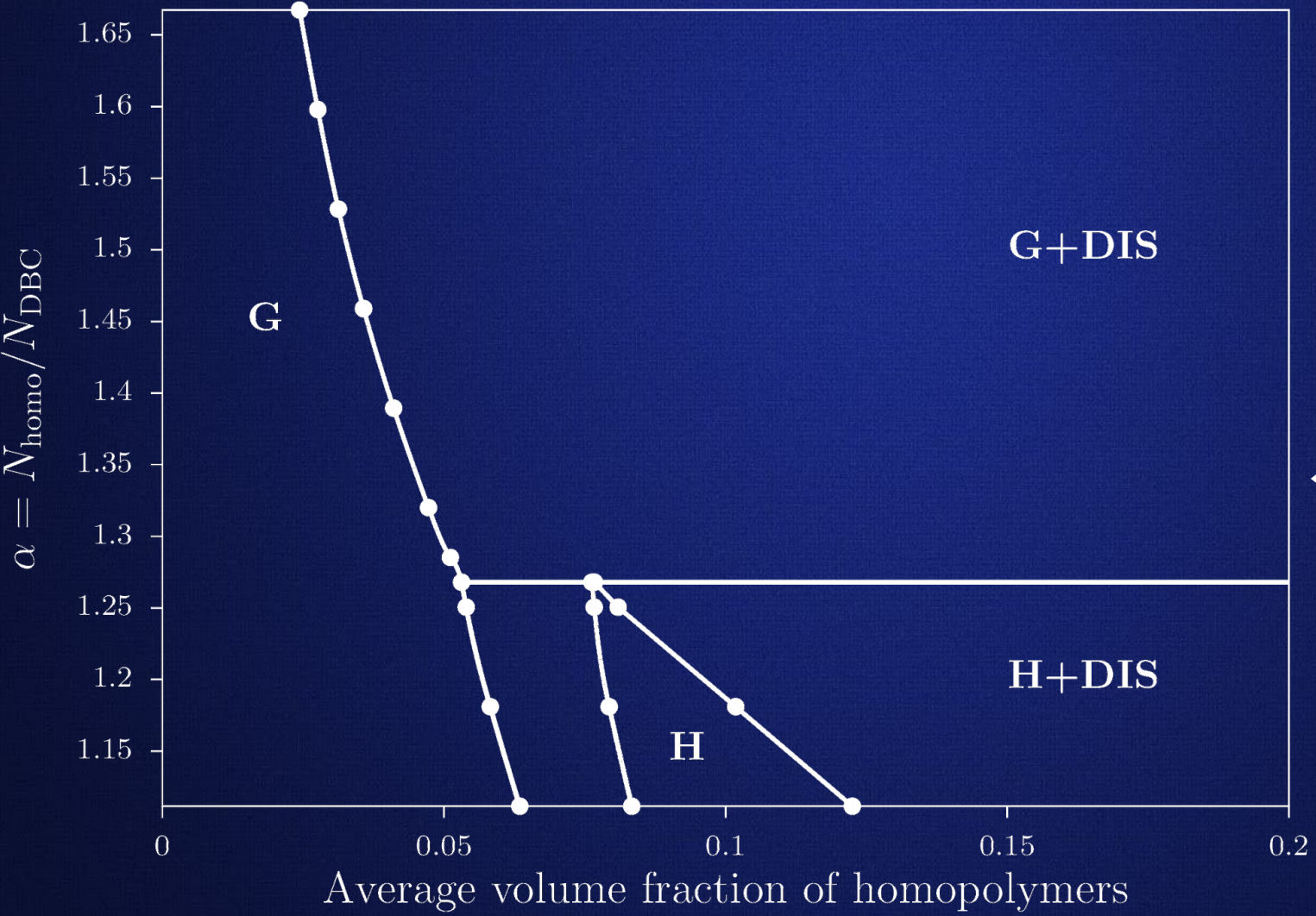
H

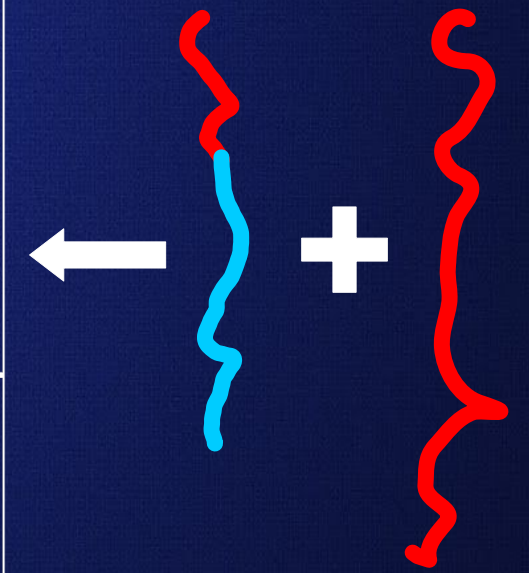
Disordered DIS

$\chi_{AB} N_{DBC} = 25.$

Gyroid-forming Species + **Homopolymer**

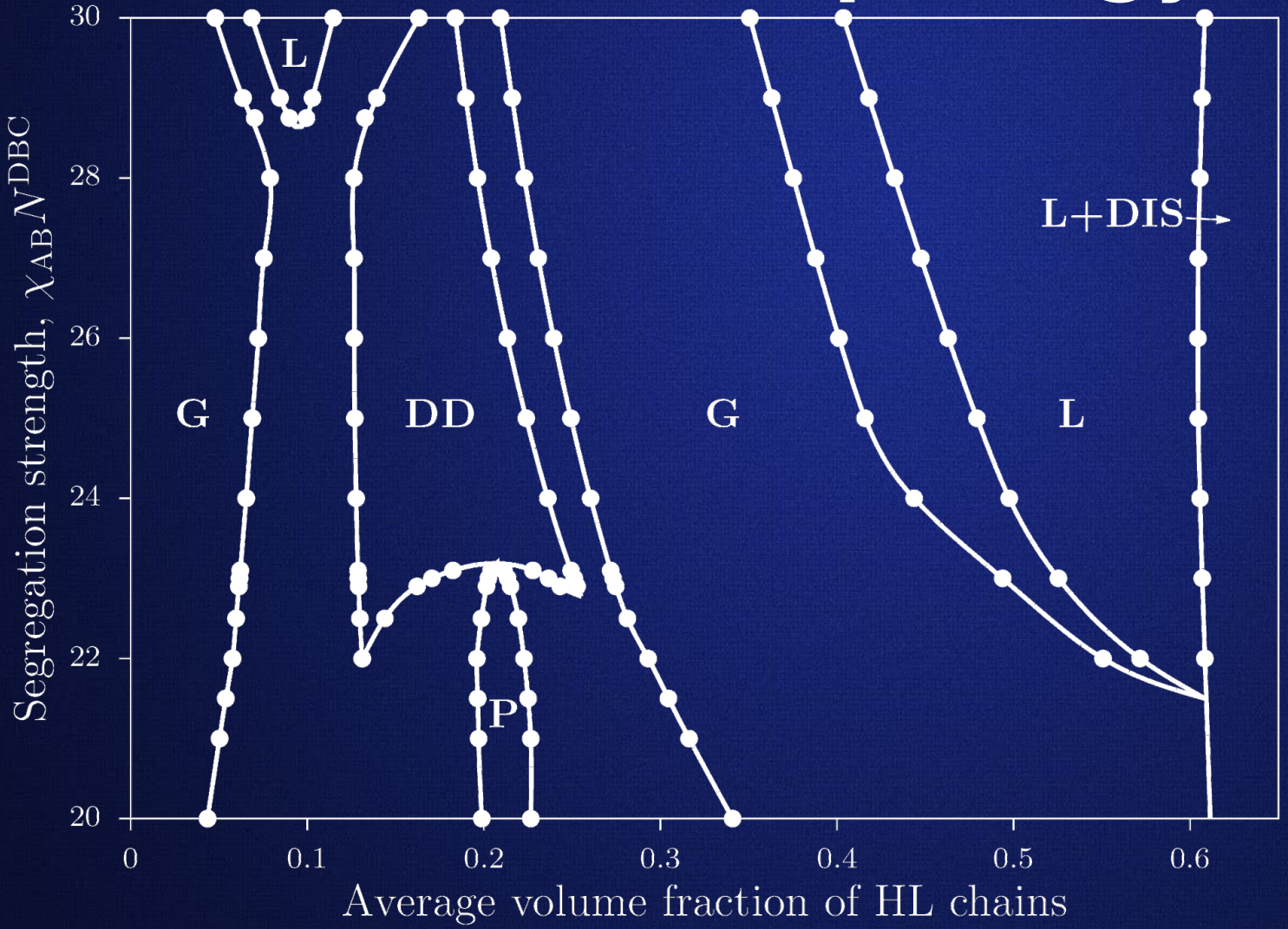
Early Macro-phase Separation

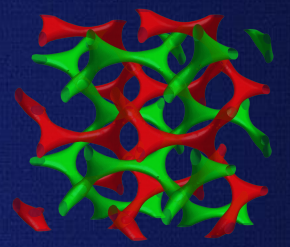




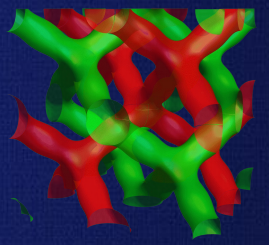
The inclusion of B monomers onto the additive is vital for stabilizing the double-diamond phase!

The Stable P Morphology

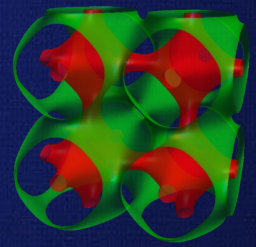




G



DD



P

L

Disordered

DIS

Gyroid-forming Species + **Homopolymer-like (HL) Chain**

Confinement to the Nodes

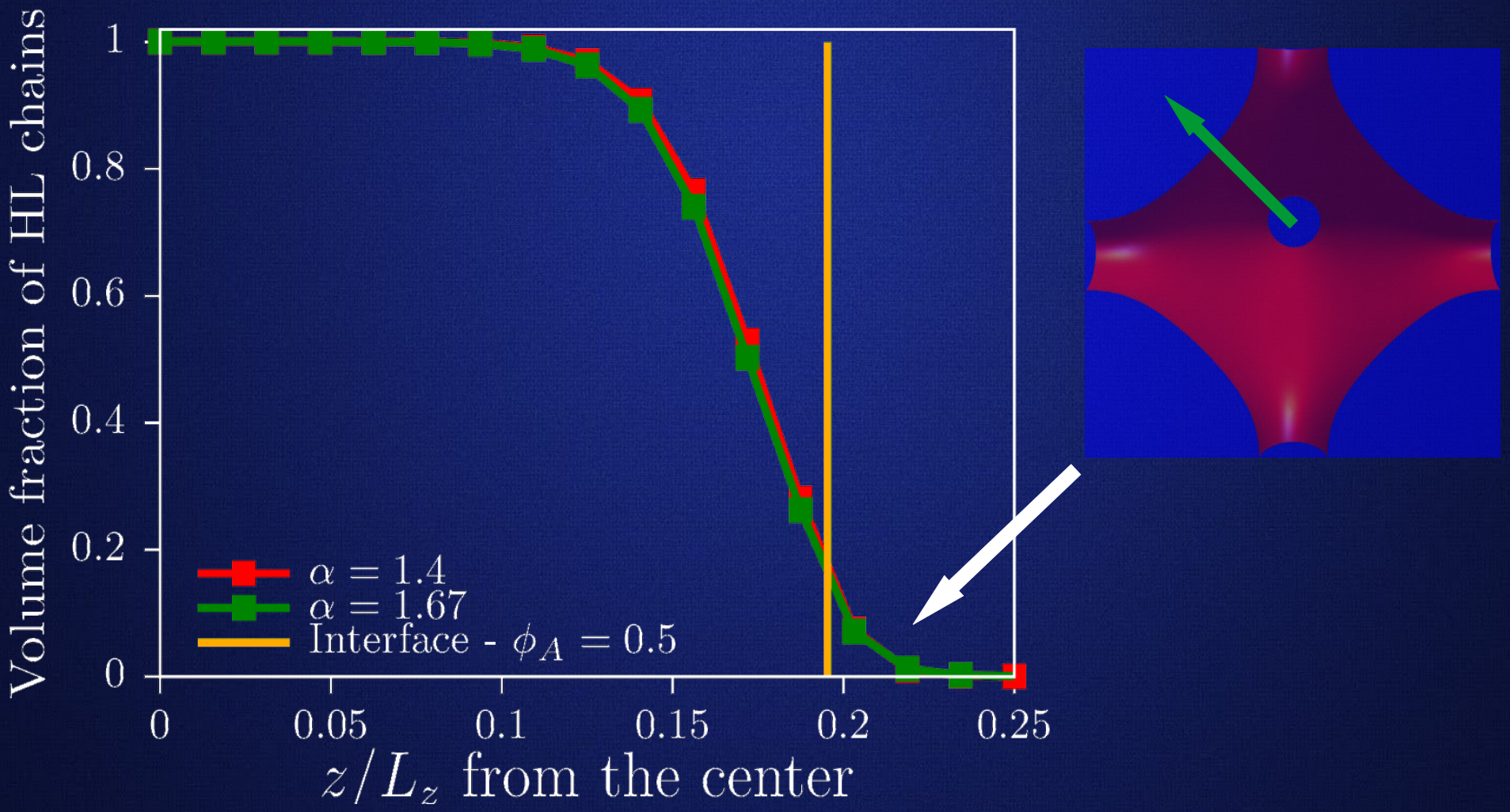
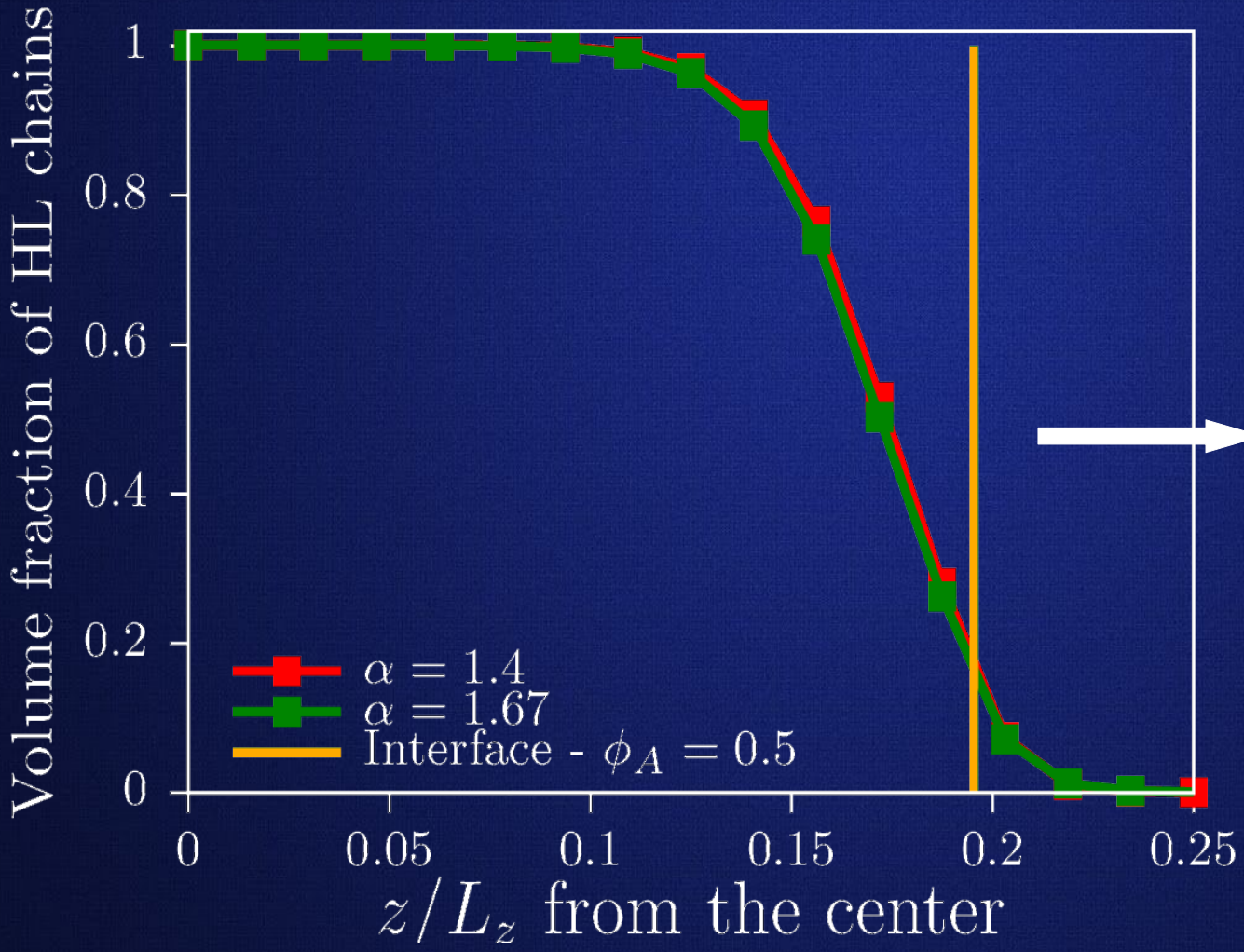
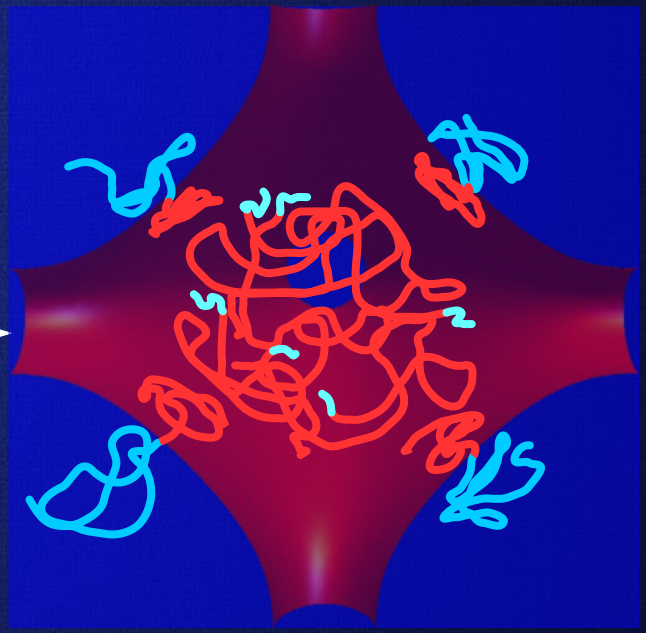


Fig. 6) Plot of the volume fraction of the homopolymer-like chain, ϕ_{HL}, as a function of the relative distance from the center of the node for a metastable P phase at $\overline{\phi}_{HL} = 0.4$.

Alleviation of Packing Frustration

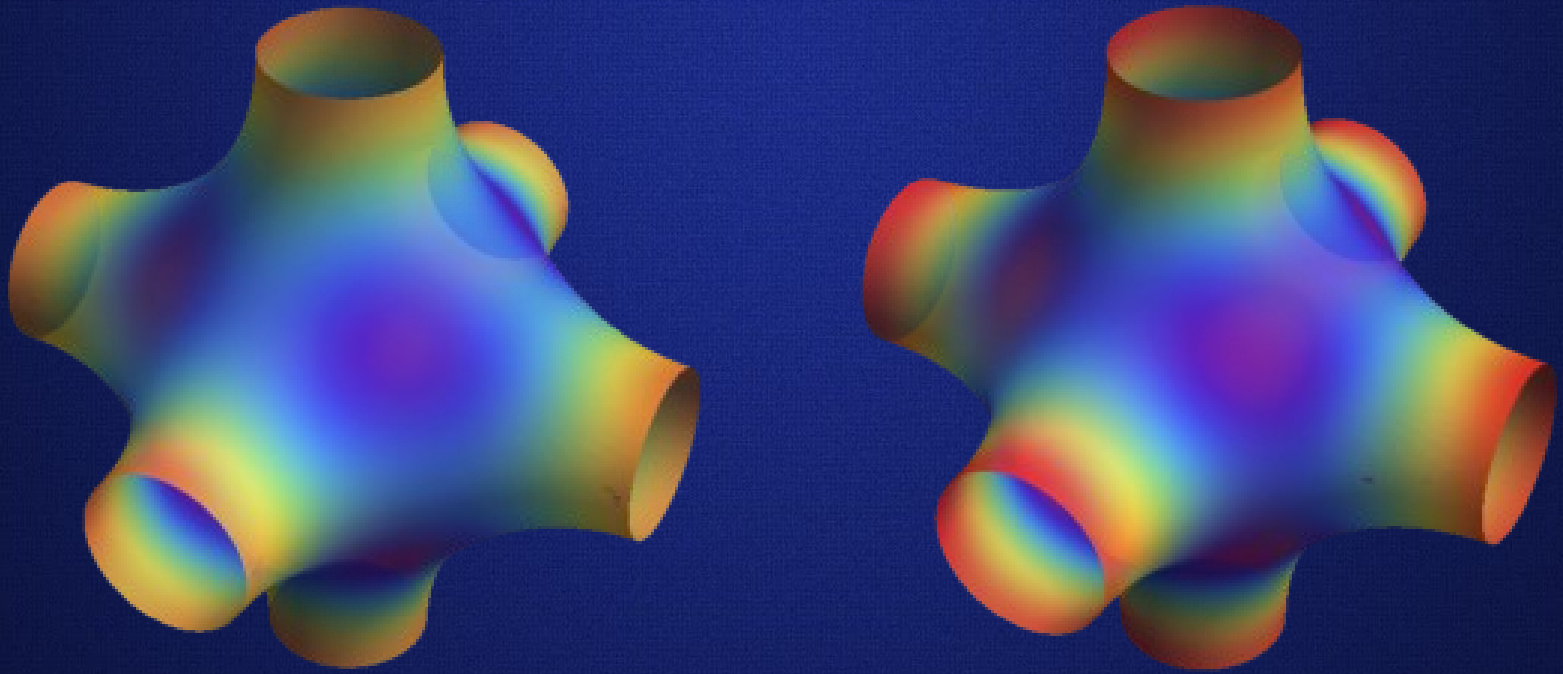


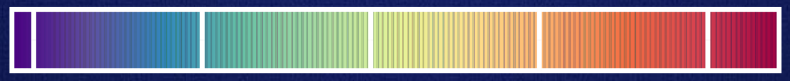


The observed behavior suggests that packing frustration is indeed relieved!

Examining the Mean Curvature

(a) $H_{\min} R_g = 0.155$ (b) $H_{\min} R_g = 0.130$





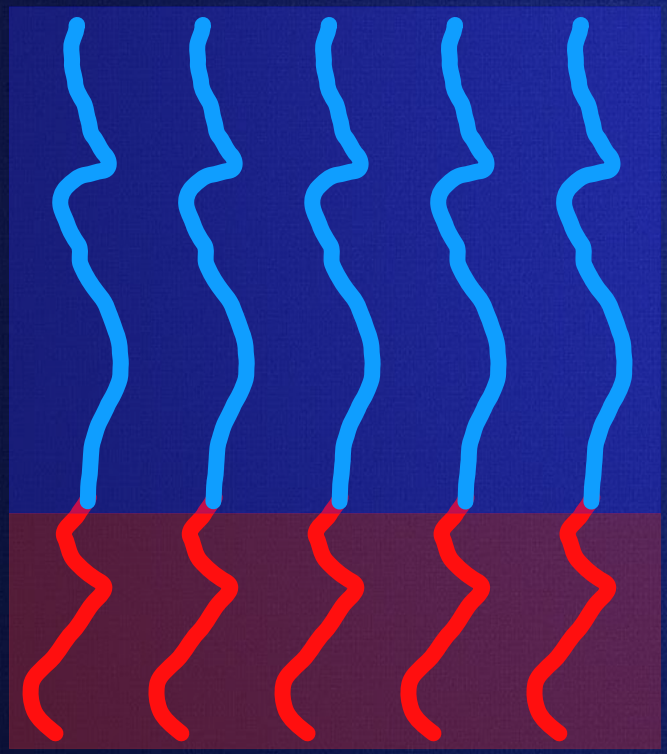
HR_g

0.15 0.3 0.45 0.6 0.75

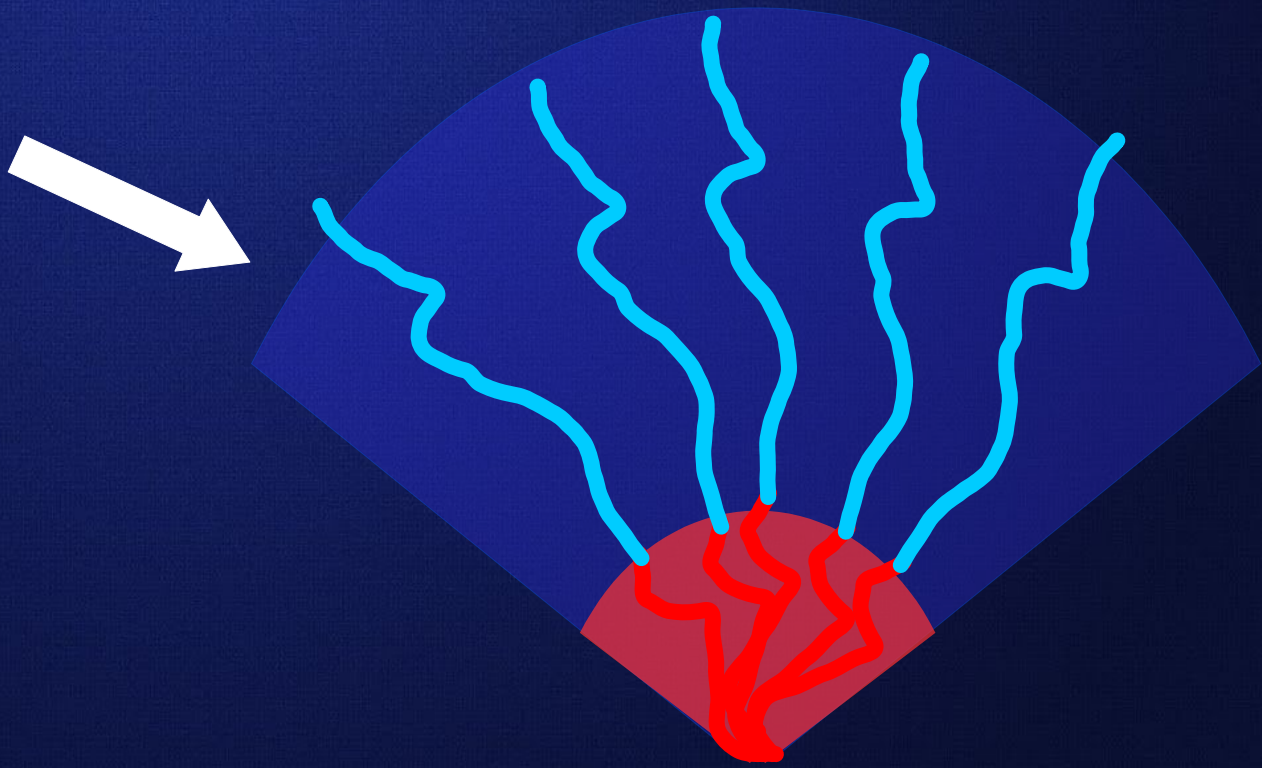
16% 16%

α = 2.32, and $\chi_{AB} N_{DBC}$ = 25

Entropy-driven Curvature

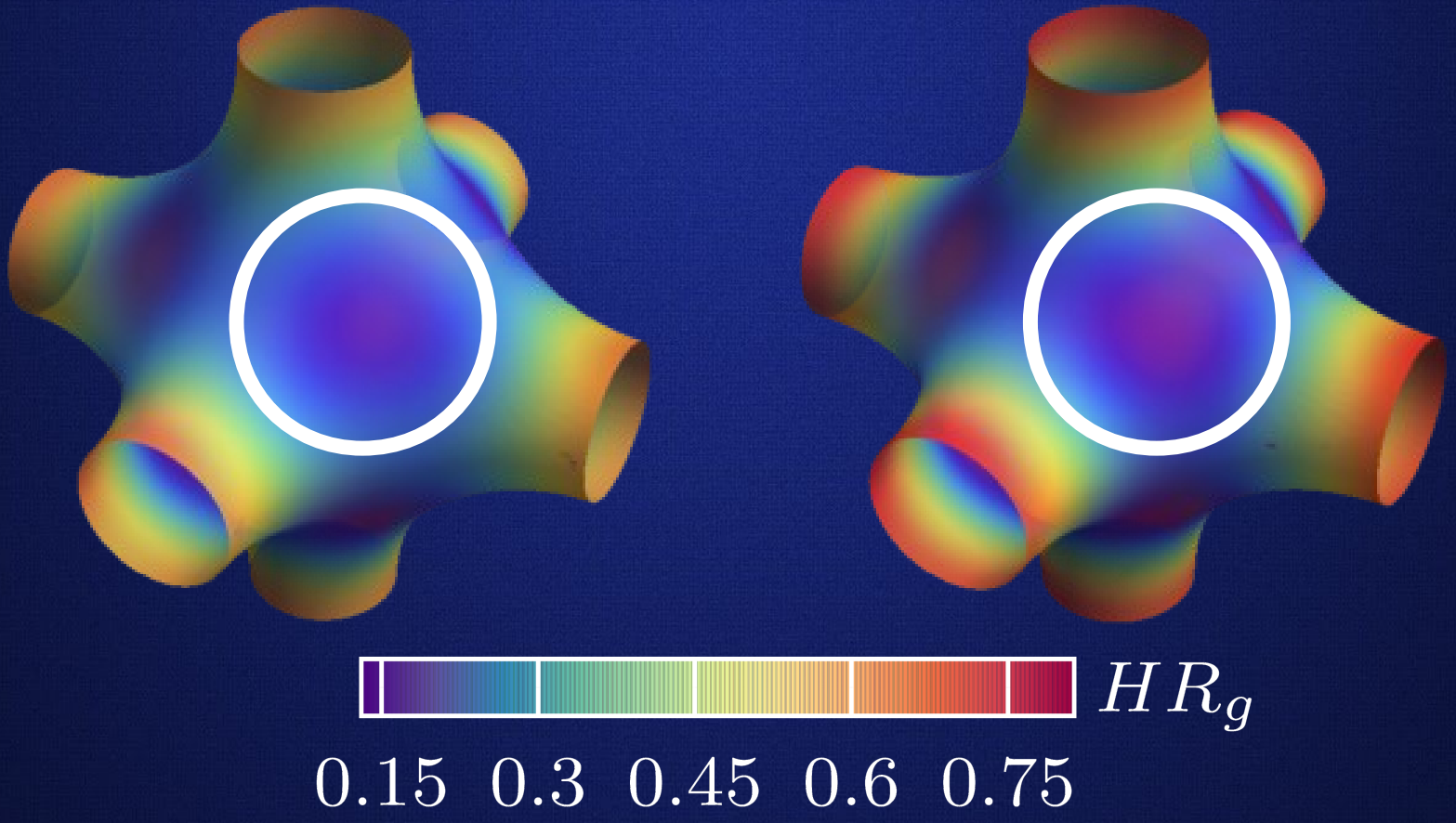


Melt incompressibility and maximization of conformational entropy



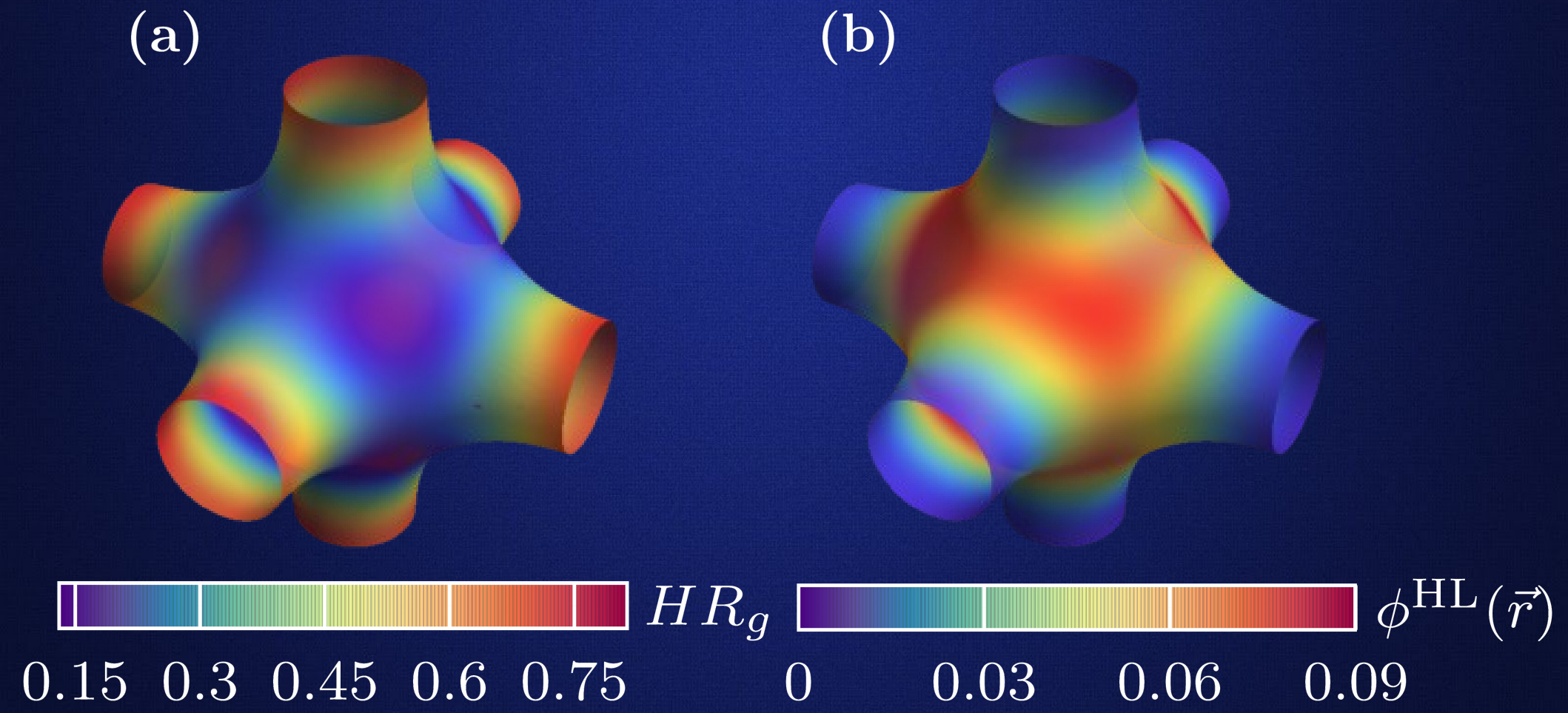
Flattening of the Interface

(a) $H_{\min} R_g = 0.155$ (b) $H_{\min} R_g = 0.130$



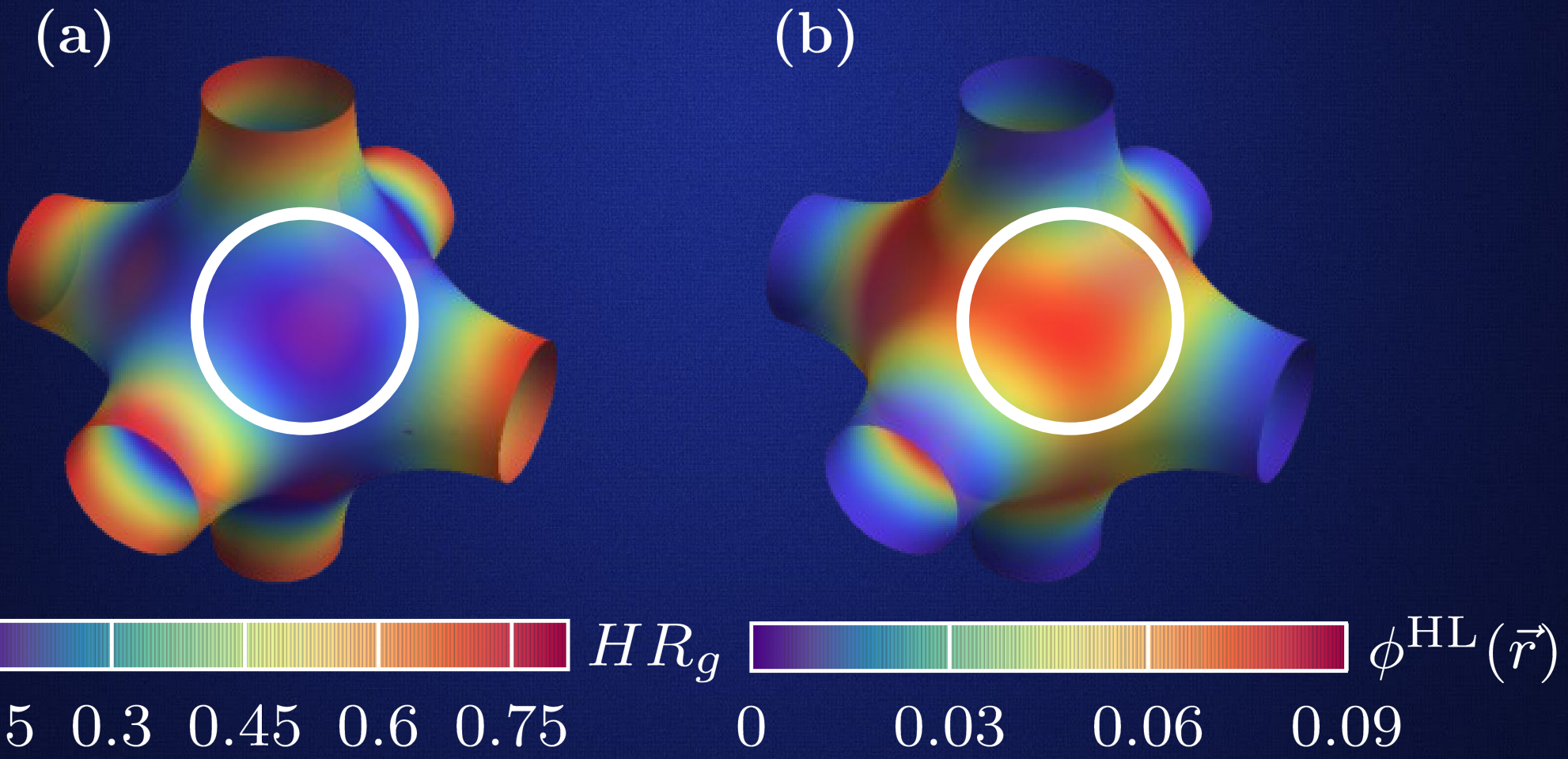
Encircled areas are slightly flatter for the homopolymer-like species, which increases the conformation entropy.

Segregation on the AB-Interface



Gyroid-forming Species + **16% HL Chains**

Dual-Purpose Additive



The homopolymer-like species serves two purpose:

(1) “Space” filler relieving packing frustration

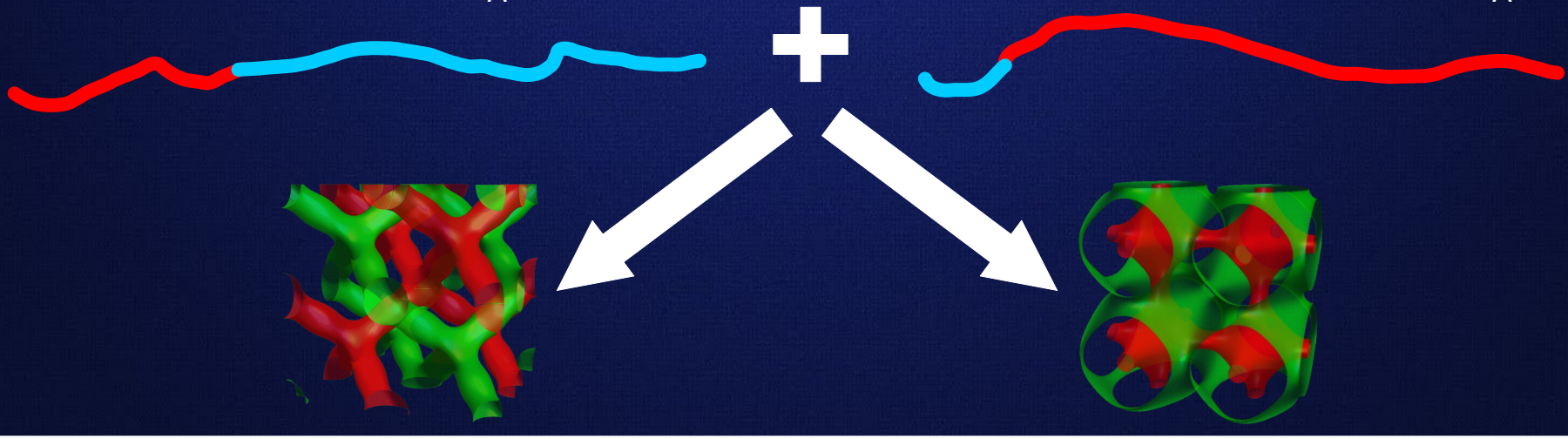
(2) Flattens the interfacial curvature, making it more entropically favorable for the G-forming species

Recap

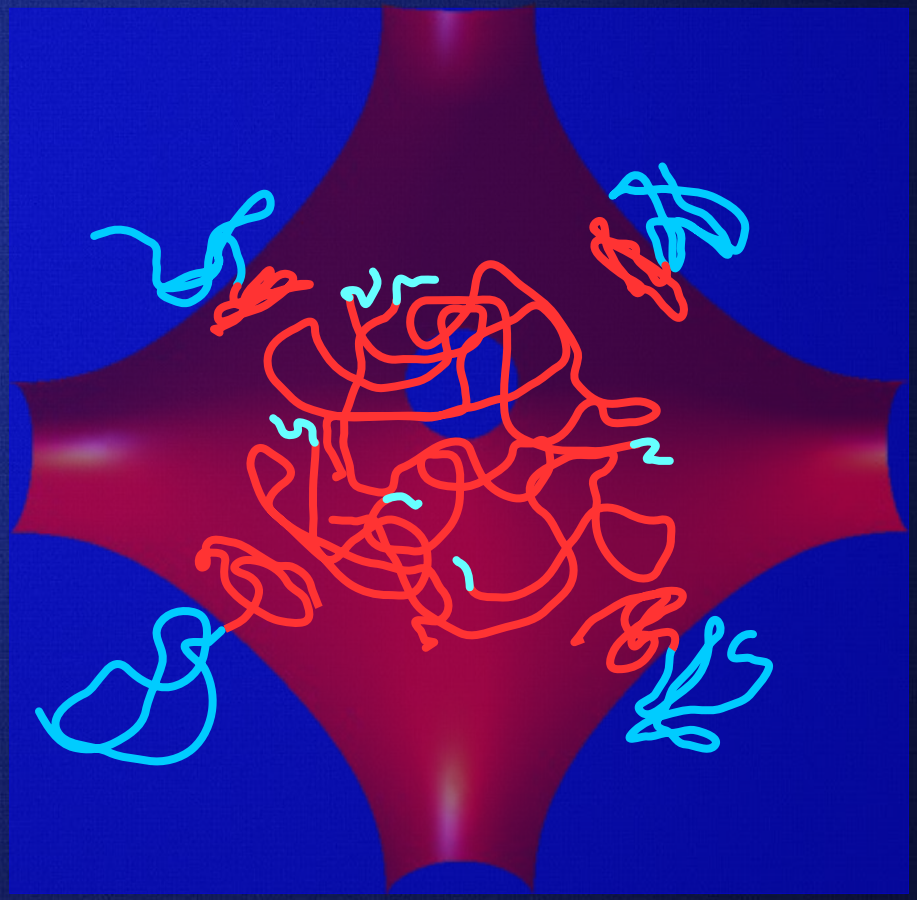
Using self-consistent field theory, we have showed in binary mixtures of diblock copolymers

- The stabilization of the double-diamond, and plumber's nightmare phase.
- The resulting stability regions of the novel bicontinuous phases can be extended by using homopolymer-like chains.

Gyroid-forming (f_A = 0.33) **Homopolymer-like** (f_A = 0.95)



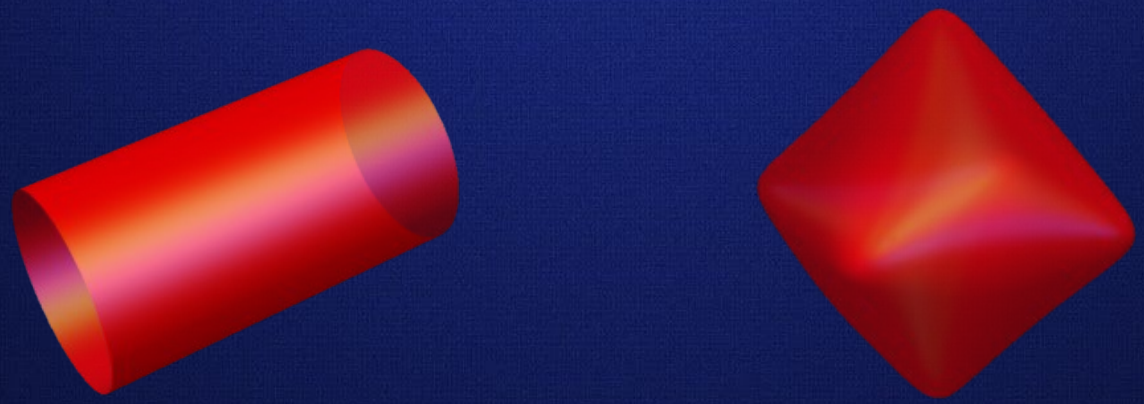
BONUS SLIDES



Minimization of Interfacial Area

The system ideally wants to form a constant-mean-curvature structure in order to minimize the interfacial surface energy. This results in [1]

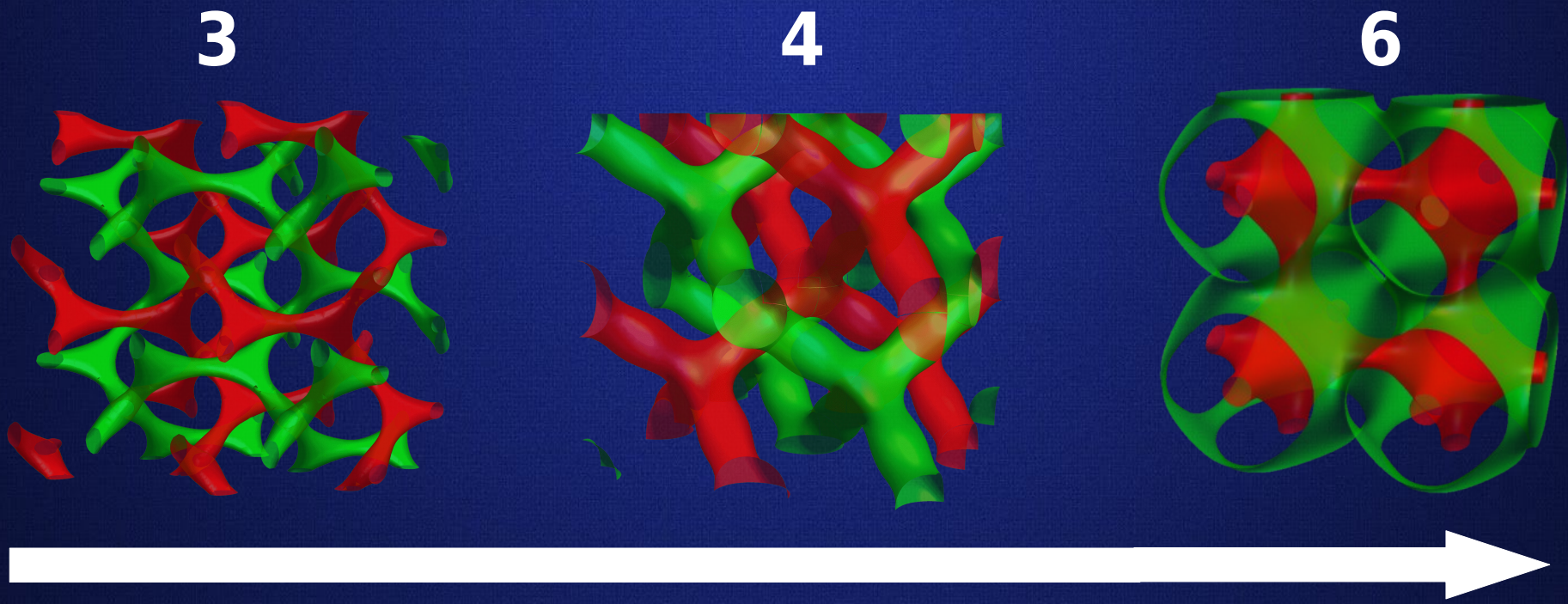
Strut volume < Node volume



[1] Macromolecules 1995 28 (17), 5765-

The Sole Representative

Number of struts per node:



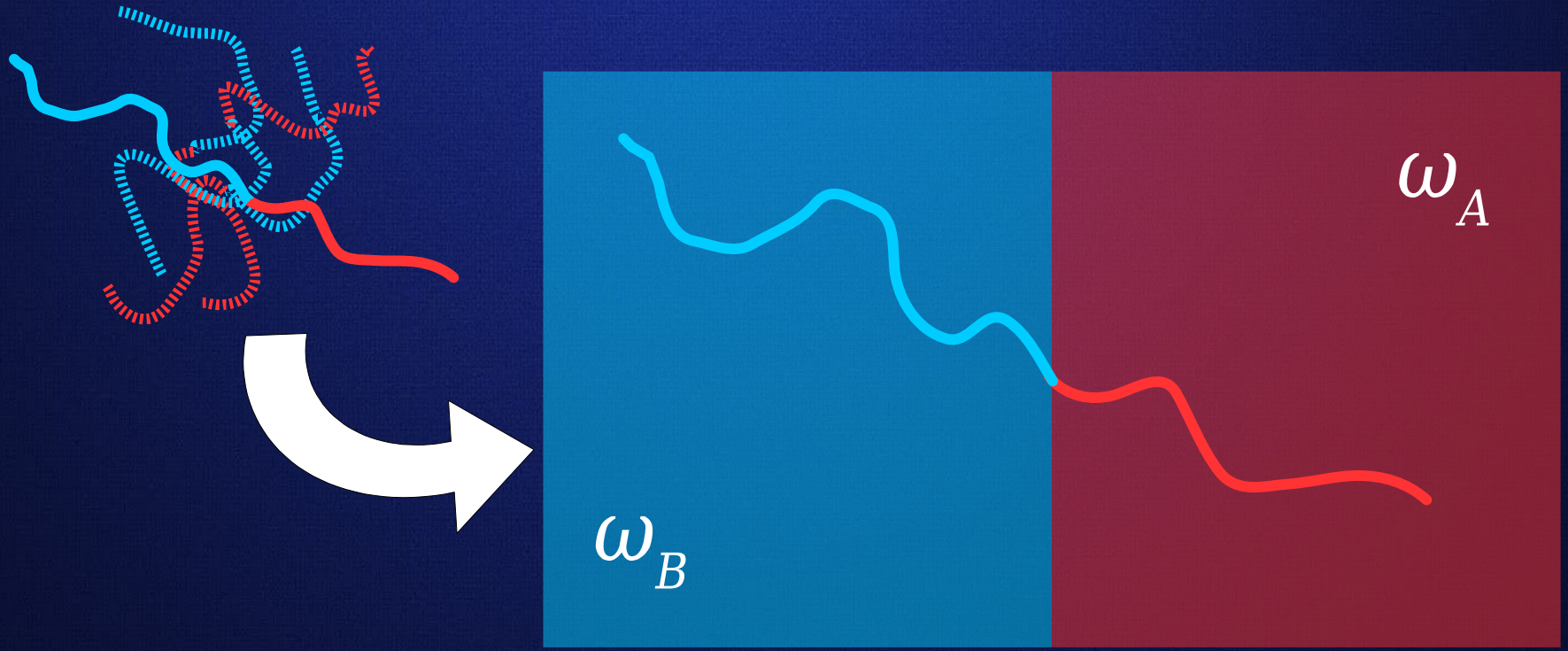
Degree of experienced packing frustration

With the least number of struts per node, 3, the G phase will experience smallest degree of packing frustration, explaining why is the sole representative for the cubic bicontinuous phases in monodispersed AB-diblock melts.

Methodology

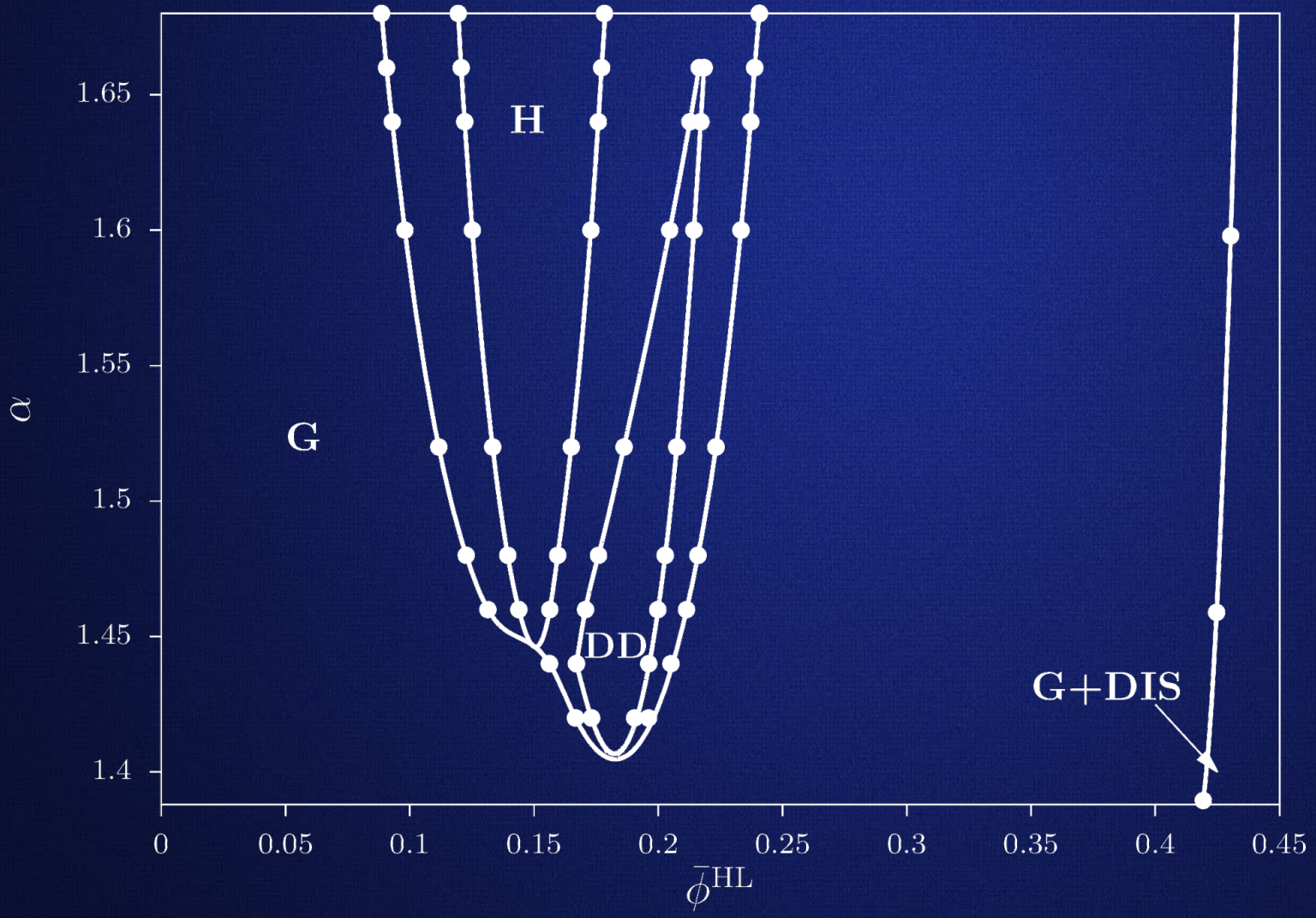
Self-consistent field theory [1-3] is used to study to the resulting phase behavior.

Basic idea:



[1] Physical Review E 2002 65, 041806
[2] Journal of Polymer Science Part B: Polymer Physics 2002 40, 1777 (2002).
[3] Macromolecules 2006 39 (19), 6661-6671

Stabilization of the DD Phase



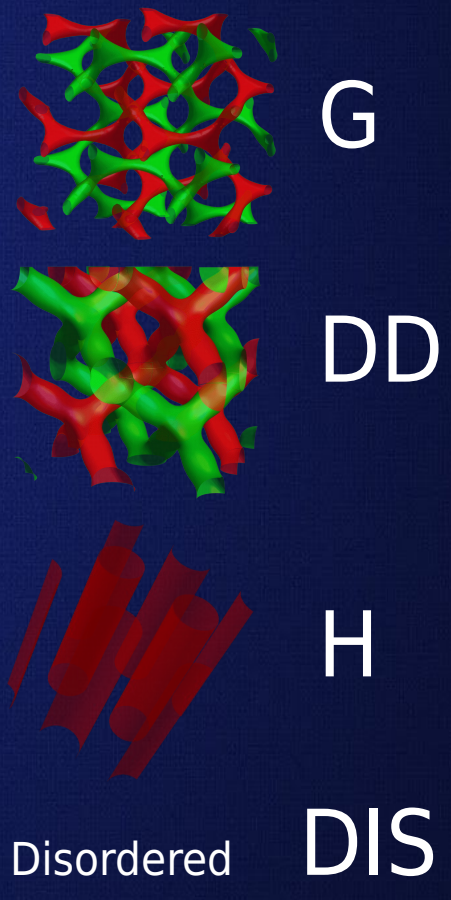
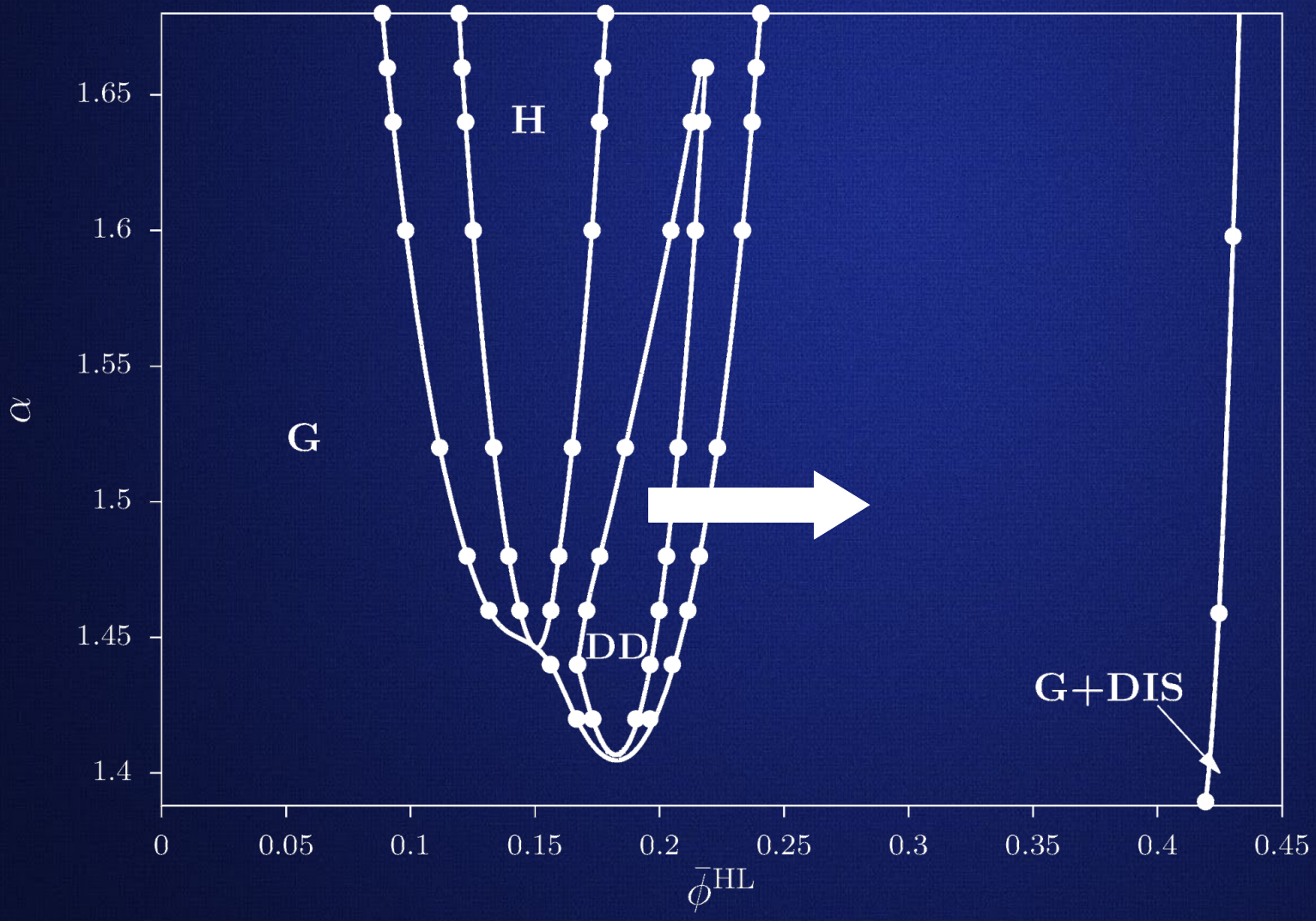
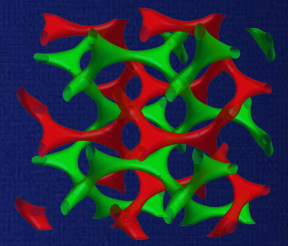


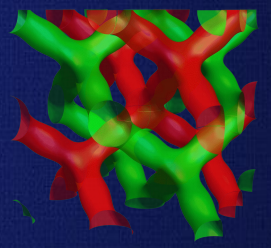
Fig. 3) Phase diagram of diblock copolymers (f_A = 0.33) and a homopolymer-like species (f_A = 0.05) at different compositions of HL chains, $\bar{\phi}^{HL}$, and values of α. The interaction strength is $\chi_{AB} N_{DBC}$ = 25. The phases are labelled as follows: H for the cylindrical phase, G for the double gyroid phase, D for the double diamond phase, and DIS for the homogeneous phase.

BONUS: Diamond → Gyroid Transition





G

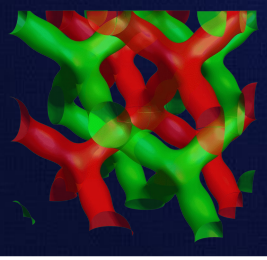


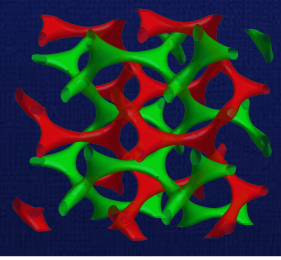
DD

H

Disordered

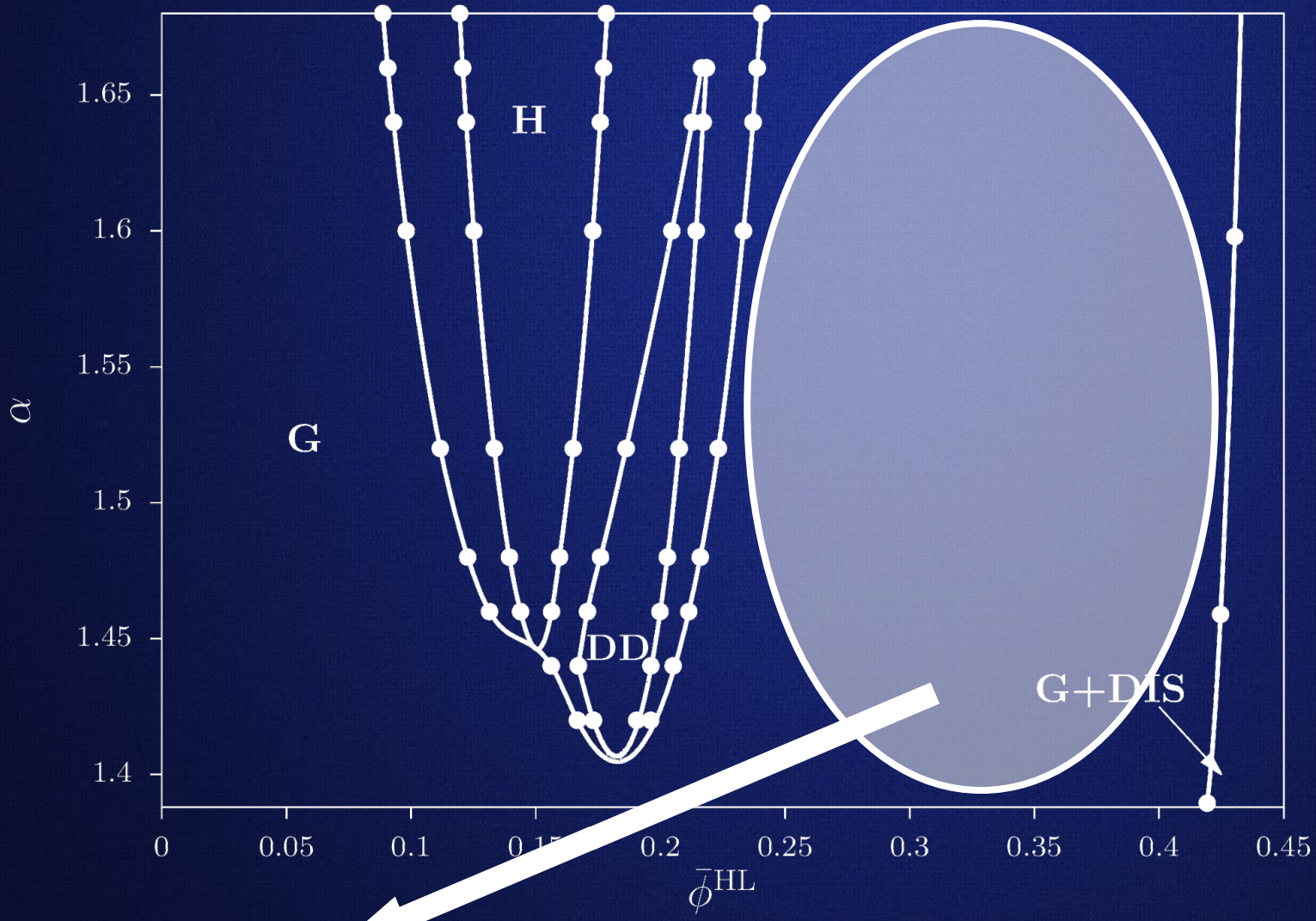
DIS

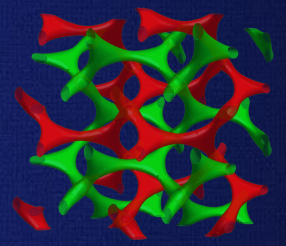




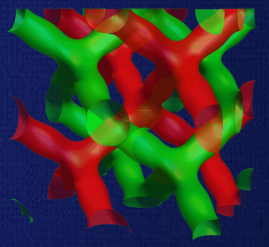
as concentration of additives continues to increase for all studied values of α

A-Majority Gyroid Phase





G

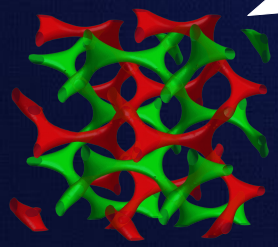


DD

H

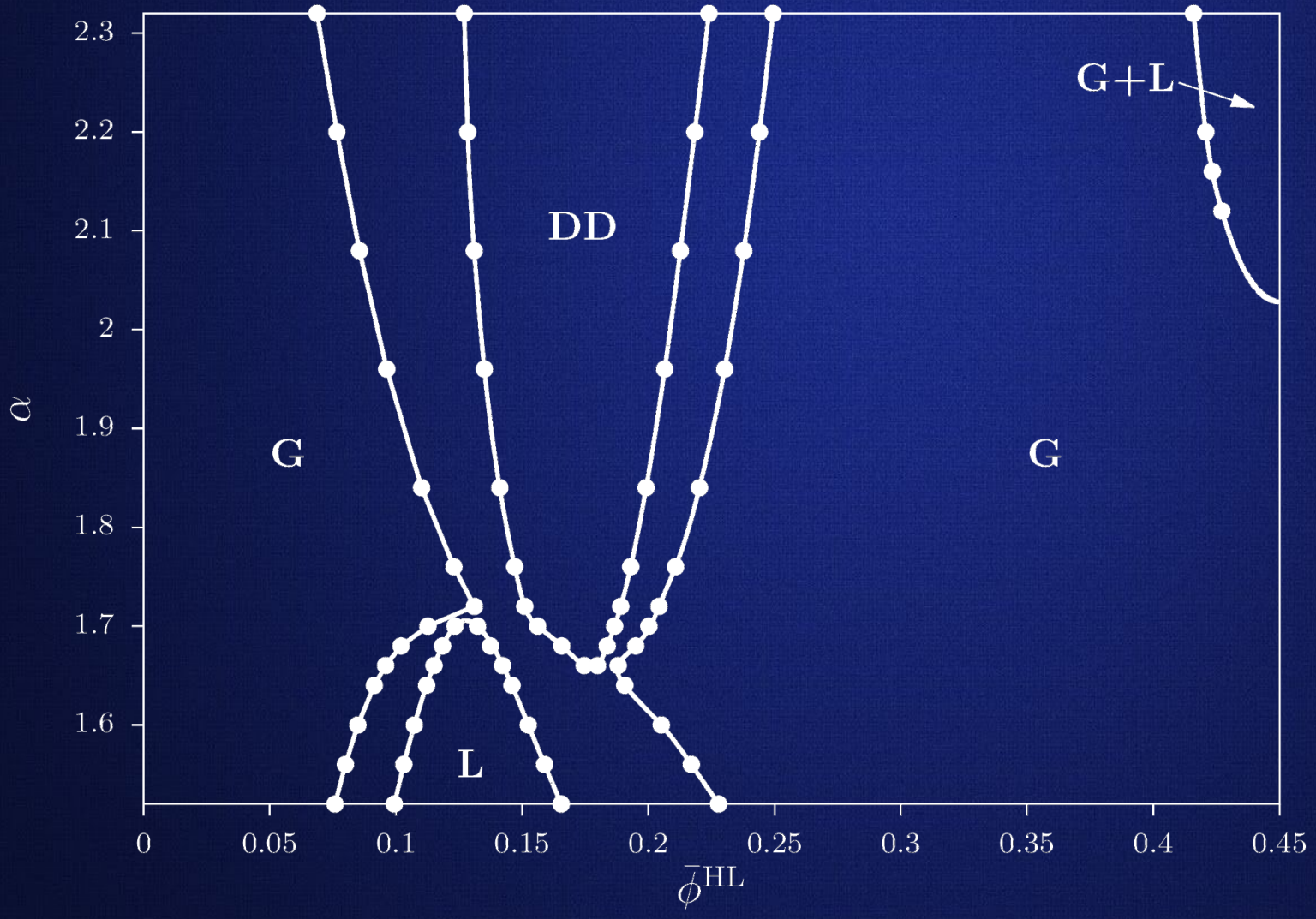
Disordered

DIS



for an average A-monomer volume fraction, $\bar{\phi}_A$, ranging from 45% to 60%! The G morphology only exists for $\bar{\phi}_{A,B}$ ≈ 0.30 to 0.35 in monodispersed melts [?].

Improved Stability of DD Phase



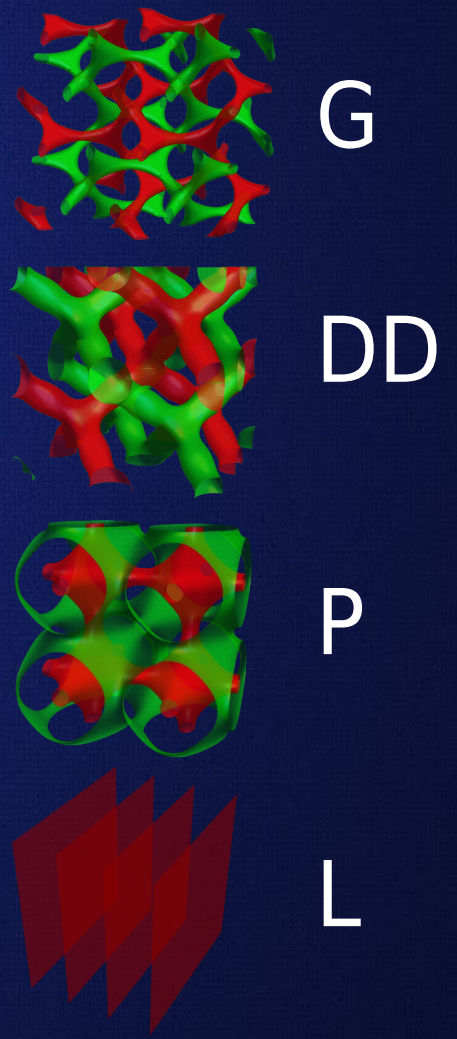
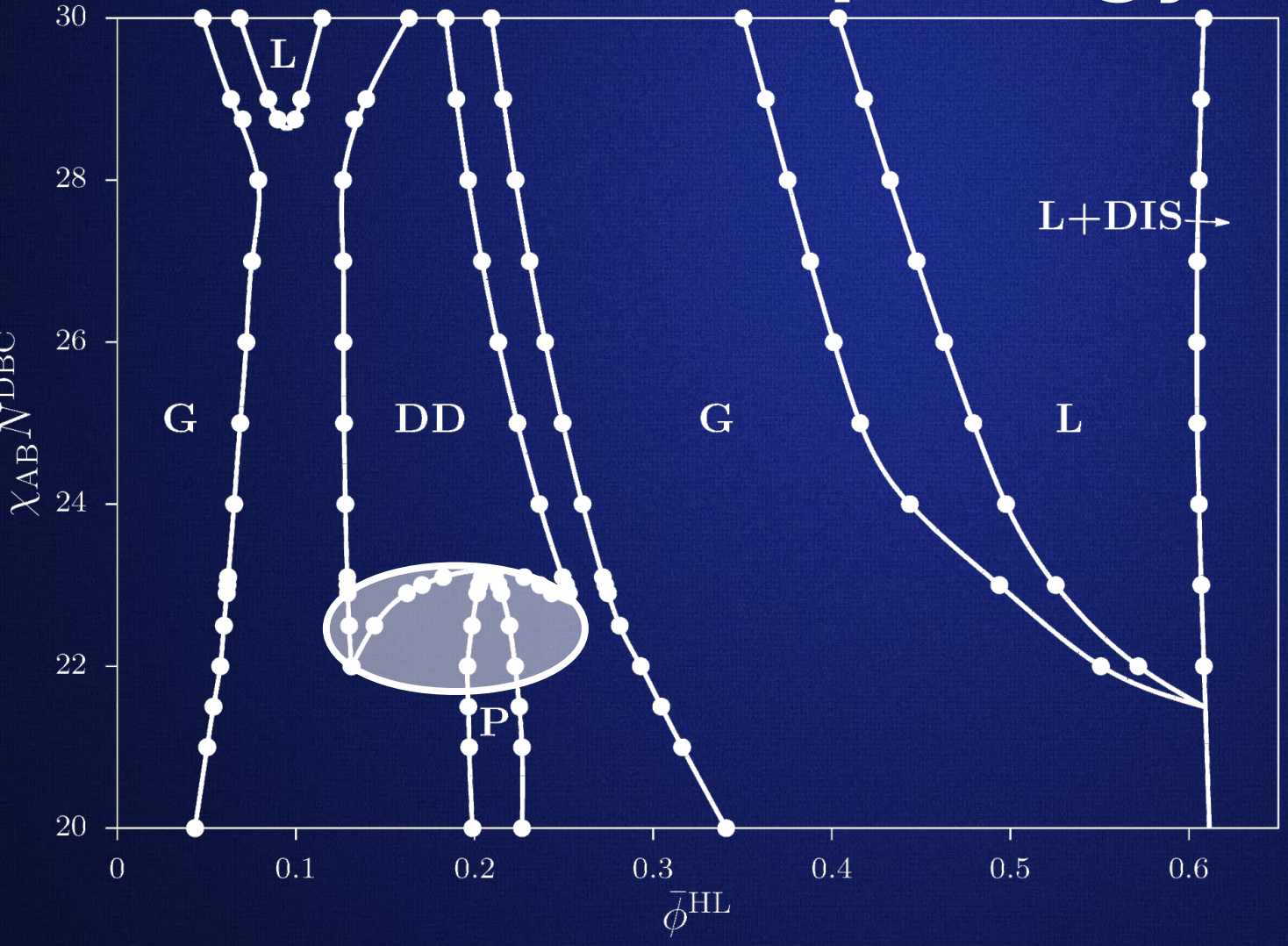
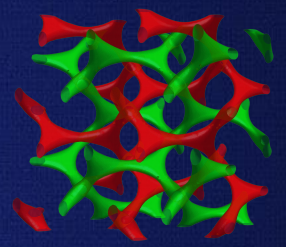


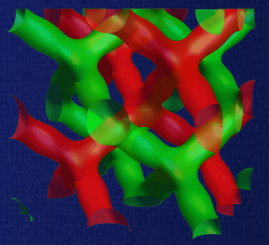
Fig. 3) Phase diagram of diblock copolymers (f_A = 0.34) and a homopolymer-like species (f_A = 0.05) at different compositions of HL chains, $\bar{\phi}^{HL}$, and values of α. The interaction strength is again $\chi_{AB} N_{DBC}$ = 25. The lamellar phase is labelled as L.

The Stable P Morphology 2

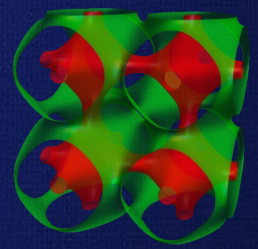




G



DD



P

L

Disordered

DIS

An elaborate sequence of stable bicontinuous phases is found near $\chi_{AB} N_{DBC} \approx 23$ as the concentration of the additive species is increased, G → DD → P → DD → G.

Pausing for a moment...

We have so far looked at the effects of the

- Chain length ratio, α
- Volume concentration of the homopolymer-like species, $\overline{\phi}^{HL}$
- Segregation strength

Next part of the journey is to understand the formation of the novel bicontinuous phases arising from blending the homopolymer-like chains.